Effects of Size and Polarizability on Ion Partitioning at the Aqueous Liquid-Vapor Interface: a Molecular Simulation Perspective

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Despite a long history of both experimental and theoretical investigations, the microscopic picture of ions at the aqueous liquid-vapor interface remains controversial, particularly with regard to ion partitioning between the bulk fluid and the surface. Despite thermodynamic predictions that the interface should be void of ions, many recent studies demonstrate that certain anions, such as Cl- or I-, seem instead to prefer a surface location. Reasons for this apparent preference remain unclear, but are often attributed to the increasing polarizablity of these ions. While the radius of these ions also increases with the polarizability, little has been said about the effects of size in explaining this phenomenon. In an effort to further explore the driving force of the observed partitioning, we perform configurational-bias Monte Carlo simulations in the Gibbs ensemble to investigate the liquid-vapor interface for neat water and water-ion mixtures at 298 K. We consider two types of ion mixtures: one with ions of varying size all having the same fixed charge (i.e., the same polarizability), and the other with ions of varying polarizabilty all having the same size. By comparing the effects of both ion size and polarizablity, we are able to better understand what role these attributes play in determining ion partitioning. System properties studied include surface tension, interfacial width, coordination number, surface relaxation, and an analysis of hydrogen-bonding at the interface.