INTERFACIAL WATER STRUCTURE AND CATION BINDING WITH THE DPPC PHOSPHATE AT AIR /AQUEOUS INTERFACES STUDIED BY VIBRATIONAL SUM FREQUENCY GENERATION SPECTROSCOPY

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Molecular-level knowledge of water structure and cation binding specificity to lipid headgroups at lipid/water interfaces plays a key role in many relevant chemical, biological, and environmental processes. To obtain information on the molecular organization at aqueous interfaces, vibrational sum frequency generation (VSFG) has been applied extensively as an interface-specific technique. Dipalmitoylphosphocholine (DPPC) is a major component of cell membranes and has been used as a proxy for the organic coating on fat-coated aerosols. In the present work, in addition to conventional VSFG studies on cation interaction with the phosphate headgroup moiety of DPPC, we employ phase-sensitive vibrational sum frequency generation (PS-VSFG) to investigate the average direction of the transition dipole moment of interfacial water molecules. The average orientation of water structure at DPPC/water interfaces is inferred. DPPC orients interfacial water molecules on average with their net transition dipole moment pointing towards the surface. The influence of Na^+, K^+, Mg^{2+}, Ca^{2+} is identified in regard to interfacial water structure and DPPC headgroup organization. Ca^{2+} is observed to have greater impact on the water structure and a unique binding affinity to the phosphate headgroup relative to other cations tested. In highly concentrated Ca^{2+} regimes the already disturbed interfacial hydrogen-bonding network reorganizes to resemble that of the neat salt solution interface.