Using Density Functional Theory to Study Shape-Reactivity Relationships in Keggin Al-Nanoclusters

Katie W. Corum^a and Sara E. Mason^{a*}

^aDepartment of Chemistry, University of Iowa, Iowa City, IA 52242

*Corresponding author: Sara-mason@uiowa.edu

Abstract

Keggin-based aluminum nanoclusters have been shown to be efficient sorbents for the removal of arsenic from water. Obtaining a molecular-level understanding of the adsorption processes associated with these molecules is of fundamental importance, and could pave the way for rational design strategies for water treatment. Due to their size and the availability of experimental crystal structures, Al nanoclusters are computationally tractable at the density functional theory (DFT) level. Here, we compare the reactivity of three aluminum polycations: $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}), $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$ (Al_{30}), and $[\text{Al}_{32}\text{O}_8(\text{OH})_{60}(\text{H}_2\text{O})_{30}]^{20+}$ (Al_{32}). We use DFT calculations to determine reactivity as a function of particle topography, using sulfate and chloride as adsorption probes. Our comparative modeling of outer-sphere adsorption of Cl^- and SO_4^{2-} on Al_{13} , Al_{30} , and Al_{32} supports that the unique “hourglass” shape characteristic to Al_{30} gives rise to relatively strong adsorption in the molecular beltway, as well as a wide range of reaction energies as a function of particle topography. The DFT trends in outer-sphere adsorption energy stated in this paper suggest that the apparent shape-reactivity relationship supersedes reactivity predictions based on oxygen functional group type alone.

Keywords: Al Keggin; Al polycations; DFT; Al_{30} ; reactivity; adsorption

Introduction

Al-based materials are known to exhibit high reactivity towards polyoxoanion species such as arsenate, and therefore are frequently used in coagulation-coprecipitation and adsorption-based water remediation. Studies point to the utility of the Keggin-based aluminum hydroxide nanocluster $[\text{Al}_{30}\text{O}_8(\text{OH})_{56}(\text{H}_2\text{O})_{26}]^{18+}$ (Al_{30}) in the efficient removal of arsenic from water. Mertens et al. have been prime investigators in researching the removal of inorganic sodium arsenate from contaminated water samples. (Mertens et al., 2012a) In a recent study, the reactivity of several Al-based sorbents was compared by measuring the uptake capacity of arsenic, specifically As(V). (Mertens et al., 2016) The materials tested included Al_{30} solution, Al_{30} enriched polyaluminum chloride (PAlCl_{30}), polyaluminum granulate (PAG), and the natural Al mineral phase, gibbsite. The pure Al_{30} and PAlCl_{30} showed similar As uptake efficiency, suggesting that the Al_{30} content of PAlCl_{30} is responsible for its reactivity towards the contaminant. All of the nanocluster sorbents adsorbed at least 93% of arsenic from solutions of initial arsenic concentration ranging from 0.133-0.667 mmol/L, while the gibbsite sample only decreased the As(V) concentration by 50%. While Al nanoclusters can adsorb contaminants at a variety of pH conditions it has been shown that PAlCl_{30} efficiency is highest near neutral pH, making it an excellent candidate for the purification of natural waters. (Mertens et al., 2012a, Mertens, 2011, Mertens et al., 2012b)

Conceptually, the high reactivity of the Al_{30} molecule has been rationalized through structure-reactivity relationships that were developed for extended mineral surfaces and based on Pauling's rules of inorganic crystal stability. (Pauling, 1929) Mineral-water interfaces are well-defined models for geochemical systems. Surface energetics for mineral-water interfaces have been extracted experimentally, but it is time consuming and relative to UHV conditions. (Israelachvili and Adams, 1978, Jordan and Geiger, 2014) Theoretical studies using methods

such as DFT and *ab initio* molecular dynamics (AIMD) can help to fill in the conceptual gap between macroscopic experiments and molecular understanding. However, information from atomistic modeling currently trails the information obtained from over a decade of experimental studies of hydrated single-crystal surfaces (see, for example, Catalano et al. (2008), Fenter et al. (2000), Fenter and Sturchio (2004), Eng et al. (2000), Catalano (2010), Rosso et al. (2010), Abadia et al. (2014)). In the absence of more robust chemical modeling, bond-valence theory has been a popular and useful means of mapping experimental information about adsorption to structure-property relationships. The bond-valence model as formulated by Brown relates bond length to bond strength through the bond valence s of atom type i . (Brown, 2009) The model is parametrized such that the sum over s_i for each atom should equal its formal valence, where $s_i = (R/R_0)^{-N}$, R is the observed bond length while R_0 and N are fitted bond valence parameters. The conceptual result born out of bond-valence theory is that functional group type is a key predictor of mineral surface reactivity. (Hiemstra et al., 1989) In a recent review, Brown and Calas (2011) discuss the oxygen functional groups exposed as “long-term docking stations”. They explain that the formation of (partially covalent) inner-sphere (IS) adsorption complexes immobilizes the adsorbate. On the other hand, outer-sphere (OS) adsorption is considered to be relatively weak on mineral-water interfaces. Here, when we refer to an OS adsorption complex involving an Al Keggin molecule, we specifically mean that no ligand exchange occurs between the Al atoms of the Keggin and the adsorbate. Conventionally, the interaction between the adsorbate and the Keggin would be thought to be weaker in an OS complex than in an IS complex.

It is easy to see why, in conjunction with high reactivity noted in the literature, the importance of functional group number and type is assumed to govern the reactivity of Al

nanoclusters. The Al_{13} molecule has two types of exposed doubly bridging ligands ($\mu_2\text{-OH}$) and twelve equivalent bound water molecules ($\eta\text{-H}_2\text{O}$). Al_{30} and Al_{32} are comprised of two $\delta\text{-Al}_{13}$ Keggin units, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (Al_{13}) connected by four Al linkers. (Abeyasinghe et al., 2012, 2013a) There are three surface functional group categories in the Al_{30} and Al_{32} molecule – bound water molecules ($\eta\text{-H}_2\text{O}$), doubly bridging ligands ($\mu_2\text{-OH}$), and triply-bridging ligands ($\mu_3\text{-OH}$). (Rustad, 2005, Casey, 2006, Casey and Rustad, 2007, Sun et al., 2011) The Al_{32} molecule contains two additional Al atoms on the Al_{30} molecule but contains the same types of oxygen functional groups. Indeed, the existence of numerous distinct functional groups on the surface of the Al Keggin molecules has been highlighted as an argument for adopting these species as geochemical models. (Casey and Rustad, 2007, Casey, 2006)

The Keggin structural motif common to the Al nanoclusters studied here is of general interest to a wide range of chemistry beyond adsorption. For example, Furrer et al. has studied aluminum flocs and have found that the Al flocculants that precipitate from streams contain a significant amount of $\text{Al}(\text{O})_4$, which is the building blocks of the $\epsilon\text{-Al}_{13}$ Keggin. (Furrer et al., 2002) The ferrihydrite structure of Michel et al. based on pair distribution function analysis exhibits similarities to the $\delta\text{-Keggin}$ structure. (Michel et al., 2010) More recently, an $\alpha\text{-Keggin}$ Fe_{13} cluster was characterized by Sadeghi et al., providing further evidence that the growth of both natural and synthetic phases proceeds by aggregation of clusters. (Sadeghi et al., 2015) The Keggin motif in prenucleation clusters has also been observed in Nb-polyoxometalate systems. (Hou et al., 2013) Other aspects of the reactivity of Keggin clusters have been shown to depend on composition. For example, Rustad and Casey have determined heteroatom substitution can impact the kinetics of ligand exchange reactions. (Rustad and Casey, 2012, Rustad et al., 2004, Reusser et al., 2014)

These examples of broad interest in Keggin clusters provides further motivation for modeling studies aimed at assigning their reactivity to underlying physical properties.

In our previous work, we carried out DFT calculations to rationalize the crystal structure of an Al_{30} Keggin species with two surface-bound Cu^{2+} , referred to as $\text{Cu}_2\text{Al}_{30}\text{-S}$. (Abeyasinghe et al., 2013b) The crystallization was done in the presence of disulfonate ions (2,6-NDS), and the structure exhibited Cu^{2+} bound to Al_{30} in a corner-sharing bidentate fashion, while the sulfonate groups had an OS relationship to the molecule. DFT modeling of IS Cu^{2+} adsorption and/or OS SO_4^{2-} adsorption (as a simplified approximation to the bulky 2,6-NDS counter ions used in the experiment) was carried out. When Cu^{2+} and SO_4^{2-} adsorption was considered separately, the cation and anion showed opposite trends in adsorption site preference as a function of location on the particle surface. Specifically, Cu^{2+} adsorption was preferred at the ends or “caps” of the molecule, while SO_4^{2-} adsorption was preferred in the molecular center or “beltway” region. Furthermore, while OS adsorption is generally thought of as a weak interaction, the reaction energies associated with the OS adsorption of SO_4^{2-} were relatively large. When co-adsorption was modeled, the preferred structure had both Cu^{2+} and SO_4^{2-} adsorbed in the beltway, congruent with the crystal structure and suggested that the strong OS adsorption controlled the coadsorption site preference. The variation in the Cu^{2+} and SO_4^{2-} adsorption energies as a function of molecular topography, specifically between the beltway and caps, was greater than 1 eV per ion, despite the fact that all of the inner-sphere adsorption geometries involved two $\eta\text{-H}_2\text{O}$ groups. These results suggest that reactivity factors other than oxygen functional group identity were governing the DFT energy trends. Plots of the electrostatic potential (V_{el}) mapped onto the charge density of the molecule revealed that the unique “hourglass” shape of Al_{30} gives rise to more positive values in the beltway and less positive values at the caps. The reason for this

variation is attributed to how the topography of the particle surface affects the distribution of η -H₂O functional groups. In the former, SO₄²⁻ can only interact with the oxygen functional groups directly beneath it, while in the latter the SO₄²⁻ can interact with a larger area of the Al₃₀ surface.

In the present work, we aim to directly assess how shape affects adsorption trends on Al₁₃, Al₃₀, and Al₃₂, using DFT calculations and AIMD. We model OS adsorption of SO₄²⁻ and Cl⁻ to sample the potential energy surfaces of the three Al nanoclusters. SO₄²⁻ and Cl⁻ are chosen as representative probe adsorbates based on their common use in crystallization experiments. Additionally, these ions allow us to compare reactivity trends as a function of adsorbate size and charge, and can be considered an analog for contaminant polyoxoanions such as selenate and molybdate. These different ions all have a different ionic radii and this could lead to a more complete discussion of how the size of the ion effects reactivity.

Computational and Theoretical Methods

AIMD simulations and DFT geometry optimizations are carried out using the DMol³ package developed by Delley,(Delley, 1990, 2000) with aqueous effects accounted for by the conductor-like screening model (COSMO).(Klamt and Schüürmann, 1993) The AIMD trajectories are used to search for minimum energy adsorption configurations, which allows for a better sampling of the potential energy surface than through static DFT calculations alone. AIMD simulations were carried out in the (N,V,T) ensemble with trajectories of 1000 steps of 0.463 fs. The temperature was set at 330 +/- 2K and controlled by using the Nosé-Hoover chain (NHC)(Nose, 1984, Hoover, 1985) method. A temperature higher than normal environmental conditions was intentionally chosen to give the system additional thermal energy such that more of the potential energy surface would be accessible to the adsorbate. The lowest energy configurations from the AIMD simulations were then subjected to geometry optimization at the

DFT level, and all of the reported energetics in this study are from those DFT results. An additional reason to consider higher temperature in a system with many bound water groups is the fact that the GGA style exchange correlation functional used in our calculations has been shown to over-structure water.(Leung et al., 2006) The inversion symmetry of Al_{30} and Al_{32} is maintained in the adsorbed systems by modeling two anions with atomic coordinates that are also related by inversion symmetry.

Select configurations of SO_4^{2-} and Cl^- adsorption at distinct positions (in terms of molecular topography) were then subjected to DFT geometry optimization. The geometry optimization calculations were carried out at the GGA-PBE (Perdew et al., 1996) level with a structural convergence criterion of 0.03 eV/Å. A DNP numerical atom-centered basis set (with a cutoff radius of 3.5 Å) was used to expand the single electron orbitals. Further details of the computational optimization methods (including prior benchmarking and convergence studies) are reported in our previous work.(Abeyasinghe et al., 2013b, Corum and Mason, 2015, Fairley et al., 2015)

In order to use probe adsorbates to sample the potential energy surface of the Al nanoclusters, it is necessary to model the isolated molecular form. Molecular Al nanocluster geometries are generated based on the experimental crystal structures of Al_{13} .(Johansson, 1960) Al_{30} .(Abeyasinghe et al., 2012) and Al_{32} .(Abeyasinghe et al., 2013a) Protonation states of the exposed oxygen functional groups are determined based on a bond-valence analysis. The molecular structures are then embedded in the COSMO continuum solvent model (with a dielectric constant of 78.54 to simulate water), and fully optimized at the DFT level. The average bond distances between the tetrahedral Al and the four bound O atoms for all three aluminum nanoparticles are tabulated and compared to the experimental structure in Table 1,

showing excellent structural agreement between the modeled molecular structure and the experimental crystal structure.

Two adsorption configurations (for each adsorbate) were fully optimized for Al_{13} and Al_{30} , and three configurations were fully optimized for Al_{32} . The initial adsorption configurations for all three molecules are shown schematically in Figure 1. The two adsorption configurations for Al_{13} are labeled A_{13} and B_{13} . The configurations for Al_{30} have the adsorbate located in the beltway of the cluster, labeled A_{30} , or at the caps of the cluster, B_{30} . The Al_{32} adsorption configurations were based off of the Al_{30} configurations. In the A_{32} and B_{32} configurations, the adsorbates are in the beltway region (which is now partially blocked by the additional Al atoms relative to Al_{30}), and in the C_{32} configuration the adsorbates are above the molecular caps.

As previously reported, the 16+ form of the Al_{30} molecule was shown to be more stable than the 18+ form by using vibrational analysis, while several stable 16+ isomers were found.(Abeyasinghe et al., 2013b) Therefore, in modeling adsorption on Al_{30} , we have the additional consideration of which 16+ isomer(s) to consider. While not exhaustive, we chose two 16+ Al_{30} isomers on which to model adsorption, in which two (symmetry-related) $\eta\text{-H}_2\text{O}$ groups are deprotonated. In one Al_{30}^{16+} , the deprotonated $\eta\text{-H}_2\text{O}$ groups are in the beltway, labeled as “a”, and in the other, the deprotonated $\eta\text{-H}_2\text{O}$ groups are at the cap sites, labeled as “b”, also shown in Figure 1. The difference in the DFT total energy of the two 16+ isomers is 0.86 eV.(Casey et al., 2005) Therefore, we consider both deprotonation states as possible starting points for subsequent adsorption. The two deprotonation sites, a and b, and two adsorption configurations, A and B, results in 4 possible configurations: A_{a30} , B_{b30} , A_{b30} , and B_{a30} . The A_{a30} structure is where the beltway sites are deprotonated to form the 16+ molecule and OS adsorption is at the beltway, the B_{b30} structure is where the cap sides are deprotonated to form the

16+ molecule and OS adsorption is at the caps, the A_{b30} structure is where the cap sites are deprotonated to form the 16+ molecule and OS adsorption is at the beltway, and the B_{a30} structure is where the beltway sites are deprotonated to form the 16+ molecule and OS adsorption is at the caps.

DFT reaction energies, E_{rxn} , are calculated based on Scheme 1 using the total energy information for each reactant and product species, weighted by the appropriate stoichiometric coefficients. In forming $(SO_4)_y\text{---}Al_x$ and $Cl_y\text{---}Al_x$, Al_x interacts electrostatically with the anion species, where x equals the number of Al atoms: $x=13, 30$, and 32 and $y=1$ or 2 depending on the number of ions adsorbing to the molecule. In order to calculate values of E_{rxn} by Scheme 1, the following molecular aqueous species were modeled: Al_{13} , Al_{30} , Al_{32} , SO_4^{2-} , Cl^- , $SO_4\text{---}Al_{13}$, $Cl\text{---}Al_{13}$, $(SO_4)_2\text{---}Al_{30}$, $Cl_2\text{---}Al_{30}$, $(SO_4)_2\text{---}Al_{32}$ and $Cl_2\text{---}Al_{32}$, where “---” denotes OS adsorption between the adsorbing ion(s) and Keggin molecule, and the double adsorption on Al_{30} and Al_{32} reflects the molecular inversion symmetry.

Results and Discussion

Values of E_{rxn} for sulfate and chloride adsorption configurations are reported in Table 2, with the optimized geometries shown in Figure 2 (Al_{13}), Figure 3 (Al_{30}), and Figure 4 (Al_{32}). The range of E_{rxn} values for each adsorbate system, ΔE_{rxn} , is also reported for convenience. For simplicity, we discuss the A_{a30} and B_{b30} results to represent Al_{30} , as they show the greater range in E_{rxn} .

The magnitude of the most favorable values of E_{rxn} on the Al_{30} and Al_{32} molecules is greater than that for adsorption of either ion on the Al_{13} molecule. This begs the question if the trends are dictated by the overall formal charge on each Keggin species. As previously discussed in the literature, the total formal charge on each Al nanocluster (7+, 18+, and 20+ respectively

for Al₁₃, Al₃₀, and Al₃₂) does not represent how charge is distributed, motivating the definition of a surface specific charge, σ , that effectively normalizes the molecular charge per Al: $\sigma = (Z + \Sigma_{\max}) / \text{Al}_{\text{surf}}$. Here, Z stands for the average number of protons lost per Al nanocluster, $\Sigma_{\max}$ represents the total charge at the fully protonated state, and Al_{surf} is the total number of Al atoms in each Al nanocluster. (Casey et al., 2005) Using this definition of σ and the 16⁺ state of Al₃₀ we model here, all three of the Al polycations have σ values in the range of 0.53 to 0.66 charge units. Here, we use the DFT results and Mulliken (Mulliken et al., 1949) population analysis to investigate if there are significant variations in the local charges of Al atoms in the Al nanoclusters. The Mulliken charges on the Al atoms are on average 1.51 e, 1.52 e, and 1.53 e for Al₁₃, Al₃₀, and Al₃₂, confirming that the distribution of charge per Al atom is similar in all of the Al nanoclusters.

As no direct bonds are formed in OS adsorption, there is no single adsorbate-cluster distance to characterize the optimized configurations. We report the average distance of the sulfate (sulfur atom) and chloride on the Keggin structures to the tetrahedral Al (Al_{tet}) center for Al₁₃, Al₃₀, and Al₃₂. For sulfate adsorption the average S-Al_{tet} bond distance is 6.070 Å, 6.479 Å, and 6.390 Å for Al₁₃, Al₃₀, and Al₃₂ respectively and 6.454 Å, 5.679 Å, and 6.133 Å for chloride adsorption on Al₁₃, Al₃₀, and Al₃₂ respectively. Since each Keggin contains its own unique shape we cannot make an equal comparison between all three Keggin structures, but note that there is no simple correlation between E_{rxn} and these distances.

We also report an O---O distance on the surface of Al₃₀ and Al₃₂ in order to observe how the nanocluster geometry changes in response to adsorption. The O---O distance we measure is circled in Figure 3 and Figure 4. On the bare clusters the O---O interatomic distance is 3.530 Å and 3.456 Å for Al₃₀ and Al₃₂, respectively. For Al₃₀ we observe that when sulfate and chloride

adsorb to the beltway this O---O distance expands. This is due to the fact that the H atoms on one of the O atoms wants to hydrogen bond with the adsorbate. For sulfate adsorption the O---O distance expands by 0.244 Å and for chloride adsorption the O---O distance expands by 0.270 Å. When the adsorbate is on the cap there is only at most a 0.035 Å elongation of the O---O distance. For chloride adsorption on Al₃₂ both beltway structures (A₃₂ and B₃₂) have an elongation of the O---O distance but only by 0.017 Å and the cap site, C₃₂ has a contraction of 0.015 Å. For sulfate adsorption the only structure that has an elongation of this O---O distance is A₃₂. The A₃₂ structure is where the sulfate is trying to fit into this pocket, the O---O distance expands by 0.056 Å. For B₃₂ and C₃₂ the O---O bond distance contracts by 0.022 Å and 0.011 Å respectively. The analysis of surface O-O separations shows that adsorption can induce significant changes in the cluster geometry, which may contribute to trends and variations in E_{rxn} .

Charge population analysis is carried out to further characterize the adsorption configurations, and is reported in Table 3. Charge population analysis is a semi-quantitative approach in which the electron density (obtained from the DFT calculation) within a region is summed, along with the nuclear charge, to yield an atomic partial charge. Atomic partial charges can be summed to determine the charge on a molecule or fragment in a system. On Al₁₃, the sulfate and chloride charge is unchanged between the A₁₃ and B₁₃ configurations. The largest variation in adsorbate charge between configurations is seen for SO₄²⁻ on Al₃₂. In the B₃₂ configuration, the charge on SO₄²⁻ has been reduced by 0.65 e, while in the C₃₂ configuration the charge has only been reduced by 0.44 e. There are also variations in adsorbate charge in the chloride Al₃₂ configurations and the Al₃₀ SO₄²⁻ and Al₃₀ Cl⁻ configurations. The trend can be summarized as showing that when anions adsorb in beltway configurations on Al₃₀ and Al₃₂,

there is a greater extent of charge transfer with the Al nanocluster, and this trend correlates with the larger magnitude values of E_{rxn} for beltway configurations.

The comparison of E_{rxn} values on Al_{13} , Al_{30} , and Al_{32} nanoclusters and the charge population analysis supports that there is a shape-reactivity relationship governing adsorption behavior on the Al nanocluster surfaces: On the spherical Al_{13} , E_{rxn} varies by at most 0.11 eV, while the variation between configurations with adsorbates at the beltway versus cap configurations on Al_{30} and Al_{32} is 0.28-1.27 eV. The Mulliken population analysis in Table 3 shows that the relatively strong adsorption in the beltway configurations is accompanied by a greater extent of charge transfer between the adsorbate and the Al nanocluster. In order to visualize the interactions between the anions and the Al nanoclusters, we calculate and plot the induced charge density, $\Delta\rho$, taken as $\rho_{\text{SO}_4/\text{Al}_x} - \rho_{\text{Al}_x} - \rho_{\text{SO}_4}$, where $\rho_{\text{SO}_4/\text{Al}_x}$ is the charge density from the sulfate adsorbed cluster, ρ_{Al_x} is the charge density from the Al nanocluster, and ρ_{SO_4} is the charge density from just the sulfate ions in their same geometry as if there were adsorbed onto the Al nanoclusters. The resulting isosurfaces are shown in Figure 5. Figure 5 shows $\Delta\rho$ for the sulfate B configuration on Al_{13} as well as the A and C configurations for Al_{32} . All of the $\Delta\rho$ plots use the same isosurface value. Comparing the beltway (A_{32}) and cap (C_{32}) configurations, it is qualitatively apparent that there is a larger volume bound by the isosurfaces for A_{32} . The same can also be seen for beltway adsorption of SO_4^{2-} on Al_{30} , as previously shown in Abeysinghe et al (2013b). Again using a piece of paper as an analogy for how the functional groups are distributed on the Al_{32} particle surface, the caps are like a flat page, which sterically limits how many functional groups interact with SO_4^{2-} in C_{32} . The beltway corresponds to the inside of a rolled piece of paper, which increases Al_{32} - SO_4^{2-} interactions in A_{32} . In contrast, the

round shape means that $\text{Al}_{13}\text{-SO}_4^{2-}$ interactions are both limited relative to the Al_{30} and Al_{32} beltway, and are also uniform throughout the Al_{13} particle surface.

The shape-reactivity relationship supported by the DFT calculations can be represented by considering the V_{el} as shown in Figure 6. The electrostatic potential for Al_{13} is relatively uniform as a function of location on the particle surface while Al_{30} and Al_{32} show variation in V_{el} , with the most positive values in the beltway and the least positive values at the caps. We interpret the correlation between V_{el} and E_{rxn} as evidence that V_{el} may be useful as a predictor of the relative strength and range of OS adsorption energies on differently shaped Al nanoclusters. However, V_{el} is not the only factor governing reactivity, as steric effects can also influence adsorption trends. For example, while both Al_{30} and Al_{32} exhibit more positive regions of V_{el} in the molecular beltway, the beltway surface of Al_{32} is less accessible due to the additional Al atoms in the structure.

Conclusion

The DFT modeling of OS adsorption of SO_4^{2-} and Cl^- on the surfaces of Al_{13} , Al_{30} , and Al_{32} supports the existence of a shape-reactivity relationship in Al nanoclusters. Combined with our previous adsorption modeling, we conclude that the shape-reactivity relationship affects both IS and OS adsorption, but particularly gives rise to unusually strong OS anion adsorption in the beltway of the larger Al Keggin nanoclusters. There are implications of these results for the use of Al Keggin nanostructures in precipitation-based water treatment. Once a contaminant has been bound by the sorbing Al nanocluster, precipitation of the aluminum polycation complex requires counterions. The results here demonstrate that SO_4^{2-} and Cl^- counterions interact more strongly with Al_{30} and Al_{32} (the Keggin that exhibit gradients in V_{el} due to their shape) relative to Al_{13} . This suggests that shape and gradients in V_{el} should be considered in optimizing the

298 performance of Al sorbents to be used in precipitation-based water remediation. The shape-
299 reactivity relationship may be of particular use in comparing adsorption trends on nanocluster
300 sorbents of the same composition, but varying shape and size. The need for sustainable water
301 remediation strategies is a driving force for ongoing efforts to fundamentally understand
302 nanocluster reactivity and adsorption processes.

303 **Acknowledgements**

304 This work was supported by NSF grant CHE-1254127, and utilized computational resources
305 provided by the University of Iowa College of Liberal Arts and Sciences.

306

References

- Abadia, M., Gonzalez-Moreno, R., Sarasola, A., Otero-Irurueta, G., Verdini, A., Floreano, L., Garcia-Lekue, A. and Rogero, C., 2014. Massive surface reshaping mediated by metal-organic complexes. *J. Phys. Chem. C* 118(51), 29704-29712.
- Abeysinghe, S., Corum, K.W., Neff, D.L., Mason, S.E. and Forbes, T.Z., 2013b. Contaminant adsorption on nanoscale particles: structural and theoretical characterization of Cu^{2+} bonding on the surface of Keggin-type polyaluminum (Al_{30}) molecular species. *Langmuir* 29(46), 14124-14134.
- Abeysinghe, S., Unruh, D.K. and Forbes, T.Z., 2012. Crystallization of Keggin-type polyaluminum species by supramolecular interactions with disulfonate anions. *Cryst. Growth Des.* 12(4), 2044-2051.
- Abeysinghe, S., Unruh, D.K. and Forbes, T.Z., 2013. Surface modification of Al_{30} Keggin-type polyaluminum molecular clusters. *Inorg. Chem.* 52(10), 5991-5999.
- Brown, G.E. and Calas, G., 2011. Environmental mineralogy - understanding element behavior in ecosystems. *C. R. Geosci.* 343(2-3), 90-112.
- Brown, I.D., 2009. Recent developments in the methods and applications of the bond valence model. *Chem. Rev.* 109(12), 6858-6919.
- Casey, W.H., 2006. Large aqueous aluminum hydroxide molecules. *Chem. Rev.* 106(1), 1-16.
- Casey, W.H. and Rustad, J.R., 2007. Reaction dynamics, molecular clusters, and aqueous geochemistry. *Annu. Rev. Earth. Pl. Sc.* 35, 21-46.
- Casey, W.H., Rustad, J.R., Banerjee, D. and Furrer, G., 2005. Large molecules as models for small particles in aqueous geochemistry research. *J. Nanoparticle Res.* 7(4-5), 377-387.
- Catalano, J.G., 2010. Relaxations and interfacial water ordering at the corundum (110) surface. *J. Phys. Chem. C* 114(14), 6624-6630.
- Catalano, J.G., Park, C., Fenter, P. and Zhang, Z., 2008. Simultaneous inner- and outer-sphere arsenate adsorption on corundum and hematite. *Geochim. Cosmochim. Ac.* 72(8), 1986-2004.
- Corum, K.W. and Mason, S.E., 2015. Establishing trends in ion adsorption on the aqueous aluminium hydroxide nanoparticle Al_{30} . *Mol. Simulat.* 41(1-3), 146-155.
- Delley, B., 1990. An all-electron numerical-method for solving the local density functional for polyatomic-molecules. *J. Chem. Phys.* 92(1), 508-517.
- Delley, B., 2000. From molecules to solids with the DMol³ approach. *J. Chem. Phys.* 113(18), 7756-7764.
- Eng, P.J., Trainor, T.P., Brown, G.E., Waychunas, G.A., Newville, M., Sutton, S.R. and Rivers, M.L., 2000. Structure of the hydrated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface. *Science* 288(5468), 1029-1033.
- Fairley, M., Corum, K.W., Johns, A., Unruh, D.K., Basile, M., de Groot, J., Mason, S.E. and Forbes, T.Z., 2015. Isolation and characterization of the $[\text{Ga}_2\text{Al}_{18}\text{O}_8(\text{OH})_{36}(\text{H}_2\text{O})_{12}]^{8+}$ cluster: cationic variations on the Wells-Dawson topology. *Chem. Comm.* 51(62), 12467-12469.
- Fenter, P., Cheng, L., Rihs, S., Machesky, M., Bedzyk, M.J. and Sturchio, N.C., 2000. Electrical double-layer structure at the rutile-water interface as observed in situ with small-period X-ray standing waves. *J. Colloid Interface Sci.* 225(1), 154-165.
- Fenter, P. and Sturchio, N.C., 2004. Mineral-water interfacial structures revealed by synchrotron X-ray scattering. *Prog. Surf. Sci.* 77(5-8), 171-258.

352 Furrer, G., Phillips, B.L., Ulrich, K.U., Pothig, R. and Casey, W.H., 2002. The origin of
 353 aluminum flocs in polluted streams. *Science* 297(5590), 2245-2247.
 354 Hiemstra, T., Vanriemsdijk, W.H. and Bolt, G.H., 1989. Multisite proton adsorption modeling at
 355 the solid-solution interface of (hydr)oxides - a new approach .1. model description and
 356 evaluation of intrinsic reaction constants. *J. Colloid Interface Sci.* 133(1), 91-104.
 357 Hoover, W.G., 1985. Canonical dynamics - equilibrium phase-space distributions. *Phys. Rev. A*
 358 31(3), 1695-1697.
 359 Hou, Y., Zakharov, L.N. and Nyman, M., 2013. Observing assembly of complex inorganic
 360 materials from polyoxometalate building blocks. *J. Am. Chem. Soc.* 135(44), 16651-16657.
 361 Israelachvili, J.N. and Adams, G.E., 1978. Measurement of forces between 2 mica surfaces in
 362 aqueous-electrolyte solutions in range 0-100nm. *J. Chem. Soc. Faraday Trans.* 74(4), 975-
 363 1001.
 364 Johansson, G., 1960. On the crystal structures of some basic aluminium salts. *Acta Chem. Scand.*
 365 14(3), 771-773.
 366 Jordan, D.S. and Geiger, F. M., 2014. Interaction of aluminum ions with fused silica/water
 367 interfaces in the presence of oxalic acid tracked by second harmonic generation. *J. Phys.*
 368 *Chem. C.* 118(50), 28970-28977.
 369 Klamt, A. and Schüürmann, G., 1993. Cosmo - a new approach to dielectric screening in
 370 solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc.*
 371 *Perk. T. 2* (5), 799-805.
 372 Leung, K., Rempe, S.B., and Lorenz, C.D, 2006. Salt permeation and exclusion in hydroxylated
 373 and functionalized silica pores. *Phys. Rev. Lett.* 96(9), 095504-1-095504-4.
 374 Mertens, J., 2011. Al nanoclusters in coagulants and granulates: application in arsenic removal
 375 from water. *Rev. Environ. Sci. Biotechnol.* 10(2), 111-117.
 376 Mertens, J., Casentini, B., Masion, A., Pothig, R., Wehrli, B. and Furrer, G., 2012.
 377 Polyaluminum chloride with high Al₃₀ content as removal agent for arsenic-contaminated
 378 well water. *Water Res.* 46(1), 53-62.
 379 Mertens, J., Rose, J., Kagi, R., Chaurand, P., Plotze, M., Wehrli, B. and Furrer, G., 2012b.
 380 Adsorption of arsenic on polyaluminum granulate. *Environ. Sci. Technol.* 46(13), 7310-
 381 7317.
 382 Mertens, J., Rose, J., Wehrli, B. and Furrer, G., 2016. Arsenate uptake by Al nanoclusters and
 383 other Al-based sorbents during water treatment. *Water Res.* 88, 844-851.
 384 Michel, F.M., Barron, V., Torrent, J., Morales, M.P., Serna, C.J., Boily, J.F., Liu, Q.S.,
 385 Ambrosini, A., Cismasu, A.C. and Brown, G.E., 2010. Ordered ferrimagnetic form of
 386 ferrihydrite reveals links among structure, composition, and magnetism. *P Natl. Acad. Sci.*
 387 *USA* 107(7), 2787-2792.
 388 Mulliken, R.S., Rieke, C.A., Orloff, D. and Orloff, H., 1949. Formulas and numerical tables for
 389 overlap integrals. *J. Chem. Phys.* 17(12), 1248-1267.
 390 Nose, S., 1984. A unified formulation of the constant temperature molecular-dynamics methods.
 391 *J. Chem. Phys.* 81(1), 511-519.
 392 Pauling, L., 1929. The principles determining the structure of complex ionic crystals. *J. Am.*
 393 *Chem. Soc.* 51, 1010-1026.
 394 Perdew, J.P., Burke, K. and Ernzerhof, M., 1996. Generalized gradient approximation made
 395 simple. *Phys. Rev. Lett.* 77(18), 3865-3868.
 396 Reusser, D., Casey, W.H. and Navrotsky, A., 2014. Energetics of heterometal substitution in
 397 epsilon-Keggin [MO₄Al₁₂(OH)₂₄(OH₂)₁₂]^{6/7/8+} ions. *Am. Mineral.* 99(11-12), 2337-2343.

- 398 Rosso, K.M., Yanina, S.V., Gorski, C.A., Larese-Casanova, P. and Scherer, M.M., 2010.
399 Connecting observations of hematite (α -Fe₂O₃) growth catalyzed by Fe(II). *Environ. Sci.*
400 *Technol.* 44(1), 61-67.
- 401 Rustad, J.R., 2005. Molecular dynamics simulation of the titration of polyoxocations in aqueous
402 solution. *Geochim. Cosmochim. Ac.* 69(18), 4397-4410.
- 403 Rustad, J.R. and Casey, W.H., 2012. Metastable structures and isotope exchange reactions in
404 polyoxometalate ions provide a molecular view of oxide dissolution. *Nat. Mater.* 11(3), 223-
405 226.
- 406 Rustad, J.R., Loring, J.S. and Casey, W.H., 2004. Oxygen-exchange pathways in aluminum
407 polyoxocations. *Geochim. Cosmochim. Ac.* 68(14), 3011-3017.
- 408 Sadeghi, O., Zakharov, L.N. and Nyman, M., 2015. Aqueous formation and manipulation of the
409 iron-oxo Keggin ion. *Science* 347(6228), 1359-1362.
- 410 Sun, Z., Wang, H., Tong, H.G. and Sun, S.F., 2011. A giant polyaluminum species S-Al₃₂ and
411 two aluminum polyoxocations involving coordination by sulfate ions S-Al₃₂ and S-K-Al₁₃.
412 *Inorg. Chem.* 50(2), 559-564.
- 413

414 **Schemes**

415
 416 **Scheme 1.** Model reactions for the outer-sphere adsorption of SO_4^{2-} and Cl^- , where x stands for
 417 the number of Al atoms in the nanoparticle (13, 30, or 32) and y stands for the number of SO_4^{2-}
 418 or Cl^- ions. There are 2 SO_4^{2-} and Cl^- ions for Al_{30} and Al_{32} due to the inversion symmetry of the
 419 nanocluster and one SO_4^{2-} and Cl^- ion per Al_{13} .

420
 421

Figure Captions

Figure 1. The initial outer-sphere adsorption configurations for SO_4^{2-} and Cl^- on Al_{13} , Al_{30} , and Al_{32} . The small a and b on Al_{30} represents the two different protonation sites on Al_{30} while the large A and B represents the adsorption configurations. The Al^{3+} octahedrons are represented by the blue, turquoise, and green polyhedrons.

Figure 2. DFT geometry optimized structures of $\text{SO}_4\text{---Al}_{13}$ and Cl---Al_{13} . Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and green spheres, respectively. From left to right: $\text{SO}_4\text{---A}_{13}$, $\text{SO}_4\text{---B}_{13}$, Cl---A_{13} , and Cl---B_{13} .

Figure 3. DFT geometry optimized structures of $(\text{SO}_4)_2\text{---Al}_{30}$ and $\text{Cl}_2\text{---Al}_{30}$. Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and green spheres, respectively. From left to right: $(\text{SO}_4)_2\text{---A}_{30}$, $(\text{SO}_4)_2\text{---B}_{30}$, $\text{Cl}_2\text{---A}_{30}$, and $\text{Cl}_2\text{---B}_{30}$. The black circle around the two oxygen atoms on the left most structure show which oxygen atoms are used to monitor an O---O interatomic distance before and after adsorption.

Figure 4. DFT geometry optimized structures of $(\text{SO}_4)_2\text{---Al}_{32}$ and $\text{Cl}_2\text{---Al}_{32}$. Aluminum, oxygen, hydrogen, sulfur, and chlorine are shown by blue, red, gray, orange, and green spheres, respectively. From left to right and top to bottom: $(\text{SO}_4)_2\text{---A}_{32}$, $(\text{SO}_4)_2\text{---B}_{32}$, $(\text{SO}_4)_2\text{---C}_{32}$, $\text{Cl}_2\text{---A}_{32}$, and $\text{Cl}_2\text{---B}_{32}$, $\text{Cl}_2\text{---C}_{32}$. The black circle around the two oxygen atoms on the left most structure show which O atoms are used to monitor an O---O interatomic distance before and after adsorption.

Figure 5. From left to right induced charge density $\Delta\rho$ for sulfate adsorption for the B_{13} , A_{32} , and C_{32} configurations. Adsorption causes electron flow from the regions bound by black isosurfaces to regions bound by yellow isosurfaces. The same isosurface value is used in all of the figures, thus the relative volume bound by the isosurfaces in each structure correlates to the relative amount of charge transfer between the adsorbate and Keggin molecule.

Figure 6. Plots of V_{el} mapped onto charge density isosurfaces of Al_{13} , Al_{30} , and Al_{32} . The electrostatic potential is positive throughout, with higher positive values shown in red and lower positive values shown in blue. For all three, the same scale is used and all three have a range of 16 eV/e. The relative lack of gradient in the V_{el} of the Al_{13} molecule compared to Al_{30} and Al_{32} correlates with the relatively small range in E_{rxn} for the former.

Tables

Table 1. Average tetrahedral bond length (in Å) comparison between the DFT optimized nanoparticles and the experimental crystal structures.

Bond Lengths (Å)	Al ₁₃	Al ₃₀	Al ₃₂
DFT	1.815	1.824	1.824
Experimental	1.838 ^a	1.797 ^b	1.805 ^c

a.(Johansson, 1960)

b.(Abeyasinghe et al., 2012)

c.(Abeyasinghe et al., 2013a)

Table 2. Calculated values of E_{rxn} (in eV) for sulfate and chloride adsorption on Al₁₃, Al₃₀, and Al₃₂. In the two rows for Al₃₀ A_a and B_b represents that adsorption and deprotonation are occurring in the same location while A_b and B_a represents that adsorption and deprotonation are occurring in mismatched locations, as described in the text.

E_{rxn} (eV)	A	B	C	Δ_{max}
SO ₄ ---Al ₁₃	-1.76	-1.87		0.11
(SO ₄) ₂ ---Al ₃₀ (A _a and B _b)	-2.34	-1.39		0.95
(SO ₄) ₂ ---Al ₃₀ (A _b and B _a)	-2.84	-1.96		0.88
(SO ₄) ₂ ---Al ₃₂	-2.89	-2.44	-1.63	1.27
Cl---Al ₁₃	-1.18	-1.30		0.12
Cl ₂ ---Al ₃₀ (A _a and B _b)	-1.85	-0.99		0.86
Cl ₂ ---Al ₃₀ (A _b and B _a)	-1.62	-1.34		0.28
Cl ₂ ---Al ₃₂	-1.95	-1.60	-1.14	0.81

Table 3. Mulliken population analysis values for the sulfate and chloride ions in the DFT geometry optimized configurations. In the two rows for Al₃₀ A_a and B_b represents that adsorption and deprotonation are occurring in the same location while A_b and B_a represents that adsorption and deprotonation are occurring in mismatched locations, as described in the text.

Mulliken Values (e)	A	B	C	Δ_{max}
SO ₄ ---Al ₁₃	-1.53	-1.53		0.00
(SO ₄) ₂ ---Al ₃₀ (A _a and B _b)	-1.50	-1.57		0.07
(SO ₄) ₂ ---Al ₃₀ (A _b and B _a)	-1.40	-1.54		0.14
(SO ₄) ₂ ---Al ₃₂	-1.45	-1.35	-1.56	0.21
Cl---Al ₁₃	-0.65	-0.65		0.00
Cl ₂ ---Al ₃₀ (A _a and B _b)	-0.61	-0.74		0.13
Cl ₂ ---Al ₃₀ (A _b and B _a)	-0.60	-0.67		0.07
Cl ₂ ---Al ₃₂	-0.59	-0.58	-0.66	0.08

Figure 1

FIGURES

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Nanocluster

Shape