Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

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BSc (University of Victoria, 2015)

“Surface Water as a Reporter on the Interfacial Microenvironment During Biomolecular Adhesion to Aqueous Interfaces”

Department of Chemistry

Tuesday, April 20, 2021
9:00 A.M.
Conducted Virtually

Supervisory Committee:
Dr. Dennis Hore, Department of Chemistry, University of Victoria (Supervisor)
Dr. Frank van Veggel, Department of Chemistry, UVic (Member)
Dr. Jay Cullen, School of Earth and Ocean Sciences, UVic (Outside Member)

External Examiner:
Dr. Keng Chou, Department of Chemistry, University of British Columbia

Chair of Oral Examination:
Dr. Christopher Bose, Department of Mathematics and Statistics, UVic

Dr. Stephen Evans, Acting Dean, Faculty of Graduate Studies
Abstract

The roles of solvation and solution conditions during biomolecular and cell adhesion to surfaces are integral to gaining insight into these processes, yet remain poorly understood. Surface-specific nonlinear vibrational spectroscopy is used to characterize the silica–water interface. Sum frequency generation (SFG) experiments revealed the presence of two distinct water populations in the electrical double layer that respond differently to changes in the bulk ionic strength and pH. These results provide a new understanding of the structure of the double layer at silica–aqueous interfaces at high salt concentrations (where a Stern layer is present), which has important implications for biomolecular and cell adhesion to silica. Further SFG experiments, combined with bulk solution measurements and imaging, are then used to study silica surface conditions during the growth of E. Coli. As a result of the high surface charge density of silica, the water structure at the silica–aqueous interface is known to be especially sensitive to pH and ionic strength, and surface concentration profiles develop that can be appreciably different from the bulk solution conditions. We illustrate that, in the presence of growing cells, a unique microenvironment is established near the surface as a result of biopolymers and metabolites accumulating above it. Even in the subsequent absence of cells, these charged exopolymers and osmolytes work to reduce the interfacial ionic strength as revealed by the enhanced signal from surface water molecules. In the presence of growing bacteria, an additional boost in surface water signal is attributed to a local pH that is higher than that of the bulk solution. Zeta potential measurements of silica beads with adhered bacteria—both normal and those stripped of their extracellular polymeric substances (EPS)—show an increasingly positive trend that suggests an increase in negative surface potential is not responsible for the observed changes in the sum frequency response of interfacial water. In addition, spatial correlation with SFG intensity on the surface reveals that the surface water response is independent of the number of cells adhered, and therefore the surface charge density. Finally, vibrational SFG spectroscopy, in combination with QCM-D, is used to investigate the adsorption of a hydrophobic amino acid (leucine) onto a hydrophobic surface (polystyrene) in water and heavy water. QCM-D experiments showed that more than twice the amount of leucine adsorbed to the surface when in heavy water. When this ratio of adsorbed masses is used in a model of the SFG response, the intensity and appearance of the spectral features are entirely accounted for. This suggests a similar adsorbed structure in the two
solvent environments, highlighting the role solvent plays in dictating the extent of biomolecular adsorption to hydrophobic surfaces, while not altering the adsorbed structure. All of these results provide new insight into surface conditions during biomolecular and cell adhesion to hydrophilic and hydrophobic surfaces, and the important role that solvent plays in mediating these interactions.