Wednesday Morning, October 4, 2000

Biomaterial Interfaces

Room 202 - Session BI+SS-WeM

Water at Biointerfaces

Moderator: B. Kasemo, Chalmers University of Technology, Sweden

8:20am BI+SS-WeM1 Role of Water in Biological Processes, E.A. Vogler, The Pennsylvania State University INVITED

Water is so familiar and ubiquitous in our environment that we frequently forget, ignore, or underestimate the role its special properties play in the biological and material sciences. Likewise in the hybrid field of biomaterials, where water-surface interactions apparently control and/or moderate the biological response to materials applied in medicine and biotechnology. In fact, the behavior of water near surfaces is becoming increasingly relevant in these fields as surface-to-volume ratios increase with the ever-decreasing size imposed by micro-to-nano-scale analytical and medical devices, especially as applied in nanobiotechnology. This lecture reviews some important water properties from both a thermodynamic and molecular perspective. The occasionally forgotten biological/environmental importance of thermodynamic attributes such as heat capacity, (latent) heats of fusion/vaporization, density, and interfacial tension are briefly recapitulated, leading to the conclusion that terrestrial life simply could not and would not work the way it does without the special mediating influence of water. Molecular aspects that give rise to these important bulk-water properties will be discussed along with the impact these have on the mechanisms of water wetting. It will be suggested that current theories of wetting substantially ignore some of these unique aspects of molecular water that distinguish it from all other room-temperature fluids. Against this backdrop, evidence suggesting that the role of water in the acute biological response to materials has been underestimated will be presented, concluding that the interfacial behavior of water must be explicitly included in any comprehensive biophysical theory attempting to explain or predict performance of biology at aqueous interfaces.

9:00am BI+SS-WeM3 Neutron Reflectivity Studies on the Interaction of Water with Biocompatible Monolayer Films, D. Schwendel, University of Heidelberg, Germany; R. Steitz, Hahn-Meitner Institute, Germany; J. Pipper, R. Dahint, M. Grunze, University of Heidelberg, Germany

Since the early 1990s protein resistance has been obtained for surfaces coated with poly- or oligo(ethylene glycol) (PEG or OEG) derivatives ((CH@sub2@-CH@sub2@-O)@subn@). While the inertness of PEG has been explained by the steric repulsion theory associating the inertness of the polymer brushes with the high conformational freedom of PEG chains in the near surface region, FT-IRRAS studies related the protein resistance of OEG to its molecular conformation. Whereas the helical and amorphous conformers on Au are inert towards protein adsorption, the planar all-trans conformer on Ag does adsorb protein. In Small Angle Neutron Scattering (SANS) studies we found experimental evidence for a strongly bound water layer on helical OEG-terminated alkanethiolate self assembling monolayers (SAMs). The experimental observations have been predicted by ab initio calculations simulating the adsorption of water molecules on methoxy terminated OEG with 3 EG units (EG3-OMe) and Monte Carlo simulations of water close to the SAM surfaces. Both theoretical studies postulate easy accommodation of water at helical OEG strands and a lower density of water near the SAM surface. This strongly bound water film is identified as the physical cause that these surfaces are inert against protein adsorption and cell attachment. SANS studies showed that the data for a hydroxy terminated helical OEG-SAM with 6 EG units (EG6-OH) on Au correlate satisfactorily with the model assuming a boundary water layer of 56 Å at the solid/liquid interface with a density of 92 % of that of bulk water. Also for the investigation of amorphous EG3-OMe immobilized on Au the assumption of a 36 Å water layer with a density of 78 % compared to bulk D@sub2@O yielded a much lower @chi@@super2@ deviation between the experimental data and the fit than the assumption of no interphase water.

9:20am BI+SS-WeM4 Hydrogen Bond of Water in Ih Ice Probed by Corelevel Spectroscopies, *H. Ogasawara*, *D. Nordlund*, *M. Cavalleri*, *L.-A. Näslund*, *M. Nagasono*, *L.G.M. Petterson*, *A. Nilsson*, Uppsala University, Sweden

In biological complexes, DNA, protein and so on, materials consist of two types of chemical bonds. A shorter covalent bond has the strength of a few eV to construct molecular flame, and longer hydrogen bond has the strength of a few tenth meV. This energetically weak nature of hydrogen bond gives flexibility and enables the self-organization of molecules at ambient temperature. Ice is a unique material that hydrogen and oxygen atoms in the crystal are connected both covalent and hydrogen bonds where each oxygen atom has two covalent O-H bonds and two hydrogen O-H bonds. Here we report electronic structure of water in Ih ice, a thin film grown on Pt(111), studied with combination of core-level spectroscopies, X-ray absorption spectrosocpy (XAS), X-ray emission spectroscopy (XES) and theoretical simulation (DFT calculation). The experiments were performed at MAX-LAB, Sweden. The details of the endstation is described elsewhere.@footnote 1@ The theoretical simulation of spectra was done using the deMon program@footnote 2@ XAS and XES results indicate a reconfigration of molecular orbitals of water in ice beside the binding energy shift. In O 1s XAS, 4a@sub 1@ resonance is severely suppressed indicating the enhancement of s-character of this orbital compared to that of the gas phase. In O 1s XES, 3a@sub 1@ emission is suppressed showing the strong s-character of this orbital. From these observations we conclude that a water molecule in ice has a pseudo-totally-symmetric character. This pseudo-totally-symmetric character of water in ice is confirmed by excitation profile of 3a@sub 1@ photoemission peak and theoretical simulation. @FootnoteText@ @footnote 1@ R. Denechke et al, J. Electron Spectrosc. Relat. Phenom. 101-103, 971(1999). @footnote 2@ deMon-KS version 4.0, deMon Software, (1997).

9:40am BI+SS-WeM5 Tyrosine Derivatives Adsorbed on Gold for Surface Modification, K. Uvdal, J. Svensson, P. Konradsson, B. Liedberg, Linköping University, Sweden

Model molecules can be very useful when searching for mechanisms of protein folding. We intend to use model molecules to study if the changed conditions for binding of water, caused by binding and cleavage of ATP, is the main reason for protein conformational changes. In this very first study we are investigating tyrosine derivatives linked to 3-mercaptopropionic acid through an amide bond. Two different tyrosine derivatives, one with the OH group free and one with the OH group phosphorylated are studied. These molecules are adsorbed on gold and studied by X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection-Absorption Spectroscopy (IRAS). The techniques are used to investigate the coordination to the surface and the molecular orientation of adsorbates relative to the surface. Molecular surface interactions causing chemical shifts in the core level XPS spectra of the adsorbates on gold are investigated using multilayer films as references. IR in transmission mode is used as a reference to the IRAS results and thus the surface selection rule is used to identify the orientation of certain vibrations relative to the surface. The S(2p) core level XPS spectrum for the adsorbate of the tyrosine derivative shows only one type of sulfur. The S(2p3/2) peak is shifted about 2.5 eV to lower binding energy when compared to multilayer showing a chemical adsorption through the sulfur atom. A phosphorylated tyrosine derivative adsorbed on gold shows an enhanced signal from PO3 in surface sensitive mode in good agreement with a molecular orientation with the PO3 group pointing away from the surface. The IR spectrum of the tyrosine derivative is showing several strong bands in transmission mode (KBr). Most of these peaks are also strong in the spectrum for the adsorbate. However, some significant differences are observed which are correlated to the molecular orientation relative to the surface. In a second step these monolayers are to be used for water interaction studies.

10:00am BI+SS-WeM6 Stretching of a Macromolecule: A First Principles Theory, H.J. Kreuzer, Dalhousie University, Canada INVITED

The statistical mechanics to describe the stretching of a single polymer strand (in particular in an AFM experiment) is formulated. As ingredients one needs the potential energy surfaces of the various conformers of the macromolecule. These have been calculated for oligo (ethylene glycol) resulting in quantitative agreement for the force/extension curves measured for PEG, both in hexadecane and in water. The interaction of water with PEG is discussed in great detail. We also present results for the effect of strong electric fields on PEG, such as surprisingly large electrostriction.

10:40am BI+SS-WeM8 A Fundamental Approach to Protein Adsorption: Changes in Free Energy for Adsorption of Individual Peptidyl Residues onto Functionalized SAM Surfaces, *R.A. Latour*, Clemson University; *L.L. Hench*, Imperial College, UK

Cellular response to biomaterial surfaces has great importance for the design of bioactive substrates for implant, drug delivery, and tissue engineering applications and is greatly influenced by protein/surface adsorption. All proteins are made up of amino acids (peptidyl residues); thus protein adsorption must be fundamentally governed by the submolecular interactions between a protein's residues and surface

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functional groups. The objective of this research was to develop an approach to quantitatively determine changes in Gibbs free energy for individual mid-chain residue/surface (R/S) functional group interactions and apply it to selected R/S group pairs. Molecular models (MOPAC/COSMO; CAChe software, Oxford Molecular Inc.) were created of 3 residues (Ala, Ser, Lys) and 3 SAM surfaces (CH@sub 3@, OH, COO-) to represent hydrophobic, hydrophilic, and charged systems in an aqueous environment. Adsorption enthalpy for each R/S pair was determined by positioning the residues over the surfaces and calculating the system energy as they were sequentially separated from the surface. Additional enthalpy and entropy contributions due to water restructuring effects were estimated based on changes in solvent accessible surface area and experimental wetting data. This was combined with the modeling data to calculate the net @DELTA@G@sub ads@. Ala was predicted to tightly bind to the CH@sub 3@ surface with @DELTA@G@sub ads@ = -5.8 kcal/mol with Ser and Lys each having @DELTA@G@sub ads@ > 0. All 3 residues exhibited @DELTA@G@sub ads@ > 0 for adsorption to the OH surface. Lys was predicted to be attracted to the COO- surface with @DELTA@G@sub ads@ = -5.4 kcal/mol, but only through intervening water layers with a 5 - 7 Å surface separation distance. Ala and Ser had @DELTA@G@sub ads@ > 0 for their interaction with the COO- surface. Further work is planned to integrate this type of data to develop a universal model for predicting protein-surface adsorption behavior.

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