Chemical Fractionation at Environmental Interfaces

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Jie Cheng

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Abstract

Chemical processes at the interfaces often differ kinetically and mechanistically from the bulk counterparts, partly due to the concentration inhomogeneity of different chemicals at the interfaces. The fractionation of chemicals at the interfaces not only determines their interfacial concentrations, but also affects the physicochemical properties of the interfaces. In this thesis, three sets of chemicals/interfaces with important environmental implications are studied: (1) anion fractionation at the gas–liquid microdroplet interfaces, (2) fractionation of perfluoroalkyl surfactants and matrix components at the bubble–water interface in ultrasonically irradiated solutions, and (3) ion fractionation across the ice–water interface during the freeze–thaw cycle of electrolyte solutions.

The relative anion affinity for the air–water interface, as measured by Electrospray Mass Spectrometry (ES–MS), is exponentially correlated with ionic radius. The affinities respond differently to different additives, suggesting that specific anion effects are due to different energy levels of physical interactions. Relative anion affinities at the air–methanol interfaces are almost identical to those at the air–water interface, suggesting that surface structure is not the primary driving force for interfacial anion fractionation.

Perfluoroalkyl carboxylates and sulfonates can be transferred from the ocean to marine aerosols due to their high affinity for the air–water interface, but transfer to gas phase is unlikely as they remain deprotonated in aqueous phase because of their low pKa. Organic matrix components may reduce the sonochemical kinetics of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) by competitive adsorption onto the bubble–water interface or by lowering the interfacial temperatures. Inorganic anions, but not cations, may significantly enhance or reduce the sonochemical kinetics of PFOS and PFOA. The

specific anion effects following the Hofmeister series are likely related to anions' partitioning to and interaction with the bubble–water interface.

Time–resolved confocal fluorescence microscopy of freezing electrolyte solutions reveals that the thickness of interstitial liquid films depends non–monotonically on electrolyte concentration. It also confirms that selective incorporation of cations (anions) into the ice lattice decreases (increases) the pH of the interstitial liquid films. Since the magnitude of pH change during freezing is smaller than during the subsequent thawing process, it is likely to be limited by the seepage of H^+ (OH^-) slowly produced via water dissociation.

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