Phospholipid self-assembly at oxide surfaces

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A critical event in the origin of cellular life involved encapsulation of RNA and other organelles into a membrane envelope [1]. A fundamental question is whether cellular organization occurred preferentially at mineral surfaces. Converesely, certain metal oxides lyse (rupture) cell-membranes whereas others do not [2]. Yet, no coherent model exists to explain the differential organizational versus membranolytic ability of oxides.

Biological cell-membranes are composed primarily of a bilayer of phospholipids and of integral membrane-proteins. We explore, here, whether heterogeneous self-assembly of phospholipids into organized structures (e.g., micelles, bilayers) at mineral surfaces is thermodynmcailly favored relative to homogenous assembly in aqueous solution. We used Isothermal Titration Microcalorimetry to measure the enthalpy of micellization of phosphatidylcholine (PC), a common membrane-phospholipid. In particular, we examined the sorption and micellization behavior of 1,2-dihexanoyl-*sn*-glycero-3-phosphate, where both hydro-carbon chains are six carbons long, at physiological pH 7.2 and 0.1M NaCl ionic strength. The oxides studied include anatase (β-TiO_2), corundum (α-Al_2O_3), and amorphous silica (am. SiO_2).

Preliminary results indicate that the enthalpy of micellization is exothermic for all the oxides studied, becoming less favorable in the order am. SiO_2 > β-TiO_2 > α-Al_2O_3. This sequence is similar, but not identical, to the order predicted by a thermodynamic model based on crystal-chemical and solvation considerations, where it was assumed that the quaternary ammonium moiety of the phospholipid head-group interacts with the oxide surface [3]. Future work includes measuring the micellization entropy and identifying the functional group that interacts with the oxide surface.

References

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Comparative biochemistry of acidiophilic and neutrophilic metal-reducing bacteria

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Summary

Comparative biochemical and physiologic studies have revealed interesting similarities and differences between neutrophilic and extremophilic mineral transforming bacteria. Acidophilic dissimilatory iron-reducing bacteria (DIRB) have not been extensively studied, in contrast to their neutrophilic (i.e. *Geobacter*) counterparts. Acidophiles are important organisms in metal and mineral transformation in acidic environments, and could represent bioremediative agents in metal- and radionuclide-contaminated low pH systems. Our work is focused on the physiology and biochemistry of a representative acidophilic iron reducer, *Acidiphilium cryptum* JF-5. Analytical and preparative methods for isolating and characterizing outer membrane and extracellular polymeric substance (EPS) of *Acidiphilium* and *Geobacter* have been developed. Physiology studies show that *A. cryptum* cells and cell/membrane extracts effectively reduce both Fe(III) and Cr(VI), similar to many neutrophilic DIRB. Preliminary biochemical analysis of Fe(III)-grown *Acidiphilium* shows the presence of several c-type cytochromes in cell surface/EPS extracts, including two high-mass (42 and 48 kDa) outer membrane associated cytochromes c and two ~10kDa cytochromes c. All of these cytochromes have been purified by ion exchange and gel filtration techniques, and spectrophotometric analyses confirm all four proteins contain heme c, with no evidence of other heme types or cofactors. Spectroelectrochemical analysis suggests that some of these proteins are capable of Cr(VI) and Fe(III) reduction *in vitro*. Neutrophilic DIRB also contain a suite of c-type cytochromes, but in much greater overall abundance as compared to *A. cryptum*. Both acidiphilic and neutrophilic DIRB form biofilms when grown on mineral surfaces, although EPS composition probably differs due to enironmental pH. Differences in overall cytochrome and EPS composition may be a result of the pH-influenced availability of Fe(III) substrates.