Methodology for Studying Physical and Chemical Properties of the Air/Water Interface by Observing Excitation and Emission Spectra of Adsorbed Soluble Molecules with a Confocal Fluorescence Microscope

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論文題名：Methodology for Studying Physical and Chemical Properties of the Air/Water Interface by Observing Excitation and Emission Spectra of Adsorbed Soluble Molecules with a Confocal Fluorescence Microscope (水面吸着した可溶性分子の共焦点蛍光顕微鏡を用いた蛍光励起・発光スペクトル観測による水面の物理化学特性研究の方法論)

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論 文 内 容 の 要 旨

The air/water interface is a universal but unique region. It is of great importance to understanding the air/water interface in physical, analytical, and environmental chemistry. Some physical and chemical properties of the air/water interface, like the pH at the air/water interface, are still controversial. Unlike commonly used surface-selective analytical methods including second-harmonic generation, sum-frequency generation and two-photon ionization, the sensitivity of a confocal fluorescence microscope (CFM) is so high that it enables us to observe the fluorescence emission of water-soluble fluorescent dyes adsorbed at the air/water interface even under the surface density of solute molecules being 1-10^3 molecule/μm^2. However, when it comes to broader and deeper application of studying physical and chemical properties of the air/water interface, there are still large rooms to completely improve the CFM equipment and to modify experimental procedures including theoretical and analytical developments.

In this dissertation, methodology is described for studying physical and chemical properties of the air/water surface by observing excitation and emission spectra of adsorbed soluble molecules with CFMs: a renovated-CFM calibrated and a semi-confocal fluorescence microscope (ScFM). Five chapters are successively developed to contribute to the methodology for understanding physical and chemical properties of the air/water interface, revolving with three central objectives: 1), to develop a CFM equipment in order to obtain a complete and corrected fluorescence spectra of soluble molecules at the air/water interface; 2), to develop a new method for determining pH at the air/water interface; and 3), to develop a ScFM as a new type of CFM for utilizing wavelength-tunable excitation in an ultraviolet region and for observing excitation spectra of soluble molecules adsorbed at the air/water interface. All conclusions in these chapters will significantly contribute to understanding the physical and chemical properties of the air/water interface.

In Chapter 1, backgrounds and objectives are described. Basic knowledge closely correlated was reviewed, including surface chemistry, the air/water interface, spectroscopic methods, tunable lasers, and fluorescence methods. Regarding studying physical and chemical properties of the air/water interface, and analytical methods for studying the air/water interface, research works are summarized, classified, and evaluated. For the CFM and fluorescent probes, fundamental knowledge as well as common research work are reviewed. Based on research works from predecessors, three original, essential and complicated research objectives are proposed.

In Chapter 2, development of a calibrated CFM equipment is described. A complete and corrected fluorescence spectrum of a fluorescent dye (rhodamine B, RhB) adsorbed at the air/water interface is first obtained with the CFM developed. The experimental procedure to acquire such a fluorescence spectrum at the air/water interface is introduced. An updated alignment way proposed; a number of basic parameters for calibration obtained, including the time dependency of fluorescence intensity; the solution concentration dependence of fluorescence intensity; the depth resolution for the CFM; and the optimal data processing, which helps us to know the instrument of the CFM more and better.

In Chapter 3, a highly sensitive method for estimating pH at the air/water interface based on two pH-dependent dyes and the CFM is innovatively proposed. A relationship between the pH at the air/water interface and that in bulk solution is formulated in connection with the adsorption equilibrium and dissociation equilibrium of the dye adsorbed. Two ways for determining the unknown property $pK_{a,surf}$ of RhB molecules at the air/water interface are pointed out. The adsorption properties, the maximum surface density, and the adsorption equilibrium constants are estimated for both cationic and zwitterionic forms of RhB molecules at the air/water interface, with surface-tension measurements. As the basic fluorescence pH indicator, 5-(and-6)-carboxyseminaphthorhodafluor-1 is tried to be applied with this method, and some preliminary results are obtained. Owing to high sensitivity of this new method, this work provides new insight and inspiration for studying the water surface's acidity.

In Chapter 4, in order to observe fluorescence excitation spectra of soluble molecules adsorbed at the air/water interface, especially for aromatic hydrocarbons having no visible light-absorption, a ScFM is originally designed and constructed based on a total internal reflection illumination of tunable monochromatic ultraviolet light from a xenon lamp and a CFM. The theoretical feasibility to obtain fluorescence spectrum of soluble molecules adsorbed at the air/water interface surface-selectively with this microscope is confirmed. The fluorescence spectra of pyrene molecules are observed with this microscope. It is found that pyrene has a weak surface activity for observing fluorescence surface-selectively with the developed ScFM.

In Chapter 5, common conclusions for this dissertation are summarized, with future prospects proposed.