Surface Science Division
Room 320 - Session SS2+CA+AS-FrM
Environmental, Atmospheric and Astronomical Surfaces

Moderators: Kathryn Perrine, Michigan Technological University, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:20am **SS2+CA+AS-FrM-1 Combining Synchrotron X-ray and SFG Spectroscopy Techniques to Illuminate Aqueous Interfaces***, S. Nayak, R. Kumal, A. Carr,* Argonne National Laboratory, USA*; S. Lee,* Argonne National Laboratory*; **Ahmet Uysal,*** Argonne National Laboratory, USA **INVITED**

Chemical separations are central to our energy, environment, and security needs. From efficient refinery and recycling of rare earths to cleanup of contaminated underground waters, chemical separations cover a wide range of processes such as liquid-liquid extraction (LLE), membranes, and sorbents. A common theme in most processes is that the target ions need to adsorb on or go through an interface. Understanding aqueous interfaces at molecular scale, require special experimental techniques that can distinguish the interfacial structures from the overwhelmingly larger bulk.

Surface sensitive synchrotron X-ray scattering and fluorescence, and vibrational sum frequency generation (SFG) spectroscopy techniques are among the most advanced tools available to study aqueous interfaces. Interestingly, these techniques have been developed in separate communities and there are only a handful of studies that take advantage of complementary nature of them. In this presentation, I will summarize our group's efforts in understanding aqueous interfaces in chemical separations, by combining these two experimental techniques. I will provide specific examples where a single method is not enough to decipher the complex interactions at the interface. The examples cover ion-amphiphile interactions in LLE [1-4] and ion adsorption on graphene-oxide thin films [5].

1. Nayak, S.; Kumal, R. R.; Liu, Z.; Qiao, B.; Clark, A. E.; Uysal, A., Origins of Clustering of Metalate–Extractant Complexes in Liquid–Liquid Extraction. ACS Appl. Mater. Interfaces 2021, 13 (20), 24194-24206.

2.Kumal, R. R.; Nayak, S.; Bu, W.; Uysal, A., Chemical Potential Driven Reorganization of Anions between Stern and Diffuse Layers at the Air/Water Interface. J. Phys. Chem. C 2021.

3.Kumal, R.; Wimalasiri, P.; Servis, M.; Uysal, A., Thiocyanate Ions Form Antiparallel Populations at the Concentrated Electrolyte/Charged Surfactant Interface. ChemRxiv 2022, https://doi.org/10.26434/chemrxiv-2022-x8s7x

4.Nayak, S.; Kumal, R. R.; Uysal, A., Spontaneous and Ion-Specific Formation of Inverted Bilayers at Air/Aqueous Interface. Langmuir 2022, https://doi.org/10.1021/acs.langmuir.2c00208

5.Carr, A. J.; Kumal, R. R.; Bu, W.; Uysal, A., Effects of ion adsorption on graphene oxide films and interfacial water structure: A molecular-scale description. Carbon 2022, 195, 131-140.

9:00am **SS2+CA+AS-FrM-3 X-Ray Studies of Extractant and Lanthanide Ion Ordering at Liquid Interfaces Relevant to Solvent Extraction***, **Mark Schlossman,*** University of Illinois at Chicago **INVITED**

Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. Complexation of metal ions with extractants and complexants is believed to take place at or near the organic-aqueous interface, as demonstrated recently by synchrotron x-ray measurements which locate and characterize metal ions and their complexes in the liquid-liquid interfacial region. This presentation will describe recent X-ray studies of model liquid interfacial systems relevant to the extraction of rare earth ions. These results suggest a connection between the observed interfacial structures and the extraction mechanism, which ultimately affects the extraction kinetics.

9:40am **SS2+CA+AS-FrM-5 Probing Surface Chemistry in Complex Environments: Water Disinfectants and Ionic Solutions at the Air/Liquid/Iron Interface***, **Kathryn Perrine,*** Michigan Technological University

Water disinfectants are used to treat pathogens in the water supply, but chlorine is known to react with organic matter to produce toxic disinfectant by-products (DBP). Other disinfectants, such as monochloramine, provide a higher level of disinfection without producing chlorinated DBP's. However, studies have shown that monochloramine can corrode copper and lead surfaces, but little is known for iron-based materials. Iron interfaces are prevalent in soils, minerals, and atmospheric dust, and are known to undergo redox reactions. Iron is a known catalyst in several processes due to its different active sites. Due to the advent of degradation of disinfectants in the water supply, the reaction of monochloramine was investigated on iron interfaces in complex environments.

The interaction of monochloramine was studied at the air/solution/iron interface using *in situ* polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS). These studies are compared with the iron interfaces exposed to aqueous solutions that were used to synthesize monochloramine, NH_4Cl(aq), NaOH(aq), and NaOCl(aq). After exposure to each solution, ATR-FTIR spectroscopy and X-ray photoelectron spectroscopy were used to measure the chemical composition at the interface region exposed to atmospheric O_2 and CO_2 and the region submerged in solution. This builds upon our previous work where we have investigated alkali and alkaline chloride solutions at the air/electrolyte/iron interface. There the anion acts to corrode the surface to produce nucleation sites for carbonate film growth, while the cation influences the mineral film identity and the rate of carbonation from the uptake of CO_2. These findings show that water disinfectants at solution/metal interfaces result in unexpected reactions in complex aqueous systems, which may provide insight for related surface catalytic and environmental processes.

10:00am **SS2+CA+AS-FrM-6 The Surface Chemistry of Martian Mineral AnalogsDuring Triboelectric Charging in Sand Storms***, **Mikkel Bregnhøj**, T. Weidner, K. Finster,* Aarhus University, Denmark

The surface chemistry of the Martian regolith has a significant impact on the atmospheric composition on the Red Planet. For example, methane concentrations vary by a factor of ~3 or more during a Marsian year. Theories based on established photochemical and environmental mechanisms, have so far failed to accurately model the seasonal variation. The currently known gas/solid interfacial chemistry that forms and removes methane from the Marsian atmosphere is insufficient to explain the observed dynamics.

We propose an alternative driver of Martian surface chemistry: wind-driven triboelectric charging of minerals. Sand storms, saltation, and erosion are common phenomena on the Red Planet. In proof-of-principle laboratory experiments, we have shown how Martian mineral analogs can erode each other and induce electric discharges with sufficient energy to (1) ionize and/or dissociate gasses like argon, methane, and carbon dioxide and (2) drive gas/solid interfacial chemistry of organic species present on the surface of these minerals. Using advanced surface spectroscopies (XPS, NEXAFS, etc.) we show how saltation can drastically alter the gas and mineral surface composition. For example, tumbling quartz sand in a methane atmosphere will change the colour of the sand from pristine white to reddish/brown (see attached figure). Using a custom-built container, we also simulate a sand storm with realistic Martian atmospheres and mineral analogs, sealed inside a container made of the very same mineral. In this way, we exclude possible interference effects from the container walls, and come as close to the actual conditions of a sand storm on Mars as is possible on Earth.

10:20am **SS2+CA+AS-FrM-7 Unraveling Water Formation on Planetary and Astrophysical Bodies: The Role of Surface Science***, T. Orlando, **Brant Jones,*** Georgia Institute of Technology **INVITED**

The sources of molecular water in planetary systems is a subject of general interest in astrophysics and astrochemistry and its presence and persistence are critical for life on Earth and for space missions involving long term human exploration.The Moon is the nearest exploration target and sources of water include primordial water, delivery via comets and meteorites, formation and release during small impact events, and solar wind interactions. Our controlled surface science experiments have demonstrated that thermally activated recombinative desorption (RD) or associative desorption (AD) from lunar regolith and other solar wind irradiated grains can be an additional source term for water formation. This involves hydroxyl (-OH) defects made by implantation of solar wind protons. Using several Apollo lunar samples, temperature program desorption (TPD) experiments conducted under ultra-high vacuum conditions yielded first order activation energies for desorption of chemisorbed molecular water and second order activation energies for the RD mediated formation and release of molecular water. Depending on the temperature excursions, RD can occur on a diurnal basis on the Moon and is likely prevalent during impacts with meteorites and meteoroids. This is simulated by laser impact studies followed by state and velocity resolved detection of the photo-produced water. Once formed, the water can either desorb, or be transported on and within the regolith and grain surfaces.Our combined experimental and modeling effort has successfully simulated recent observational data of water on both Mercury and the Moon. Water formation via RD is also likely general under astrophysical conditions that involve proton bombardment followed by thermal excursions (> 400 K), and is critical to the formation of water in star forming regions and in developing strategies for extraction of water for future, sustainable human space exploration missions.

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