Tuesday Afternoon, October 29, 2013

Ions at Aqueous Interfaces Focus Topic
Room: 201 B - Session IA+BA-TuA

Ions and Biomolecules at Aqueous Interfaces

Moderator: J.M. Gibbs-Davis, University of Alberta, Canada

2:00pm **IA+BA-TuA1 Selective Adsorption of Ions to Aqueous Interfaces and its Effects on Evaporation Rates**, ***R.J. Saykally***, University of California, Berkeley **INVITED**

By exploiting the strong charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their interfacial adsorption properties are measured by UV-SHG spectroscopy. Temperature and concentration dependences are determined, with the goal of establishing a complete molecular description of selective ion adsorption. A study of thiocyanate reveals that its strong adsorption is driven by hydration forces and impeded by a novel entropy effect. A study of nitrite indicates adsorption as an ion pair with sodium. Evaporation rates are measured by combining liquid microjet technology and Raman thermometry. The relationship between surface propensities of ions and evaporation rates is investigated. A detailed molecular mechanism for both selective ion adsorption and aqueous evaporation is explored.

2:40pm **IA+BA-TuA3 Exploring Ion Interactions at Aqueous Interfaces**, ***P.S. Cremer***, Penn State University **INVITED**

We have employed a combination of surface specific techniques to interrogate the interactions of ions with self-assembled monolayers and proteins at aqueous interfaces. The results provide direct insight into ion pairing interactions. In particular, I will discuss the behavior of cations and anions as they relate to the Hofmeister series, which is a rank ordering of the efficacy of these species to influence the physical behavior of colloidal and interfacial systems in solution. The TiO_2/water, quartz/water, alkyl chain/water, and air/water interfaces were each explored.

Experiments consisted of a combination of sum frequency generation and thermodynamic measurements. Ion specific effects at these interfaces were found to be determined by several factors. These include the sign and magnitude of the surface potential, ion pairing effects, as well as the presence of polar and nonpolar interfacial moieties. At negatively charged, hydrophilic surfaces, we found that Na^+ adsorption and double layer formation was modulated by the nature of the counterion in solution. For the anions, it was found that SCN^- was less depleted at the interface compared with better hydrated anions such as Cl^-. The same ordering was observed for the anions whether this interface was relatively hydrophobic or hydrophilic. Changing the sign of the charge at the interface also led to a similar Hofmeister ordering. Curiously, the ordering for cations at these aqueous interfaces was found to be more sensitive to the specific surface chemistry. Moreover, at negatively charged hydrophilic surfaces, the smallest and best hydrated cations were mostly favored over more poorly hydrated cations. By contrast, well hydrated cations were repelled from more apolar surfaces. Li^+ displayed somewhat anomalous behavior. All of these results will be discussed with an eye toward a broader model for interfacial partitioning of ions in aqueous solutions.

4:00pm **IA+BA-TuA7 Revealing the Dynamics of Lipid Composition in Phospholipid Bilayers by Sum-Frequency Vibrational Spectroscopy**, ***J. Conboy***, University of Utah **INVITED**

A membrane, only two molecules thick, surrounds all cells and is responsible for controlling the passage of materials in and out of the cell in a selective manner. Our current understanding of the structure and dynamics of cellular membranes emerged in the early 1970's. However, there is still much we do not know about this seemingly simple "shell" which makes life as we know it possible. For example, the location of the negatively charged phosphatidylserine (PS) headgroup lipids has drastic effects on cell function, ranging from coagulation to apoptosis. The localization of PS in one leaflet of the membrane is governed by a complex interplay between kinetic and thermodynamic factors. However, the kinetics of PS exchange has not been studied in detail. Using methods of classical surface chemistry coupled with nonlinear optical methods, we have developed a novel analytical approach, using sum-frequency vibrational spectroscopy (SFVS), to selectively probe lipid compositional asymmetry in a planar supported lipid bilayer. SFVS has been used to measure both the compositional asymmetry and kinetics of PS and phosphatidylcholine (PC) lipid flip-flop in planar supported lipid bilayers composed of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) and 1,2-dihexadecanoyl-sn-glycero-3-phospho-L-serine (DPPS). The transition state thermodynamics of DSPC and DPPS were measured at biologically relevant compositions ranging from 10 to 35 % DPPS. The activation thermodynamics of DSPC and DPPS and their impact on compositional asymmetry will be discussed in detail.

4:40pm **IA+BA-TuA9 Characterization of Protein Secondary Structures at Interfaces Using Chiral Sum Frequency Generation**, ***C.Y. Yan***, Yale University **INVITED**

Characterization of protein secondary structures using vibrational spectroscopy is challenging because of strong vibrational background from water and spectral overlapping of vibrational signatures for various secondary structures. Here, we present chiral vibrational spectra of amide I and N-H stretch of protein backbone in various secondary structures at interfaces obtained by chiral sum frequency generation (SFG) spectroscopy. These spectra show unique signatures for parallel beta-sheets, anti-parallel beta-sheets, alpha-helices, 3-10 helices, and random-coils. Because the chiral SFG spectra are muted to achiral solvent, the N-H stretch can be detected at zero water background. Thus, the N-H stretch frequency can probe local H-bond environments, providing an additional signature to distinguish secondary structures. This allows chiral SFG to resolve secondary structures at interfaces, such as alpha-helices versus 3-10 helices, which elude conventional vibrational methods and circular dichroism spectroscopy. Hence, chiral SFG holds promises to address fundamental and engineering problems in biomedical and material sciences.

5:20pm **IA+BA-TuA11 Order Matters – Detecting Non-Isotropic Structures in Complex Biological Samples**, ***P. Koelsch***, University of Washington

Order is omnipresent in biological systems in various forms and on almost all length-scales. Here we discuss how to use order as a (label-free) contrast mechanism in microscopy or selectivity criteria in surface spectroscopy to detect and analyze non-isotropic arrangements in complex *in vitro* scenarios. Examples are fibrillar structures that can be visualized within tissue via second-harmonic-generation (SHG) microscopy or detected on surfaces via vibrational sum-frequency-generation (SFG) spectroscopy. The contrast mechanism in SHG microscopy is order and similarly is order (and chirality) the selectivity criteria when is comes to SFG spectroscopic measurements on surfaces. Examples to be discussed are fibrillar arrangements within the extracellular matrix of adherent cells on substrates or within cancerous tissue samples.

5:40pm **IA+BA-TuA12 Aqueous Solution Chemistry Studied by Soft X-ray Absorption Spectroscopy**, ***T.Z. Regier***, Canadian Light Source, Canada, *C. Phillips, D. Peak, R. Green, A. Moewes, J. Tse*, University of Saskatchewan, Canada, *A. Achkar, D. Hawthorn*, University of Waterloo, Canada

X-ray absorption spectroscopy is a sensitive probe of transition metal co-ordination and bonding environment. Excitation of 2p electrons into unoccupied 3d orbitals allows for determination of crystal field parameters and ligand field strength. Measurement of the x-ray absorption spectra of Cu and Fe ions in solutions was performed using a continuous flow cell on the SGM beamline at the Canadian Light Source. Fluorescence yields and inverse partial fluorescence yields were measured using a multielement silicon drift detector. The interaction between Cu ions and various organic ligands was studied and the difference between the absorption and fluorescence intensities was examined for aqueous ferrous and ferric solutions.

Authors Index

Bold page numbers indicate the presenter

— A —
Achkar, A.: IA+BA-TuA12, 1
— C —
Conboy, J.: IA+BA-TuA7, **1**
Cremer, P.S.: IA+BA-TuA3, **1**
— G —
Green, R.: IA+BA-TuA12, 1
— H —
Hawthorn, D.: IA+BA-TuA12, 1
— K —
Koelsch, P.: IA+BA-TuA11, **1**
— M —
Moewes, A.: IA+BA-TuA12, 1
— P —
Peak, D.: IA+BA-TuA12, 1
Phillips, C.: IA+BA-TuA12, 1
— R —
Regier, T.Z.: IA+BA-TuA12, **1**
— S —
Saykally, R.J.: IA+BA-TuA1, **1**
— T —
Tse, J.: IA+BA-TuA12, 1
— Y —
Yan, C.Y.: IA+BA-TuA9, **1**