

Computational Modeling of Ligands for Water Purification Nanocoatings

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ABSTRACT

Electronic structure calculations and molecular dynamics simulations are being used to investigate ligand-based nanocoatings for use in drinking water purification applications. The aim is to use computational chemistry to aid in the development of design principles for water purification systems based on adsorption of inorganic contaminants by inexpensive mesoporous substrates functionalized with low-cost ligands. These systems can provide simple, low-cost water purifiers that meet the needs of underdeveloped countries as well as more specialized applications for developed economies.

Keywords: nanocoatings, multilayers, water purification, metal binding

1 INTRODUCTION

Clean drinking water is not readily available globally, especially in underdeveloped nations. By 2025, the world's population will reach eight billion with water needs tripling over current levels as more regions move to industrial activity. Women and children are impacted the most from the global water crisis in that the burden of providing water for the family is typically the woman; children bioaccumulate toxins at a rate ten times that of an adult and are the most sensitive to neurotoxins such as lead and mercury. The overriding issue to providing clean drinking water is cost, for an individual and also for a government. For individuals earning less than \$5 per day their water needs must be met for a fraction of that. The technical challenge is a water purifier, which can process water of uncertain origin to at least World Health Organization drinking quality levels for less than \$0.0004 per Liter operating cost.

Crystal Clear Technologies (CCT) has demonstrated ligand-assisted filter media to remove toxic metals, such as arsenic, lead, mercury and others, from water; these metals are serious concerns in water even today, in developed countries and even more so in the developing world. Central to NMXTM technology is the use of ligand-based nano-coatings that attach to a substrate filter media and sequester water-borne metallic contam-

inates. The unique ligand capability enables CCT to enhance the adsorption capacity of all conventional media including extremely low cost adsorbent media such as boehmite, converting it into a highly effective adsorbent filter media with at least eight times its conventional capacity. The goal is to supply one person's water needs for one year for one dollar.

The water purification systems studied use a metal-oxide substrate (*e.g.*, boehmite or titania with nano-size pores) combined with ligands that bind to both the substrate and metal contaminants, forming nanoscale multilayers. This approach allows for greater flexibility and selectivity in addition to significantly increasing adsorption capacity. The key to improving existing systems of this type and expanding to other toxic metals is the identification of ligand candidates and the understanding of ligand-metal binding energies and structures.

We are addressing this issue with a combination of density functional theory and molecular modeling calculations. These approaches provide ligand-contaminate binding energies and the corresponding geometries. More importantly, by allowing rapid examination of different ligands, these computations aid in the development of design principles for the multilayer nanocoatings of interest. The focus of the present work is on arsenic and selenium as the contaminants and thiol- and carboxylic acid-functionalized ligands. Currently there is limited understanding of the binding and structures of such systems.[1]

2 METHODS

A two-fold approach has been used to investigate the properties of metal-ligand complexes important in water purification nanocoatings. Both electronic structure calculations and molecular modeling simulations have been performed.

Density functional theory (DFT) calculations have been used to determine the lowest energy structure(s) of metal-ligand complexes. The DFT computations reported here have been performed with the Gaussian 03[3] series of programs using the nonlocal hybrid Becke's three-parameter exchange functional (B3LYP).[4] The

geometry optimizations have been carried out with the Berny analytical gradient method.[5] The 6-31+G* basis set was used for all the calculations unless otherwise noted. Solvent effects were not considered during the geometry optimization process. The energy difference in solution was corrected from the gas-phase energy by accounting for the solvation energy with a single-point calculation. The solvation energies were obtained using the polarized continuum model (PCM)[6] with water ($\epsilon = 78.39$) as the solvent.

Electronic structure calculations are impractical for modeling a multilayer. Thus, molecular mechanics simulations are also being used; these must be validated by comparison with DFT and X-ray crystallography results. Molecular mechanics conformation search for the arsenic-ligand complexes was performed using the Monte Carlo minimization (MCM) method of Li and Scheraga.[7] At each step, a Monte Carlo atom move is taken followed by an energy minimization. The obtained trial structure is then subjected to the Metropolis acceptance criterion. The MCM method was implemented in the MCCCIS Towhee program[8] that was used for all the modeling.

The molecules were modeled using the molecular mechanics universal force field (UFF).[9] The non-bonded interactions are represented by a Lennard-Jones (LJ) 12-6 potential

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

where r_{ij} , ϵ_{ij} , and σ are the separation, LJ well depth, and LJ size, respectively, for interacting atoms i and j . The intramolecular interactions were modeled in the following way: a harmonic potential is used to control bond stretching

$$U_b = \frac{k_{ij}}{2} (r - r_{ij})^2 \quad (2)$$

where k_{ij} is the force constant. The angle bending is represented with a cosine Fourier expansion

$$U_\theta = k_\theta \sum_{n=0}^m C_n \cos n\theta \quad (3)$$

where θ is the bending angle, C_n is the expansion coefficient, and k_θ is the force constant. The torsional interactions are similarly described

$$U_\phi = k_\phi \sum_{n=0}^m C_n \cos n\phi. \quad (4)$$

The improper torsion is controlled by a cosine Fourier expansion

$$U_\omega = k_\omega (C_0 + C_1 \cos \omega + C_2 \cos 2\omega) \quad (5)$$

where ω is the improper torsion angle, and k_ω is the force constant, and c_i is the expansion coefficient.

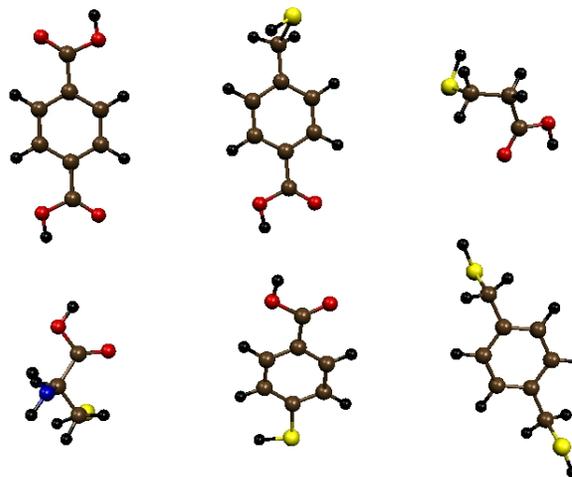
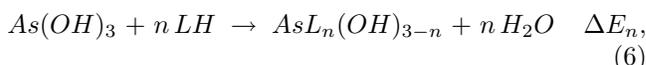


Figure 1: Several of the ligands considered in this work. (C=brown, H=black, O=red, S=yellow.)

3 RESULTS

A requisite property of potential ligands is an ability to bind strongly to a contaminate. This has been investigated for several ligands, some of which are shown in Fig. 1, for both arsenic and selenium using DFT calculations. For example, considering As(III) in aqueous solution as present primarily in the $As(OH)_3$ form, the ligand exchange reactions,



were examined for $n = 1 - 3$. In addition, the structure of the ligand coordination to arsenic was examined through DFT geometry optimizations, as this can have important consequences for the properties of a multilayer formed from the $AsL_n(OH)_{3-n}$ species.

The DFT calculations find that, for every ligand considered, the successive ligand exchange energies are more favorable. That is, AsL_3 is the thermodynamically preferred species. In general, the thiolate functional group binds more strongly than carboxylates. An important consideration in understanding the As-ligand binding is the formation of more complex structures, such as As_2L_n "dimers." It is not yet clear whether formation of a dimer is helpful or harmful in the formation of stable multilayer nanocoatings for sequestering arsenic. However, the structure of the ligand can affect whether dimer formation is favorable or not, *i.e.*, whether AsL_3 or As_2L_n is the most stable species, and what the dimer structure is, *e.g.*, As_2L_2 or As_2L_3 . The DFT calculations have shed light on what ligand properties influence these issues; these include flexibility in the functional group linkage to the phenyl ring and steric bulk on the ring. The DFT results are in agreement with the observed stable structures where data is available. The optimized structures are in very good agreement with the

corresponding X-ray crystallography data where comparisons are possible.[2] This indicates that DFT can be predictive in describing the geometries of these arsenic-ligand complexes; additional tests of these predictions are underway.

Analogous calculations are being carried out for selenium, which poses additional challenges due to its speciation. For example, Se(VI) is present primarily as selenate, SeO_4^{2-} , a $\text{pH} > 5$. Thus, an analogous ligand exchange reaction to Rxn. 6 would be



Note that, in contrast to the As(III) case, the reactants and products are ions such that solvation free energies for the different species involved can determine the favorability of binding. A similar issue arises for Se(IV) which has a more complicated speciation pattern. Preliminary DFT calculations indicate that some species undergo ligand exchange reactions much more readily than others. In addition, Se_2L_n “dimer” complexes are found to be thermodynamically stable for some species, in analogy to the arsenic chemistry discussed above. Experimental tests of the predicted binding energies and complex geometries are underway including examinations of the speciation dependence and dimerization tendencies predicted by the DFT calculations. Understanding how these binding patterns relate to multilayer nanocoating formation and properties will involve molecular dynamics calculations closely coupled with experimental studies.

Preliminary molecular modeling calculations are encouraging. For example, the structures obtained for some As_2L_3 dimers are in good agreement with DFT-optimized geometries, while others display minor differences. We are exploring whether the latter cases can be improved by simple modifications of the force field.

4 Summary

The computations presented here are generating new insight into the ligand-As and ligand-Se complexes by obtaining successive binding energies for up to three ligands, the characteristics of the lowest energy structures, the energies to form As_2L_n and Se_2L_n complexes, solvation effects, and the dependence of binding upon speciation. These are all important considerations in the design of multilayer nanocoatings for water purification. The calculated structures are in excellent agreement with crystal structures where available.[2] Experimental tests of the predicted binding patterns are currently underway.

The DFT and molecular modeling calculations are informing and will be complemented by larger-scale molecular dynamics simulations that permit the structure of the multilayers to be examined. Specifically, solvent

effects can be included more accurately and quantitative information about the competition between energetic and entropic factors important in determining multilayer stability obtained.

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