NDnano Summer Undergraduate Research
2021 Project Summary

1. Student name & home university: Elena Parial, Purdue University

2. ND faculty name & department: David B. Go, Department of Aerospace and Mechanical Engineering

3. Summer project title: Plasma-injected solvated electrons in various configurations

4. Briefly describe new skills you acquired during your summer research: Absorption spectroscopy, laser operation, experimental setup, data collection, and analysis, plasma generation, set up of plasma electrolytic cells, attention to detail, teamwork, scientific presentation skills (such as oral presentations, PowerPoints, and posters), error and data analysis.

5. Briefly share a practical application/end use of your research:
Solvated electrons are strong reducing agents that have uses in plasma medicine, radiation and analytical chemistry, water treatment, and nanomaterial synthesis.

6. 50- to 75-word abstract of your project:
Total internal reflection absorption spectroscopy is one way to observe solvated electrons produced in plasma-liquid systems. Here it will be used to characterize plasmas in nonaqueous solvents and in positive polarity configurations. In nonaqueous solvents, we expect to see different reaction dynamics, in particular, mitigating second order recombination with water. In positive polarity we hope to directly observe solvated electrons produced by incoming ions.

7. References for papers, posters, or presentations of your research:
Parial, E. P. (2021). Using total internal reflection absorption spectroscopy to measure plasma-injected solvated electrons in non-aqueous solutions. Poster presented at the Summer Undergraduate Research Symposium, Notre Dame, IN.

Anatolii et al. (1975). *Russ. Chem. Rev.* 44(906).
Bartels et al. (2005). The Journal of Physical chemistry. A. 109. 1299-307. 10.1021/jp0457141.
Buxton et al. *J Vis Chem Ref Data*. 17, (1988).
Delgado et al. *J Vis Exp*. 131, (2018) 56833.
Rumbach et al. *Nat Commun* 6, (2015) 7248.

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Plasma-liquid systems are used in a variety of applications, from wastewater purification to plasma medicine. What makes these systems of such interest is the unique chemistry they are able to induce. One powerful reducing agent they produce is the solvated electron. The goal of this research is to observe the solvated electron in a variety of plasma-liquid configurations, to better understand its behavior and subsequent reactions it drives.

The solvated electron is a free electron in a polar solvent. Existing briefly in a potential well comprised of several solvent molecules, they generally react very quickly with whatever is around them, having a reduction potential of -2.77 V [1]. Solvated electrons have already been studied in water under negative polarity operation in which the plasma acts as the cathode in an electrolytic cell and injects electrons into the solution. Since their lifetime is very short, they can be difficult to detect. By continuously injecting electrons with a plasma, a steady-state population can be produced and observed using Total Internal Reflection Absorption Spectroscopy (TIRAS). TIRAS detects the solvated electrons, which absorb light, by reflecting a laser off the plasma-liquid interface and into a photodetector. Absorbance can be found by comparing the laser intensity before and after passing through the interface. Using Beer's law, the concentration of solvated electrons can be calculated. The first objective is to study solvated electrons as a function of glycerol concentration and wavelength. The second objective is to study solvated electrons in positive polarity, in which the plasma acts as an anode.

Solvated electrons in glycerol are expected to differ from aqueous electrons in both their absorption peak and reaction dynamics. The wavelength of maximum absorbance of water solvated electrons is ~700 nm [2] while it is ~530 nm for glycerol solvated electrons [3]. Due to this difference in absorbance peak, a decrease in absorbance signal is expected when increasing the concentration of glycerol as the measurements were originally taken at a wavelength of 710 nm. On the other hand, the rate of reaction between solvated electrons and glycerol is several orders of magnitude ($\sim10^4$) smaller than the reaction rate of second order recombination with water. As such, the absorbance signal is expected to increase because the concentration of solvated electrons is increased due to a longer lifetime. Measurements at 710 nm show that TIRAS absorbance drastically decreases with increasing glycerol concentration in the electrolytic cell, much faster than would be expected from the peak shift alone. This is hypothesized to be caused by some combination of the shift in absorption and a reaction with a contaminant in the glycerol.

Positive polarity is achieved by manipulating the set up so that the electrodes are switched. In this case, the plasma acts as an anode, injecting ions into the solution. Studying TIRAS in positive polarity will allow us to measure how many electrons are produced and are solvated in this system. Methanol and nitrate solutions were used as scavengers since methanol reacts with hydroxyl (OH) radicals while nitrate reacts with solvated electrons. OH radicals react with solvated electrons which decrease the concentration. In these cases, we expect the absorbance of solvated electrons to increase with the addition of methanol and decrease with the addition of nitrate, and our results are consistent with these predictions. The addition of nitrate effectively eliminates absorption, indicating that we are observing solvated electrons, and the addition of methanol raises absorbance by a factor of 2-3.

Future work will account for the absorbance shift from water to glycerol by taking measurements at a wavelength of 532 nm which is closer to the peak of solvated electrons in glycerol. It is expected that the signal increases as the concentration of glycerol increases. In addition, the behavior of solvated electrons in other types of alcohols, such as ethylene glycol will be studied. Future work in positive polarity involves further analyzing the data to find the number of solvated electrons produced per incoming ion.

References

[1] Baxendale, J. H. (1964), Radiation Res. Suppl., 114 and 139

[2] Bartels et al. (2005). The Journal of Physical Chemistry. A. 109. 1299-307. 10.1021/jp0457141.

[3] Lin et al. *J. Phys. Chem. A* 2009, 113, 44, 12193–12198