

Influence of Surface Water Displacement on Solvation Thermodynamics

Mia Kim

South Carolina Governor's School for Science and Mathematics

Aqueous phase reforming (APR) is a process used in the field of biorefinery. In APR, chemical reactions are carried out in an aqueous solution, which results in different reaction thermodynamics and surface chemistry. This work investigates the solvation thermodynamics of several adsorbed molecules on a Pt(111) surface using classical molecular dynamics and free energy perturbation. Three goals were addressed: identification of the number of water molecules displaced by each adsorbate, calculation of the free energy of each adsorbate, and estimation of the impact water displacement has on overall solvation thermodynamics. Further understanding of APR chemistry and the relationship it and overall surface water displacement have with thermodynamics will lead to a better understanding of the development of catalytic materials in biorefinery.

Introduction

Biorefinery is a growing industry that transforms biomass products into energy or other valuable products. It has multiple goals, including supplying current fuels and building blocks to produce novel materials, creating new and more jobs, and reducing greenhouse gas emissions and fossil fuel dependency.¹

Aqueous phase reforming (APR) is one of the methods of reforming used in biorefinery. APR is a form of aqueous phase heterogeneous catalysis and has a higher energy efficiency than most other methods.² However, APR has been unable to become standardized due to issues with the cost, activity, and selectivity of the present catalysts, as well as the general lack of a comprehensive understanding of the APR mechanism.³

In theory, a unique catalyst that optimizes activity and selectivity while minimizing the cost exists for every chemical reaction. However, a complete molecular-level understanding is required to achieve this. APR is only one of several areas in which this molecular-level understanding is needed. To work towards this level of understanding, methods of catalytic simulation must first be established.²

Due to the high chemical and hydrogen bonding affinities of water, the solvent in aqueous phase heterogeneous catalysis, multiple configurations of liquid molecules must be simulated for each catalytic species of interest.⁴ This is done to account for the degree to which water will participate in reactions and potentially alter the energies of catalytic species.⁴ The two primary ways of modeling water as a solvent are as an explicit water model and as an implicit water model. In an explicit water model, water is treated as several individual molecules. In an implicit water model, water is a structureless, continuous medium. Each of these methods has positives and negatives. Since the explicit water model treats water as several individual molecules instead of one continuous medium, it has a high accuracy and computational expense, as well as previously established parameters for several molecules and catalyst interfaces. Alternatively, the implicit water model is more computationally efficient, but can often over-solvate longer chain molecules by allowing the solvent into regions that would otherwise be inaccessible.²

In addition to the choice of explicit versus implicit water model, a method of molecular dynamic simulations must also be determined. The two primary methods are *ab initio* molecular dynamics (AIMD) and classical molecular dynamics. AIMD uses quantum mechanics and has a high accuracy but can be very computationally expensive and cannot generate more than a few uncorrelated configurations per adsorbate. On the other hand, classical molecular dynamics uses a non-bonding potential model that adds the Lennard-Jones and Coulomb potentials and has pre-established parameters for liquid H₂O models and metal catalyst surfaces.²

This work employed the use of the explicit water model and classical molecular dynamics. These were used to model the adsorption of several molecules onto a Pt(111) surface. The molecules we studied were carbon monoxide, water, hexanedione, methanol, and acetone in three orientations (vertical, horizontal, and diagonal). The goals of our project were to estimate the number of water molecules displaced by each adsorbate, calculate the solvation free energy of molecules using free energy perturbation (FEP) calculations, and estimate the impact of water displacement on solvation free energy.

Methods

2.1 High-Performing Computing Resource

Clemson University's high-performing computing resource, the Palmetto Cluster (Palmetto), has 2021 compute nodes and 23,072 CPU cores. Utilized by students, faculty, and staff across all disciplines, Palmetto is one of the top ten supercomputers among US public academic institutions. Clemson's Getman Group of the Department of Chemical and Biomolecular Engineering utilizes the cluster subsection Curium to carry out their simulations and calculations.⁵

2.2 Molecular Dynamics Simulator

While our work employed the use of classical molecular dynamics, we needed a software to run those simulations. As such, we used a program called Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). LAMMPS is an open-source software that uses message-passing techniques and spatial decomposition of the simulation domain. It uses a classical molecular dynamics code that focuses on materials modeling, especially for solid-state materials (*e.g.*, metals and semiconductors), soft matter, biomolecules and polymers, and coarse-grained and mesoscopic systems. Given its focus on materials modeling, LAMMPS can be used to model atoms or as a parallel particle simulator at the atomic, meso, and continuum scales. We used LAMMPS for its particle simulator functions.⁶

Particle simulators have the capability to extract molecular trajectories and solvation enthalpies and entropies. To perform these calculations, three files are required. The data file contains the molecule's force field and atomic structure. The input file contains instructions to execute the simulation to LAMMPS (in opposition to any other programs that may be loaded). The submission file contains instructions to request resources from Palmetto that are required to complete the job.⁶

2.3 3-D Visualizer

To visualize molecules and simulations, we used Visualization for Electronic and STructural Analysis (VESTA). VESTA visualizes structural models, volumetric data, and crystal morphologies in three dimensions. Its modeling system allows for a variety of features in both structural and volumetric data, such as ball-and-stick, space-filling, and polyhedral structural models, as well as vectors, lattice structures, and various other means of graphical expression.⁷

2.4 Adsorbates

The adsorbates used in our simulations and calculations were methanol (CH₃OH), hexanedione (C₆H₁₀O₂), acetone (C₃H₆O), water (H₂O), and carbon monoxide (CO). Acetone was also analyzed in three orientations: vertical, horizontal, and diagonal.

2.5 Estimating Water Molecule Displacement

To estimate the number of water molecules displaced by each adsorbate, we first equilibrated the water configuration with molecular dynamics (MD) simulations (R. Garcia, personal communication, 2021). The simulations then yielded three files: awd.profil, Owd.profil, and Hwd.profil. These were all added to a spreadsheet (R. Garcia, personal communication, 22 June 2021) which provided the density of the first layer, the density of and prior to the bulk water, and the number of water molecules in the first layer and prior to the bulk water. These components were then used to create several density profile graphs, some of which are compiled in Figure 3. There, we observed a correlation between the adsorbate size and the displacement of water molecules from the Pt(111) surface.

2.6 Calculating the Free Energy of Solvation of Molecules

After the MD simulations completed their equilibration, another file was also generated: data.lammpsdata_nvt_samp. This was transferred into a different folder, which then contained it and a new input file (R. Garcia, personal communication, 2021). Then, the jobs were submitted to LAMMPS. After their completion, the commands “fep.py 300 < fep011.lmp” and “fep.py 300 < fep012.lmp” were run to extract the Lennard-Jones and Coulomb potential values. These were used to calculate the free energy of solvation; the results are shown in Figure 5; a bar graph comparing the adsorbate contribution to the adsorbate-surface contributions.

Results

3.1 Density and Displacement Due to Adsorbates

As adsorbate size increases, so does the number of displaced water molecules (Figures 3 and 4) for hexanedione (C₆H₁₀O₂), acetone (C₃H₆O), water (H₂O), and carbon monoxide (CO). However, methanol did not follow this trend. Methanol displaced 2.0 water molecules, which was 0.7 molecules less than the smallest adsorbate, carbon monoxide.

3.2 Solvation Free Energy

In Figure 5, like Figure 3 and Figure 4, there is a correlation between the adsorbate size and the value measured. However, rather than increasing with the adsorbate size as the number of displaced molecules do, the contributions decrease as the adsorbate size increases. While the displacement of hexanedione was much larger than methanol, methanol has a markedly higher contribution than hexanedione.

Discussion

4.1 Water Density and Displacement

The use of molecular dynamics simulations made it possible to estimate the cavity sizes of different adsorbates, which were used to generate density profile graphs. The results of some of the density profile graphs are shown in Figure 3. These graphs were then used to determine the number of water molecules displaced by each adsorbate, as shown in Figure 4. It is clear that the water displacement due to the presence of adsorbates was a contributing factor of the overall solvation thermodynamics. In fact, a change in the surface water interaction was found to enhance the solvation of adsorbed species.

However, there is one outlier to the trend: methanol, which displaces less water than carbon monoxide, the smallest adsorbate. This is likely due to the hydroxyl group and the potential hydrogen bonds and solvent interactions that occur as a result of the hydroxyl group.

4.3 Free Energy Perturbation Calculations

After running the FEP calculations, it was found that on average, the displacement of water molecules from the surface contributes to the solvation free energy by approximately -0.013eV per displaced water molecule. This contribution is expected to be negligible for small adsorbates but is a relevant factor for larger adsorbates. Furthermore, this effect may change in accordance with the surface water interactions and have a significant impact on the solvation thermodynamics for larger molecules and surfaces with a higher interaction with the solvent.

4.4 Future Research

Based on the results from this project, some potential areas worth exploring include different adsorbates on the Pt(111) surface, different catalytic materials for alternative metal-water and metal-adsorbate interactions, as well as the influence of other factors such as charges of the adsorbates on the water density, displacement, and overall solvation free energy trends.

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Notes and References

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Tables and Figures

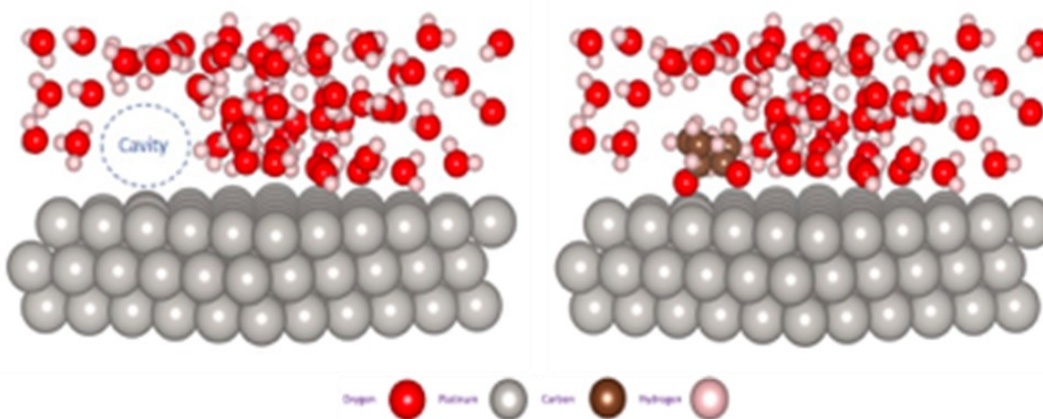


Figure 1: Two models of a Pt(111) surface in water showing the two stages of solvation. The left model shows the first step, the creation of an empty cavity in which water molecules are pushed aside, and the right model shows the second step, the adsorbate (here, hexanedione) entering the cavity.

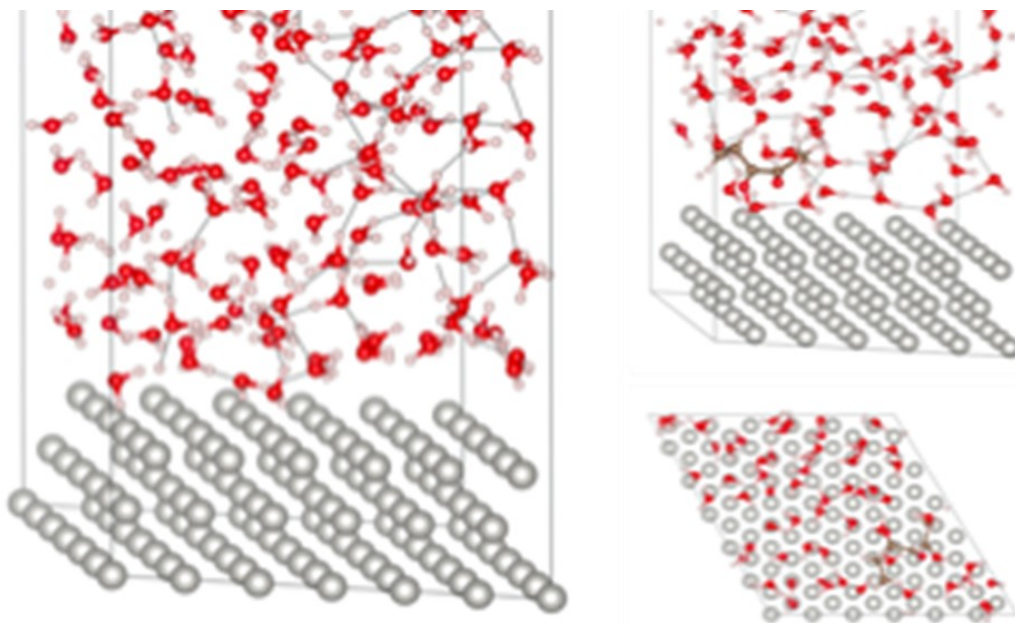


Figure 2: Three images of a Pt(111) surface; two from the front and one from the top. The largest one to the left is a clean slab, with only the Pt(111) surface in water. The two on the right contain the adsorbate, hexanedione.

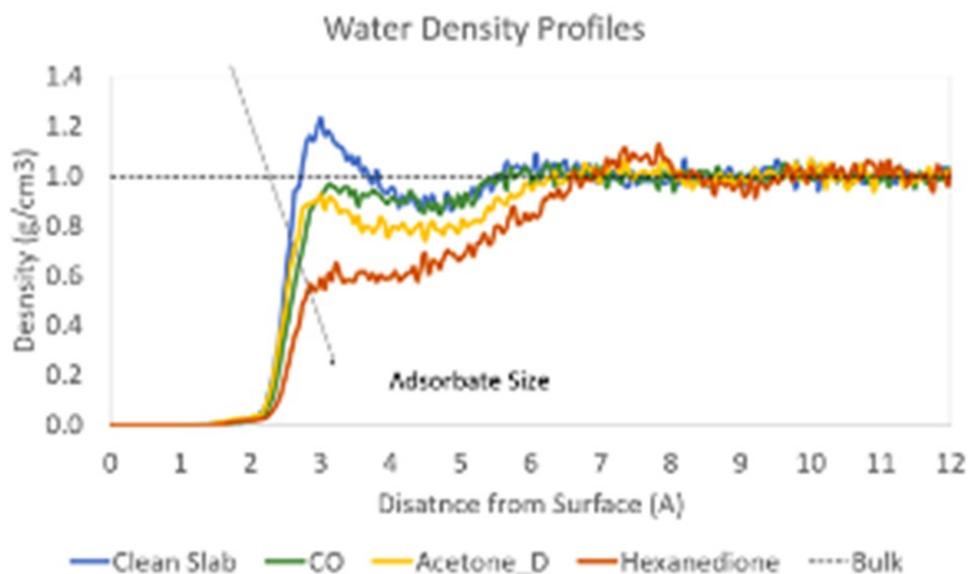


Figure 3: The trendline illustrates how the increasing adsorbate size relates to the density. From the highest to the lowest density at 3Å: Clean Slab, CO, Acetone (D), Hexanedione.

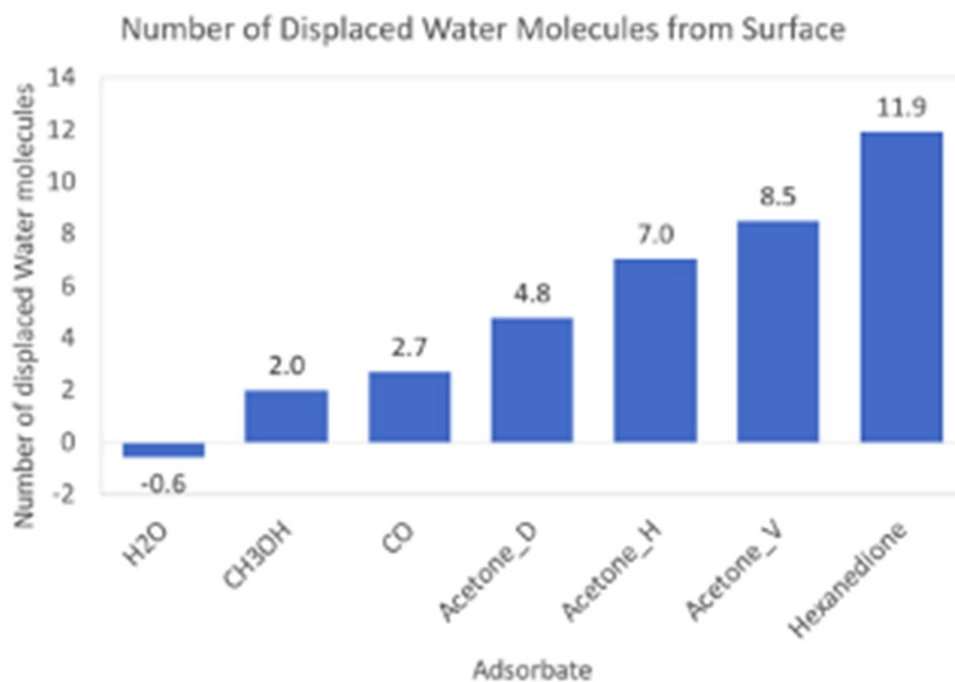


Figure 4: From the lowest to the highest number of water molecules displaced: H₂O, CH₃OH, CO, Acetone_D, Acetone_H, Acetone_V, Hexanedione. This follows the trend of increasing adsorbate size, with the exception of CH₃OH, which is the only molecule with a hydroxyl group and will thus interact differently with water molecules.

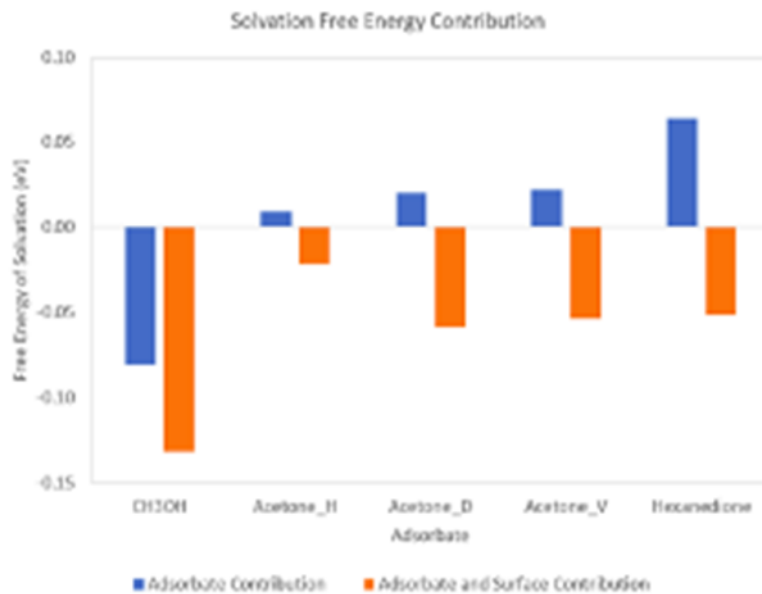


Figure 5: Regardless of whether the adsorbate contribution was positive or negative (as was only the case for CH₃OH), it is clear that the adsorbate-surface contribution was negative and favorable for CH₃OH, Acetone_H, Acetone_D, Acetone_V, and Hexanedione.