

Chemical Analysis and Imaging of Interfaces Focus Topic Room A105 - Session CA2+AS+LS+NS+SS+VT+MoM

Environmental and Energy Interfaces

Moderators: Xiao-Ying Yu, Oak Ridge National Laboratory, USA, Musahid Ahmed, LBNL

10:40am **CA2+AS+LS+NS+SS+VT+MoM-8 Probing hydrogen bonding in aerosols, and solutions with X-Ray and vibrational spectroscopy, Musahid Ahmed, LBNL** INVITED

Hydrogen and non-covalent bonding drive myriad processes which have enormous ramifications in molecular growth in soft systems. For instance, subtle changes in pH can drive dramatic changes in assembly processes relevant to biology, while a few degrees of change in temperature leads to enormous changes in plastic crystals, a phase change material (PCM) – systems of significant importance in thermal science. At Berkeley lab, we have developed an integrated suite of both synchrotron (X-Ray) and non-synchrotron-based (vibrational-THz, IR, Raman) spectroscopic techniques coupled with micro-reactors and aerosol beams to establish a molecular-level understanding of bonding & dynamics in heterogeneous systems.¹⁻³

Deep eutectic solvents (DESs), an important class of solutions, are considered as alternatives to conventional organic solvents and ionic liquids in many applications because they are highly biodegradable and renewable. DESs consist of a hydrogen bond donor and an acceptor and the ability to tune these hydrogen bonds to target required properties is what makes them attractive. At specific compositions, these forms a eutectic mixture which resemble many characteristics of ionic liquids and organic solvents thanks to its complicated inter and intramolecular hydrogen bonding network. Connecting PCM's and DES's are hydrogen bond networks and the changes impacted on it by including inorganic salts, which can be extended to build hydrogen bonded organic frameworks (HOF). Beyond enormous potential for new materials for energy storage, transport, and carbon capture, the study of HOF dynamics may also answer fundamental and controversial questions on the nature of hydrogen bonding, such as the invocation of anti-electrostatic forces in their formation. In this talk, I will describe new results using Raman spectroscopy coupled to aerosol-based X-Ray spectroscopy to probe such dynamics in choline chloride/glycerol, phosphoric acid and ammonium sulfate systems. These results also benefit from electronic structure calculations particularly for X-Ray photoelectron and absorption spectroscopy in providing exquisite insight at the molecular level on structural changes on the nanoscale.

1 Lu, W. *et al.* *Cell Reports Phys. Sci.* **3**, doi:10.1016/j.xcrp.2022.100988 (2022).

2 Weeraratna, C., Amarasinghe, C., Lu, W. C. & Ahmed, M. *JPC Lett* **12**, 5503-5511, doi:10.1021/acs.jpcllett.1c01383 (2021).

3 Weeraratna, C. *et al.* *JPC Lett* **14**, 1279-1287, doi:10.1021/acs.jpcllett.2c03748 (2023).

11:20am **CA2+AS+LS+NS+SS+VT+MoM-10 The Investigation of Degraded Historic Glass Samples Using X-ray Photoelectron Spectroscopy, G. Verhaar, Rijksmuseum, Netherlands; J. Vienes, N. Tennent, University of Texas at Dallas, United States Minor Outlying Islands (the); Amy Walker, University of Texas at Dallas**

The atmospheric deterioration of glass is a well-known phenomenon and is often referred to as glass disease, weeping or crizzling. Understanding this process and the underlying chemical mechanisms are important for a number of industries from preserving historic glass objects in museums to the long-term evaluation of nuclear waste glasses. In this talk we shall discuss the use of x-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA), to examine two fragments of heavily degraded, historic glass objects.

The two glass fragments studied originated from French wineglasses and were made available for destructive analysis by the Corning Museum of Glass. The first fragment originated from c. 1750 and is a potassium rich glass (CMG449). The second fragment was dated c. 1600-1650 and is a sodium rich glass (CMG1050). Using SEM, the thickness of the alteration layers were 60-75 μm and $\sim 30 \mu\text{m}$ for CMG449 and CMG1050, respectively.

Two types of XPS experiments were made. In the first, the surface composition of the glass fragments was examined. Second, a non-destructive cross-section analysis was performed by rotating the sample by 90° and data taken across the fracture surface providing a depth profile through the degradation layer. For example, for CMG449 an increase in the

abundance of K, Na and was observed in the first $\sim 100 \mu\text{m}$ in agreement with other studies. For CMG1050, the atomic concentration of Na also increased as a function of depth. Little, or no, K was observed as expected for a sodium rich glass.

Further, the CMG1050 surface composition did not vary across the sample. However, for CMG449 the surface composition did vary across the sample. Three different areas were identified. The outer rim of the glass contained more K compared to the inside of the foot. The middle portion contained less Na, K and Ca overall. This is a result of the manufacture of the glass. During production, the outer rim of the foot was folded over leading to the formation of a thicker rim than the inner foot region. These changes in glass thickness and stress likely lead to the observed changes in chemical composition.

Surprisingly, we also observed carbonates and formates present in the glass; their concentration varied with position and depth across the sample. There are two potential reasons for this observation. First, during the glass manufacturing process the glass melt was not completely calcined and so some carbonate was incorporated into the glass structure. Second these species are the result of aging of the glass and form in a similar manner to the formation of carbonate salts on glass surfaces. Studies are on-going to determine the origin.

11:40am **CA2+AS+LS+NS+SS+VT+MoM-11 Studying Oil-in-Water Emulsion Interfacial Changes Using Static and in Situ Imaging, Xiao-Ying Yu, Oak Ridge National Laboratory**

Bilgewater emulsion formed from the shipboard is regarded as a major pollutant in the marine environment. Bilgewater exists in a stable oil-in-water (O/W) emulsion form. However, little is known about the O/W liquid-liquid (l-l) interfacial evolution. Although some compositional information can be acquired, traditional bulk characterization approach is not capable of capturing the chemical changes at the O/W l-l interface. Surfactants are deemed essential in droplet formation, however, their roles in bilgewater stabilization are not fully understood. We have employed both static and novel in situ scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the evolving O/W interface using a NAVY bilge model for the first time. Optical microscopy was also used to confirm droplet size distribution (DSD) measurements. Our results show that the DSD of bilgewater does not change significantly without the addition of X-100 surfactants at static or rocking conditions. The in situ SEM results show that droplets coagulate even as freshly prepared emulsions. The mean DSD becomes bigger over a short course of twenty-four hours. Furthermore, both oil components and water clusters are shown to evolve over time at the O/W droplet interface by in situ liquid SIMS imaging. Of particular interest to droplet stabilization, the contribution of surfactants to the aged bilge droplets becomes more significant as the droplet size increases. The higher mass surfactant component does not appear on the droplet surface immediately while many lower mass surfactants are solvated inside the droplet. However, such interfacial information is lost when using static SIMS, because the solvent cage is collapsed during sample drying. We have provided the first three-dimensional images of the evolving O/W interface and demonstrated that in situ surface chemical mapping is powerful to reveal the complex and dynamic l-l interface in the liquid state. Our observational insights suggest surfactants are important in mediating droplet growth and facilitating effective separation of bilgewater emulsion. To conclude, our recent findings demonstrate the importance of using in situ molecular imaging to study the evolving l-l interface and offer new insights into the physicochemical changes of emulsions.

Author Index

Bold page numbers indicate presenter

— A —

Ahmed, M.: CA2+AS+LS+NS+SS+VT+MoM-8,
1

— T —

Tennent, N.: CA2+AS+LS+NS+SS+VT+MoM-
10, **1**

— V —

Verhaar, G.: CA2+AS+LS+NS+SS+VT+MoM-
10, **1**

Vienes, J.: CA2+AS+LS+NS+SS+VT+MoM-10,
1

— W —

Walker, A.: CA2+AS+LS+NS+SS+VT+MoM-10,
1

— Y —

Yu, X.: CA2+AS+LS+NS+SS+VT+MoM-11, **1**