

ABSTRACT

THESIS: Adsorption and Orientation Analysis of *p*-Nitrophenolate at Air/Aqueous Interfaces

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PAGES: 60

Numerous chemical processes occur at the interfacial region. This region is characterized as a molecularly thin region between two bulk phases. Examples of air/aqueous interface include surfaces of environmental water, rain droplets, and aerosol particles in the atmosphere. Often the interfacial chemistry is different from the chemistry in bulk solution. Thus, it is of fundamental importance to understand behavior at such interfaces.

In this thesis, surface second harmonic generation (SHG) spectroscopy has been utilized to study orientation of *p*-nitrophenolate ($p\text{-NP}^-$) as a function of its surface coverage at the air/aqueous interface. $p\text{-NP}^-$ is a small organic anion and an aquatic contaminant. Recent studies have shown $p\text{-NP}^-$ to be present at the air/aqueous interface. Previously, our group has shown the orientation of $p\text{-NP}^-$ changes with respect to the surface normal as its surface number density is increased. This contrasts with no orientation change for the neutral *p*-nitrophenol at the air/aqueous interface. Herein, this intriguing variation of $p\text{-NP}^-$ orientation at the air-aqueous interface has been further probed in the presence of a zwitterionic lipid at the air/aqueous interface and at the aqueous surface of various electrolyte solutions. Photolysis of $p\text{-NP}^-$ at the air/aqueous interface has also been performed in the presence of H_2O_2 .

It is revealed that the lipid monolayer restricts the orientation angle change of $p\text{-NP}^-$ as a function of surface population. This orientation angle at the DPPC- $p\text{-NP}^-$ interface was found to be 30° ca. with respect to the surface normal. Electrolytic environments of 1M and 2.5M NaCl solutions of $p\text{-NP}^-$ were also investigated. In comparison to the neat air/aqueous interface, the

orientation angle of $p\text{-NP}^-$ at the air/electrolyte solution interface was found to be aligned at a shallower angle for the low $p\text{-NP}^-$ concentration range. However, the orientation angle also showed variation with respect to the surface normal as surface population of $p\text{-NP}^-$ increased. The range of this change was more pronounced than that of $p\text{-NP}^-$ at the neat air/aqueous interface. The variation in the orientation of $p\text{-NP}^-$ exhibited an enhancement with increasing electrolyte concentration. To corroborate results of 1M and 2.5M NaCl solutions and their effect on the orientation of $p\text{-NP}^-$ at the air/aqueous interface, solutions of 1M and 2.5M NaBr were also investigated. It was found that 1M NaBr increased the degree of orientation change in $p\text{-NP}^-$ compared to 1M NaCl solutions, suggesting an interaction between the halide ion and $p\text{-NP}^-$ at the aqueous interface. This is consistent with the findings that the more polarizable the halide ion the greater its propensity at the surface.

Photolysis of $p\text{-NP}^-$ with H_2O_2 has been investigated at the air/aqueous interface. It has been found that the solutions of $p\text{-NP}^-$ and H_2O_2 have SHG intensity decreasing over time. When subjected to UV irradiation SHG intensity remains constant. This peculiarity eliminates the ability to describe $p\text{-NP}^-$ photo-degradation at the air/aqueous interface but does highlight a possible H_2O_2 buildup at the surface of the solution.