

Chapter 1

Introduction

1.1 Overview of Chemical Fractionation at Environmental Interfaces

Fractionation, is of, relating to, or involving a process for separating components of a mixture through differences in physical or chemical properties. In this thesis, it is occasionally used more broadly to mean partitioning, which emphasizes the separation of a species between different phases. An interface is a surface that forms the common boundary of two different phases. It can alternatively be defined by the concentration inhomogeneity of the different species, whereas the bulk is defined as the region where the species are homogeneously mixed. More broadly, gradients in not only the chemical composition but also in physicochemical properties such as dielectric constant and density are present across the interface, with the boundary values being those of the two phases the interface connects. The thickness of the interface as defined by the gradient can thus vary depending on the specific property in consideration. For example, the water-vapor interface is considered very broad as the water density gradient effectively covers a distance of roughly 0.5 nm.¹

Interfaces provide a unique chemical environment: the kinetics and mechanisms of chemical processes occurring at the interfaces are usually neither identical to nor readily extrapolated from those of the bulk processes. There are many examples in which interfacial chemical transformation is the rate-determining step of a heterogeneous chemical reaction series. The fractionation behavior of chemical species at the interface is important in that it affects not only the interfacial concentration of the chemical species of interest, but also the physicochemical properties of the interface through a variety of specific or nonspecific interactions.

Interfaces play important roles in many physical, chemical, and biological processes, many of which have important environmental implications. In this thesis, I present three independent studies on the fractionation of chemicals at environmental interfaces. The first part describes anion fractionation and reactivity at the air-liquid interfaces. The second part focuses on the partitioning of common groundwater matrix components at the bubble-water interface under ultrasonic irradiation and the effect of partitioning on the sonochemical degradation efficiency of two perfluorinated chemicals. The third part provides direct experimental evidence of the compositional change in the interstitial liquid channels during freezing of electrolyte solutions due to fractionation of ionic species at the ice-water interface.

1.2 Ions at air-water interface

The behavior of ions at aqueous interfaces is important in numerous chemical and biological systems.²⁻³ For example, the distribution and transport of ions at the air-water interface has important implications for heterogeneous atmospheric chemistry in that they affect not only the reactive uptake of gaseous species on aqueous aerosols but also the surface reactivity of ions toward gas phase reactants such as O₃ or OH radical. Understanding the equilibrium and dynamic properties of ions at the air-water interface is thus essential in modeling and even the chemical reactivity in many environmental systems that involve an air-water interface.

1.2.1 Historical view

A traditional view in physical chemistry has it that small ions are effectively repelled from the air-water interface simply due to Coulomb interactions. According to the Born model, the dehydration energy, i.e., the free energy change upon moving an ion from

water to air (vacuum), is $\Delta G = (1 - 1/\epsilon)q^2 / 4\pi\epsilon_0 R$, where $\epsilon \approx 80$ is the dielectric constant of water, ϵ_0 is the permittivity of a vacuum, q and R are the size of charge and radius of the ion, respectively. The large value of ΔG , which is on the order of 10^2 kT for small ions such as Na^+ , forces the ion to stay in bulk liquid. This concept has also been illustrated with a classical image charge model, in which an ion with charge q at the air-water interface can be conceived as being repelled by an image charge with the same sign $q' = q(\epsilon - 1)/(\epsilon + 1)$.

Given a finite ion size and a smooth gradual interface between the two phases, the energy required to bring an ion from bulk water to the water side of the air-water interface is only a few kT,⁴ and may thus be compensated by other interactions that are neglected by the classic models, including ion-water interactions, polarization and dispersion effects, and solvation entropy effects.⁵ In this more complete picture of ion solvation, it is possible for ions to be present or even enriched at the air-water interface.

1.2.2 Simulation results

Molecular simulations such as molecular dynamics (MD) and Monte Carlo (MC) methods can directly probe the molecular details of solutes at the interface. These approaches have been used to examine the equilibrium properties of neat-water surfaces, and the distribution and transport of ions at the air-water interface.⁶⁻⁷ For molecular dynamics simulations, either the classical force-field approach or the *ab initio* approach is employed.⁸ In the former case, the use of polarizable force fields is considered essential for an accurate description of ions at the aqueous interfaces.⁶⁻⁷

The traditional view of ion depletion at the air-water interface has recently been challenged by the results of molecular simulation studies, which predict that certain ions

are present or even enriched at the air-water interface. In particular, MD simulations have suggested that ions such as Cl^- , Br^- , I^- , SCN^- , NO_3^- , N_3^- and H_3O^+ are enriched at the air-water interface to varying degrees, whereas F^- , Na^+ , SO_4^{2-} prefer to stay in the bulk solution.⁹⁻¹⁵ The propensity for ions to reside at the air-water interface is believed to positively correlate with their size and polarizability. In addition, surface curvature also plays an important role in determining the solvation of ions.¹⁶

1.2.3 Experimental results

Results from surface tension and surface potential measurements have been used to infer the microscopic structures at the air-water interface. The surface tension of most aqueous salt solutions has been found to increase with increasing salt concentration.¹⁷⁻¹⁹

According to the Gibbs adsorption isotherm, $\left(\frac{\partial \gamma}{\partial \ln c}\right)_T = -RT\Gamma$, where γ is the surface tension, c is the bulk concentration, and Γ is the surface excess, i.e., the concentration at the air-water interface in excess of the bulk concentration, a positive correlation between the surface tension and electrolyte concentration is often seen as evidence for the depletion of ions at the air-water interface. However, an alternative explanation is that ions may indeed be enriched at the outermost layers of the interface, but depleted in the sublayers due to strong electrostatic repulsion, thus leading to an overall depletion of ions across the interfacial region to which the surface tension measurements are relevant. Surface potential measurements show little correlation with the surface tension measurements.²⁰ Anions play a more important role than cations in determining the sign and magnitude of the surface potential, and anions with smaller hydration energies lead to

lower surface potentials. In addition to the electrostatic effect, ions may also affect the surface potential by changing the orientation of polar water molecules at the surface.

The presence of halides at the air-water interface has been inferred from several laboratory measurements of the chemical reaction kinetics of halogen species. For example, the magnitude of the measured uptake of gas phase Cl_2 and Br_2 by their respective sodium halide solutions, and its dependence on ion concentration suggest a significant role of the reaction at the air-water interface.²¹ The kinetics of chlorine oxidation in sea salt aerosol by hydroxyl radical also suggests that chlorine occupies a significant fraction of the sea salt aerosol surface.¹²

The development of surface specific techniques such as nonlinear optical spectroscopy (vibrational sum-frequency generation, or VSFG, and second harmonic generation, or SHG),²²⁻²⁴ X-ray photoelectron spectroscopy (XPS),²⁵ X-ray diffraction and reflection, and neutron reflection,²⁶ has made it possible to directly probe the molecular details, including the behavior of ions, at the air-water interface. These experimental results are in qualitative agreement with the molecular simulation results, revealing the presence or enhancement of large and polarizable ions at the air-water interface.^{10,25,27} The interfacial depth of aqueous solutions is also found to depend on the electrolyte. For example, the interfacial depth of the NaBr and NaI solutions is observed to be greater than that of neat water, NaF, and NaCl solution, implying that there are concentration gradients of the various species that extend the interfacial region several layers into what was the bulk.

1.2.4 Hofmeister effects

The difference in the preference of ions for the air-water interface versus the bulk liquid phase is an example of specific ion effects, also known as the Hofmeister effects.

The Hofmeister series originally ranked common ions according to their ability to affect protein solubility in aqueous solution, and has since been found relevant to a wide range of interfacial phenomena such as surface tensions to ion exchange resins, zeta potentials, critical micelle concentrations, transport across membranes, and gas bubble-bubble interactions.²⁸⁻²⁹ At the air-water interface, for example, the following order is observed regarding ions' propensity to orient interfacial water molecules: $\text{SCN}^- > \text{NaClO}_4^- > \text{I}^- > \text{NO}_3^- \approx \text{Br}^- > \text{Cl}^- > (\text{pure water}) \approx \text{F}^- \approx \text{SO}_4^{2-}$.³⁰ These effects have been attributed to a wide range of “forces” such as hydration forces, specific pi electron-cation interactions, ionic bonding, hydrogen bonding, and hydrophobic forces,²⁹ but a comprehensive molecular understanding remains elusive.

1.3 Sonochemical degradation of perfluorochemicals at water-bubble interface

1.3.1 Reaction sites and mechanisms in an ultrasonically irradiated liquid

Sonochemistry, the chemical reactivity induced by ultrasonic irradiation in a liquid medium, has emerged as an alternative method for the removal of recalcitrant organic compounds in the wastewater treatment process. The efficacy of sonochemical degradation has been demonstrated for a wide variety of organic compounds such as phenol and phenolic compounds, methyl tert-butyl ether (MTBE), and perfluorinated surfactants.³¹⁻³⁵

The sonochemical effects derive principally from acoustic cavitation, i.e., the formation, growth and implosive collapse of bubbles in a liquid medium under ultrasonic irradiation. When a liquid medium is exposed to ultrasonic irradiation, acoustic pressure waves consisting of compression and rarefaction cycles are produced. During the rarefaction cycle, the acoustic pressure waves lead to the formation and growth of vapor bubbles from preexisting gas nuclei. If the intensity of the acoustic pressure waves exceeds that of the

acoustic cavitation threshold, the bubbles would overgrow and eventually collapse.³⁶ The transient collapse of bubbles leads to almost adiabatic compression of gas and vapor inside the bubbles, thus creating extremely high temperatures and pressures. The average vapor temperatures within the bubble have been shown through chemical methods to reach values as high as 4200–5000 K,³⁷⁻³⁸ consistent with the single-bubble collapse model,³⁹ and bubble-water interface temperatures have been calculated to be in the range of 600 to 1000 K.⁴⁰⁻⁴¹ These transient high temperatures lead to *in situ* pyrolytic reactions in the vapor and interfacial regions of each collapsing bubble resulting in the breakdown of gaseous water molecules to produce highly reactive radical species such as hydroxyl radicals ($\cdot\text{OH}$). These radicals react readily with compounds in the bubble gas phase or at the bubble-water interface. Some of the radical species may be dispersed into the bulk solution by nonspherical bubble collapse. The hydroxyl radicals also recombine rapidly at the bubble-water interface or in the solution bulk to produce hydrogen peroxide and water.³²

Sonochemical decomposition can occur at three potential sites in an ultrasonically irradiated liquid: (1) the cavitation bubble where the temperatures are the highest, (2) the bubble-water interface where temperatures are still high enough to induce thermal effects, and (3) the solution bulk where temperatures are ambient. The target compound can be decomposed at the first two sites via both pyrolytic decomposition and hydroxylation, or in the solution bulk via reaction with hydroxyl radicals and hydrogen peroxide. The sonochemical degradation kinetics and mechanisms of a given compound thus critically depend on its partition coefficient between the solution phase and the liquid phase, and on that between the bulk solution and the bubble-water interface. Sonochemical degradation is effective for the removal of contaminants with high Henry's law constants that readily

partition into the vapor phase of the bubble,⁴²⁻⁴³ and those preferentially partition to the bubble-water interface. Nonvolatile surfactants have been found to undergo pyrolytic decomposition at the bubble-water interface where they are oriented radially with their polar head groups pointing to the bulk solution.⁴⁴

1.3.2 Sonochemical degradation of perfluorinated chemicals

Perfluorinated chemicals (PFCs) such as perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) have been categorized as emerging contaminants. PFOS and PFOA have been consistently detected at pg L^{-1} to low ng L^{-1} in surface waters worldwide,⁴⁵⁻⁴⁸ and at mg L^{-1} in waters near point sources.⁴⁹⁻⁵³ Given their potential environmental and health effects, efforts are underway to establish regulatory standards of PFOS and PFOA in drinking water. The United States Environmental Protection Agency (EPA) recently set short-term provisional health advisories (PHA) for PFOS and PFOA of 0.2 and $0.4 \mu\text{g L}^{-1}$, respectively.⁵⁴

Not only are PFCs persistent in the environment, but they are also recalcitrant to most conventional water and wastewater treatment methods.⁵⁵⁻⁵⁷ Various other treatment techniques have been studied for PFOS and PFOA⁵⁸, among which sonochemical degradation has been shown to be effective. A representative scheme of the sonochemical degradation of PFOS into its inorganic constituents is shown in scheme 1.1. In aqueous solution, perfluorinated surfactants are found to accumulate at the air-water interface with its hydrophobic perfluorinated carbon tail pointing to the gas phase, and its ionic headgroup pointing to the aqueous phase.⁵⁹⁻⁶⁰ Thus the first step of PFOS sonochemical degradation involves its adsorption onto the bubble-water interface, where it then undergoes pyrolytic decomposition via cleavage of the C-S bond. The sulfur trioxide

hydrolyzes to form sulfate, and the fluoro-intermeidates are transformed into C₁ fluoro-radicals via pyrolysis in the bubble vapor phase. The C₁ fluoro-radicals were eventually transformed to CO, CO₂ and F⁻. The sonochemical degradation kinetics depend on the PFC concentration, and on the ultrasound parameters that determine the total bubble-water interface area and the average temperatures of the cavitation bubble and of the bubble-water interface.^{35,61}

To evaluate the application of sonochemical degradation for environmental remediation of aqueous PFCs, it is important to understand the effect of various environmental matrix components, in particular how their fractionation behaviors at the bubble-water interface would affect the PFC degradation kinetics. For example, surface active species may compete with PFCs for the bubble-water interface, and volatile species may affect the composition and thus the temperature of the cavitation bubble.

1.4 Chemical fractionation during freezing of electrolyte solutions

1.4.1 Unfrozen liquid in ice

Ice, in the form of sea ice, ice crystals in clouds, snow, glacier and polar ice, and so on, is an important medium for many chemical and photochemical reactions. The transport and transformation of chemical species in ice actually take place in a small liquid fraction in the form of microscopic films at grain boundaries and ice surfaces.⁶²⁻⁶⁴

Liquid water exists in ice at temperatures below its thermodynamic melting point due to the presence of impurities, the curvature depression of the freezing point known as the Gibbs-Thomson effect, and the formation of disordered quasi-liquid layers at ice-vapor interfaces and grain boundaries, i.e., interfacial premelting.⁶⁵ In polycrystalline ice, liquid water driven by impurity and curvature effects forms a network of microscopic channels

that are approximately 10 to 100 μm in thickness at temperatures near the bulk freezing point.⁶⁶ Bulk ice is also covered by a quasi-liquid layer of variable thickness down to about 240 K.⁶⁷ Many calibrated techniques such as x-ray scattering, atomic force microscopy (AFM), proton scattering, ellipsometry, optical microscopy, attenuated total reflection in the IR (ATR-IR), and photoelectron spectroscopy have been employed to measure the thickness of the quasi-liquid layer, but there is considerable variance between measurements using different techniques.⁶⁸ In addition, the thickness of both the quasi-liquid layer and the grain boundary liquid channels markedly depends on the presence of ice impurities,⁶⁹ although the thickness at a given temperature is not necessarily a monotonically increasing function of the impurity concentration.⁷⁰

1.4.2 Solute rejection and fractionation during freezing

During freezing of most solutions, solutes are mostly rejected from the growing ice lattice and concentrated in the remaining liquid phase.⁷¹⁻⁷³ Impurities in glacial ice are found to be preferentially located at grain boundaries and bubble surfaces.⁷⁴⁻⁷⁵ Even within the liquid layer, solute distribution within microcrystalline ice aggregates is not homogenous, but tends to peak at the triple intersection of grain boundaries. For example, it has been found that the liquid H_2SO_4 is concentrated at the junctions, but that NaCl and its ions could not be detected inside ice crystals. A spectroscopic study revealed that upon fast freezing of an aqueous methylene blue (MB) solution ($c > 10^{-7}$ M) at 77 K, the local concentration at the grain boundaries increased by approximately 3 orders of magnitude relative to the initial bulk concentration, and the concentration rose by at least 6 orders of magnitude upon "slow" freezing at 243 K.⁷⁶

It is also of note that different anions and cations are selectively incorporated into or rather rejected from the ice due to their different structural relationship with the ice lattice.^{72,77-78} For example, NH_4^+ and F^- are preferentially incorporated into ice as substitutional impurities due to structural similarity to H_3O^+ and OH^- , respectively. As a result of solute fractionation at the ice-water interface, the liquid fractions between ice grains are not simply concentrates of the initial solutions.

1.4.3 Electrical and pH changes at the ice-solution interface during freezing

Solute fractionation at the ice-solution interface during freezing may also induce significant electrical and chemical changes. Specifically, the differential partitioning of anions and cations across the water-ice interface during freezing creates a potential difference between the liquid phase and ice phase, whose sign and magnitude depend on the ionic species in the solution, their concentration, and the freezing rate.^{71,79-80} For example, a significant positive potential of liquid with respect to ice was measured during freezing of a dilute NaCl aqueous solution due to the preferential incorporation of Cl^- over Na^+ into the ice lattice.⁷¹ Since the diffusion of ions in ice is very slow,⁸¹⁻⁸² the electrical imbalance across the water-ice interface can relax on a short timescale only via migration of H_3O^+ and OH^- , the highly mobile intrinsic charge carriers of ice.⁸³ This, according to Bronshteyn and Chernov,⁸⁴ will subsequently change the acidity of the remaining liquid in grain boundaries, i.e., preferential incorporation of cations into the ice lattice leads to acidification of the remaining liquid, whereas preferential incorporation of anions has the opposite effect.

The freezing-induced pH change of electrolyte solution due to freeze-concentration and/or freezing hydrolysis has been experimentally confirmed. UV-Vis spectroscopic

measurements of cresol red (CR) in frozen aqueous solution of various acids (HF, HCl, HNO₃, H₂SO₄) showed significant enhancement in CR protonation at the grain boundaries due to increased acid concentration.⁸⁵ Solid-state ¹⁹F NMR chemical shift of 3-fluorobenzoic acid was used to probe the acidity of frozen electrolyte solutions. It was observed that upon freezing, aqueous solution of NaCl became more basic, that of (NH₄)₂SO₄ became more acidic, and that of 2-(N-morpholino)ethanesulfonic acid zwitterion retained its acidity.⁸⁶

Freezing-induced changes in the composition, in particular the increase in solute concentration and change in acidity, of the microscopic channels affect not only the exchange of chemical species between ice and gas phase,^{64,87} but also the kinetics of certain chemical reactions.⁸⁸ Most chemical and physical processes are slowed down since the phase transition radically modifies the reaction microenvironment, but certain reactions can be accelerated in partially frozen aqueous solutions. Examples of chemical reactions whose kinetics have been shown to be significantly enhanced during freezing include the oxidation of nitrate by dissolved oxygen to form nitrate,⁸⁹ the oxidative decomposition of gallic acid,⁹⁰ the photochemical nucleophilic substitution of p-nitroanisole with pyridine,⁹¹ and the reaction between nitrite and iodide to form gas-phase nitric oxide and iodine.⁹² The magnitude of the freezing-induced effect on chemical reaction kinetics is usually a function of temperature, freezing rate, and initial solution composition.

1.5 Outline of the thesis

This thesis consists of relatively independent chapters that fit into the unifying theme of chemical fractionation at environmental interfaces. Chapter 1 provides an overview of

this theme and an introduction to the topics covered in later chapters. Chapters 2 to 8, each focusing on a specific research topic, are reproduced from seven articles published in or submitted to journals such as Environmental Science and Technology and Journal of Physical Chemistry.

Chapters 2 to 3 report the studies on the fractionation and reactivity of simple anions at the air-liquid interface of aerosol droplets. In chapter 2, the relative enrichment factor of a set of anions at the air-water interface of microdroplets, as measured by the electrospray mass spectrometry (ES-MS), is found to correlate exponentially with the ionic radius rather than the polarizability. The dissimilar effects of solution pH, cationic surfactant, anionic surfactant, neutral surfactant, glycerol, and urea on relative anion enrichment factor suggest that different levels of physical forces are at play at the air-water interface.

The work in chapter 2 is extended in chapter 3 to include the large PF_6^- and the highly polarizable IO_3^- species. A strict exponential correlation between relative anion enrichment factor and ionic radius is confirmed. Experiments performed on microdroplets of water/methanol mixtures show that the relative enrichment factor is almost independent of the molar fraction of methanol. The rates of the heterogeneous reaction between the gas-phase ozone and aqueous iodide on water and methanol microdroplets are found to be virtually identical.

In this project, I also collaborated with Dr. Shinichi Enami and Dr. Chad Vecitis on the studies of heterogeneous ozone-anion reactions, which resulted in three coauthor papers that are not included in this thesis: [1] Enami S.; Vecitis C. D.; Cheng J.; Hoffmann M. R.; Colussi A. J. "Global inorganic sources of atmospheric bromine", *J. Phys. Chem. A*, **2007**, 111, 8749, [2] Enami S.; Vecitis C. D.; Cheng J.; Hoffmann M. R.;

Colussi A. J. “Electrospray mass spectrometric detection of products and short-lived Intermediates in Aqueous Aerosol Microdroplets Exposed to a Reactive Gas”, *J. Phys. Chem. A*, **2007**, 111, 13032, and [3] Enami S.; Vecitis C. D.; Cheng J.; Hoffmann M. R.; Colussi A. J. “Interfacial chemistry of aqueous S(IV)/iodide aerosol microdroplets in gaseous ozone”, *Chem. Phys. Lett.*, **2008**, 455, 316.

Chapters 4 to 7 describe a variety of interfacial processes pertaining to the transport and transformation of perfluoroalkyl surfactants such as PFOS and PFOA in the environment. In chapter 4, relative enrichment factor at the air-water interface for the perfluoroalkyl carboxylates and sulfonates of different carbon chain length, as measured by electrospray mass spectrometry, positively correlates with carbon chain length. Perfluoroalkyl sulfonates are found to be more highly enriched at the air-water interface than perfluoroalkyl carboxylates of the same carbon chain length, as the sulfonate head group is less well hydrated than the carboxylate. A hyperbolic rather than linear correlation between the logarithm of enrichment factor and chain length is due to conformational restrictions. The study suggests that marine aerosols produced from contaminated ocean surface waters may be highly enriched in these perfluoroalkyl surfactants. My role in this study was to conduct part of the experiments and to edit the manuscript.

Chapter 5 seeks to determine the acid dissociation constants, i.e., pKa values, of perfluorooctanoate (PFO) and perfluorooctanesulfate (PFOS). An acid-base titration method based on electrospray mass spectrometry is developed to determine the pKa values for chemicals that are sufficiently surface active yet poorly soluble in water, and is validated with two carboxylic acids (C₆ and C₈). Although PFO is observed to form a

very stable $(\text{PFO})_2\text{H}^-$ cluster at low pH, the pKa values of PFOS and PFOA are both well below 1.0, suggesting that the species will remain deprotonated and therefore non-volatile under environmentally relevant conditions.

Chapters 6 and 7 describe the effects of matrix components on the sonochemical degradation kinetics of two perfluoroalkyl surfactants, PFOS and PFOA. The study has important implications for the application of sonochemical techniques in the environmental remediation of these chemicals. Since the sonochemical degradation of PFOS and PFOA is actually via pyrolysis at the bubble-water interface, the fractionation of both the target compounds and the various other matrix components at the bubble-water interface can markedly affect the sonochemical reaction kinetics. In chapter 6, it is found that organic compounds in environmental matrices may reduce the sonochemical degradation rates of PFOS and PFOA by competitive adsorption onto the bubble-water interface or by lowering the average interfacial temperatures during transient bubble collapse events. The magnitude of the negative effect positively correlates with the Langmuir adsorption constant, the Henry's law constant, the specific heat capacity, and the total endothermic heat of dissociation of an individual compound.

Chapter 7 focuses on the effect of common groundwater anions and cations on the sonochemical degradation kinetics of PFOS and PFOA. The effect of anions follows the Hofmeister series; the more-surface-active species enhance the reaction rate, whereas the better-hydrated species have the opposite effect. In contrast, cations have much less pronounced effect than anions over the same concentration range. Initial solution pH enhances the degradation rates of PFOA at 3, but has negligible effects over the range of

4 to 11. The observed inorganic effects on sonochemical kinetics are hypothesized to be due to ions' partitioning to and interaction with the bubble-water interface.

In addition to the perfluorochemical remediation work presented in this thesis, I have collaborated with Dr. Chad Vecitis, Dr. Hyunwoong Park, Dr. Yajuan Wang, and Dr. Deming Zhao on the study of perfluorochemical removal in pure water and other matrices such as the aqueous film-forming foam (AFFF), using sonochemical degradation, photocatalytic reduction, and granular activated carbon (GAC) adsorption. Below is a list of related coauthor papers that have been published but are not included in this thesis: [1] Vecitis C. D.; Park H.; Cheng J.; Mader B. T.; Hoffmann M. R. "Kinetics and mechanism of the sonochemical transformation of perfluorooctane derivatives, PFOS and PFOA, into primary inorganic constituents", *J. Phys. Chem. A*, **2008**, 112, 4261, [2] Vecitis C. D.; Park H.; Cheng J.; Mader B. T.; Hoffmann M. R. "Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces", *J. Phys. Chem. C*, **2008**, 112, 16850, [3] Park H.; Vecitis C. D.; Cheng J.; Mader B. T.; Hoffmann M. R. "Reductive defluorination of aqueous perfluorinated surfactants: effects of ionic headgroup and chain length", *J. Phys. Chem. A*, **2009**, 113, 690, and [4] Vecitis C. D.; Park H.; Cheng J.; Mader B.T.; Hoffmann M. R. "Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA)", *Front. Environ. Sci. Engin. China*, **2009**, 3, 129. Two more related papers are in print.

The final chapter concerns the fractionation of ions at the ice-water interface during freezing of dilute aqueous electrolyte solutions. Time-resolved confocal fluorescence microscopy is used to monitor the composition, in particular the pH, of the interstitial liquid films in freezing electrolyte solutions. The dependence of the liquid film thickness

on electrolyte concentration is observed to be non-monotonic. In addition, moderate pH changes (± 0.4 pH) in the microscopic liquid channels are observed during freezing of dilute aqueous NaCl and NH₄Ac solutions, respectively, whereas more dramatic pH changes ($> \pm 1.0$ pH unit) are observed during the thawing process, suggesting that the pH change is limited by the relatively slow process of water dissociation. The results corroborate the theory of freezing hydrolysis by Bronshteyn and Chernov.⁸³

1.5 References

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Scheme 1.1. A representative scheme of the sonochemical PFOS transformation into its organic constituents. The inorganic products are highlighted in purple boxes.

