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Research Project Title: Impact of Alkali Halide Salt Ions on Hydrogen Bonding at the Air-Water Interface

Abstract

We present a computational study of the effect of various ions on hydrogen bonding at the water-air interface. Molecular dynamics simulations were performed using the CHARMM force field and TIP3P water. Simulations explored the impact of temperature and concentration on hydrogen bonding near the liquid-vapor interface of aqueous NaCl, KCl, RbCl, and CsCl solutions. Average coordination number was found to increase linearly with NaCl concentration, but decrease linearly with KCl, RbCl, and CsCl concentrations for several temperatures between 10-80°C. Density profiles across the liquid-vapor interface, water molecule orientations at this liquid-vapor interface, and surface tensions were calculated for each system.

Reflection Essay

Beginning in the fall of 2017 as a sophomore at Saint Rose, I began computational chemistry research with Dr. Brad Bauer. Together, we chose a topic within both of our interests which entailed the examination of various salt solutions through varying both concentration of the salt and varying the temperature of the solution. These solutions were modeled using molecular dynamics simulations, generated by the CHARMM forcefield. The solutions were examined at the water-air interface, which allowed for close examination of both the bulk liquid solution and the surface of the liquid. The Linux operating system was utilized to help create various Fortran scripts to examine several characteristics of each salt solution. The characteristics examined included surface tension, the number of hydrogen bonds, the number of coordinated molecules, the efficiency of hydrogen bonding, the anion, cation, and water densities, and the orientation of the water molecules.

Initially during my first year of research with Dr. Bauer, we did not examine nearly as many characteristics or salt solutions. After the research symposium in April 2018, several of my peers suggested in the future that I look at more salt solutions because at that point, our research project was only looking at sodium chloride solutions, cesium chloride solutions, and a mixture of alkali halides. Dr. Bauer also suggested that during the second year of our research, we should include more characteristics. Specifically, he suggested we view the orientation of the water molecules. We also turned to some journal articles for ideas on what characteristics we could examine as well. Most of the journal articles we viewed gave us a strong background on interfacial chemistry. A few of them also provided information explaining the orientation of
water molecules on a water-air interface, as well as information regarding hydrogen bonding on the interface, which strongly applied to our research.

In performing our research, the CHARMM molecular modeling package was used to simulate aqueous salt solutions at the water-air interface while holding constant NVT conditions in a cell dimension of $24\AA \times 24\AA \times 100\AA$. The z-dimension was elongated to allow enough unoccupied space to establish a vapor phase. The system contained 1024 water molecules and a set concentration of salt ions. The aqueous solutions considered were NaCl, KCl, RbCl, and CsCl, each at 0, 8, 16, 32, 48, and 64 salt pairs except KCl and RbCl. These two solutions excluded the 16 and the 48 salt pairs to save time. All molecules and ions were modeled using the CHARMM37b forcefield as well as TIP3P water. The temperatures examined were 283.15 K, 298.15 K, 310.15 K, 323.15 K, and 353.15 K. Prior to data collection, each system was allowed an equilibration time of approximately 2.0 ns. Each system was then simulated for at least 10 ns with a time step of 1.0 fs. Snapshots were obtained of the systems every 5,000 steps, resulting in a minimum of 20,000 snapshots for analysis. Post-simulation analysis on simulation trajectories was performed using custom Fortran scripts. This approach was particularly useful because there were more than enough trajectories and snapshots present with the amount of time used in generating the simulations. We were able to get great data from the methods utilized.

When looking for outside sources to help with our research, typically I would search for journal articles only, as they give the most useful information. Generally, I would start my search online using the Saint Rose Library’s database. Not only does the database generally give a lot of sources for every search, but it also contains many useful tools to help narrow down exactly what you’re looking for. The database allows you to narrow down your search to only peer-reviewed journals/sources, and also allows you to select specific publication years so that you can only be given sources that were published at a select time in history. This feature was particularly useful because a lot of old computational chemistry research may not be applicable in today’s research. In addition to the Saint Rose Library’s database, I would look for journals directly on the American Chemical Society Website, as I am a member, and occasionally I would use Google Scholar.

Journal articles can be difficult for someone to read who may not be used to reading them. However, from my experience, it was most useful to first read the abstract to get an understanding of the gist of the research performed in that article. After that, I generally would read through the experimental section to see what exactly the scientist(s) did and then I would read the results and conclusions section to see their main conclusions. Sometimes it can be difficult to see exactly what the researcher did because a lot of experimental sections are very detailed. If I ever had trouble understanding something though, Dr. Bauer was always more than willing to clarify or explain the source of confusion to me. As I have gotten more experienced with doing research, I have found that it gets easier in finding sources. Generally, you know exactly what type of journal article you are looking for to help answer what questions
you might have. For instance, if something about my research is a little confusing, usually I can look it up either on the Saint Rose Library database or elsewhere to find a journal article pertaining to that subject. In doing this, I almost always find the answers I am looking for. I am sure there are still plenty of articles out there that would be of use to our research though that I might not be able to necessarily find, so I’m sure I could still improve in my methods of searching for articles.

Several of the sources I found were used to gather a stronger understanding of the characteristics looked at in my research as well as to better understand how my research might be applied in everyday life. Specifically, source 2 was used to understand that aqueous ion-containing interfaces play a key role in atmospheric chemistry involving ocean surfaces and seawater aerosols. This source also stated that salts in seawater have been seen to cause bubble coalescence which is why when waves from the ocean break, they bubble. This however, is not seen in freshwater lakes. Another source, from the journal of physical chemistry, gave a diagram along with a detailed explanation of how the orientation of water molecules at the air-water interface works. This allowed for a stronger understanding of what is meant by the water molecules’ orientation. Two last sources examined, sources 1 and 3, both helped me understand something known as the Hofmeister Series. This series applies to my research because in looking at the number of coordinated molecules in the bulk liquid solution alone across the various salts, it can be seen that the slope of the lines formed from varying the concentration are not the same across the various salts. The NaCl slope is highly positive, where KCl’s slope is negative. RbCl and CsCl are also negative, CsCl’s being more negative than RbCl’s. These differences in the slopes are related to the Hofmeister Series, which states that some metals and some anions have different effects on a solution’s surface tension and therefore the solution’s ability to “salt in” or “salt out” a protein. Furthermore, there is a trend for metals as well as anions based on this series which involves a range from a strong chaotrope to a strong kosmotrope. A kosmotrope is a metal or anion that when in an aqueous solution, disrupts the solution’s hydrogen bonding abilities. A chaotrope has the opposite effect. On this trend, Cs⁺, Rb⁺, and K⁺ are to the left which means they are chaotropes and do not disrupt the hydrogen bonding of the solvent extensively. Na⁺ however, is the first metal placed on the right half of this series and therefore is a kosmotrope and interferes with the solvent’s hydrogen bonding abilities. Therefore, the differences in the slopes are due to the metals being placed differently on the Hofmeister Series.

My research applies to the general field of chemistry because it examines the hydrogen bonding of various aqueous salt solutions. Hydrogen bonding is one of the most basic things learned and used in chemistry as it is the strongest form of intermolecular interaction. Any aqueous solution has hydrogen bonding present in it as water molecules are highly capable of hydrogen bonding with one another. My research also examines the water density of the aqueous solutions which also applies to chemistry, especially organic chemistry with the separation of organic solutions from aqueous ones. Due to the difference in densities of organic and aqueous solutions, layers are often formed where the denser solution is on the bottom and the less dense one is on top. Knowing the densities of both the aqueous solution and the organic solution could help a researcher know which layer is which by comparing the densities.
This could allow them to be able to separate the two. Another researcher could perhaps build on my findings by seeing what happens to all of the characteristics I examined but with different salts, perhaps period two metal chlorides. Using the knowledge obtained from that research, certain trends could be drawn across the periodic table to show when varying the metal in the salt, certain effects can be seen on the hydrogen bonding, the water density, the surface tension, or even the orientation of the water molecules.

In the end, throughout my entire research experience in college, I have gained valuable knowledge about the work that goes in to performing research. I have learned how to find and utilize sources in an efficient manner. I have also learned to use databases such as the Saint Rose Library database to find such sources. From all of this, I believe that my research performed here at Saint Rose had an extraordinary outcome. Due to the general topic of my research, I am certain that it can be built upon and thus be a precursor for future projects.

References: