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Title	Molecular structures of soft matter interfaces studied by sum frequency generation (SFG) vibrational spectroscopy [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第11361号
Issue Date	2014-03-25
Doc URL	https://hdl.handle.net/2115/55568
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Aimin_Ge_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

環境物質科学専攻：博士（環境科学）

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学 位 論 文 題 名

Molecular structures of soft matter interfaces
studied by sum frequency generation (SFG) vibrational spectroscopy
(和周波発生(SFG)振動分光法によるソフトマター界面の分子構造に関する研究)

Soft matter interfaces play important roles in the functionalities of soft matter. To understand the relationship between the interfacial structures and functionalities of soft matter, one needs effective interface-specific techniques. As a second-order nonlinear optical technique, sum frequency generation (SFG) vibrational spectroscopy, which has extremely high interface selectivity and sub-monolayer sensitivity, intrinsically meets the requirement. Although there have been many SFG studies on soft matter interfaces, a general relation between the interfacial structures and functionalities of many novel soft matter systems is still not available. In this thesis, the interfacial structures of various soft matter systems including biomedical polymers and biodegradable surfactants have been evaluated by the conventional as well as the phase-sensitive SFG vibrational spectroscopy in combination with other surface characterization methods.

The thesis consists of nine chapters. Chapter 1 gives a brief introduction of soft matter interfaces and a brief review on the recent SFG studies on the interfacial structures of various soft matter systems. Chapter 2 describes a basic theoretical background of SFG technique. Chapter 3 shows the experimental details of the study.

In Chapter 4, the surface reorganization behaviors of various polyrotaxane polymers with α -cyclodextrin (α -CD) terminated by $-\text{OH}$ or $-\text{OCH}_3$ have been characterized by SFG spectroscopy. It was found that the hydrophobic interaction between the $-\text{OCH}_3$ groups of the methylated α -CDs and CH_3 groups of the *n*-butyl methacrylate (BMA) chains forming a hydrophobic domain on the polymer surface after immersion into water. Such structure was not observed on the surfaces of OH-terminated α -CDs and random copolymer containing 2-methoxyethyl acrylate (MEA) side chains, indicating the unique interaction in the methylated α -CDs. The adsorption structures of fibrinogen molecule on these polymer surfaces, which plays crucial roles in platelet adhesion, have been investigated. Fibrinogen molecules adsorb with a densely packed conformation on the hydrophobic domain of methylated α -CDs, in which the binding sites of the protein to platelets are heavily blocked.

This is attributed to the low adhesion level of platelet on its surface.

In Chapter 5, the interfacial structures of fresh and aged polyelectrolyte multilayer (PEM) films made of poly(dialkyldimethylammonium chloride) (PDDA) and poly(sodium 4-styrenesulfonate) (PSS) were characterized by SFG vibrational spectroscopy. It was found that the surface structures of PEM significantly depend on the salt concentrations. The freshly prepared PEM in 1.0 M NaCl solution are well stratified with well-defined interfacial structures. As the salt concentration decreases, the interface of the PEM film becomes fuzzier together with the increase of surface charge density. Both polycation and polyanion components appear on the surface of PEM film prepared in a salt-free solution, similar to that of polyelectrolyte mixture. The aging effect is attributed to the diffusion of the polyelectrolytes in the PEM. The present results suggest that the fresh PEM film, especially for the PEM prepared in salt, is non-equilibrium and will reorganize with aging process.

In Chapter 6, SFG spectroscopy combined with π -A isotherms, surface potential, AFM and XPS measurements have been used to study the monolayers of the biodegradable quaternary ammonium surfactants with amide (QDA) and ester groups (QDE) in the subphase containing different counterions, in comparison with a typical quaternary ammonium surfactant, DOAC. The present results revealed that in the loosely packed monolayers of DOAC, the electric repulsive interaction between the terminal ammonium moieties can be largely reduced by the screening effect of the halide ions in the subphase. Furthermore, the hydrogen bonding between the amide groups in the QDA monolayers plays important roles in forming the densely packing structure. QDE forms the highest packing density of the monolayer among these cationic surfactants to which the flexibility of the ester groups is believed to significantly contribute.

In Chapter 7, SFG and π -A isotherms were employed to study the molecular interactions between a quaternary ammonium surfactant of DOAC and a long-chain deuterated stearyl alcohol (dSA) at the air/water and air/solid interfaces. Thermodynamic analysis based on the surface excess free energy of mixing demonstrates that the two components are miscible in the monolayer. SFG observations demonstrate that molecular packing and conformational ordering of DOAC molecules are significantly improved by mixing with dSA which shows densely packing structure. These results suggest that the dSA has a strong condensing effect on DOAC by reducing the repulsive interaction between the headgroups of DOAC and increasing the van der Waals interaction between the long alkyl chains.

In Chapter 8, a broadband phase-sensitive SFG optical system was built for determination of real and imaginary $\chi^{(2)}$ spectrum at the solid/air as well as solid/liquid interfaces, which provides the direct information about the vibrational modes of the interfacial molecules. The reliability of the present phase measurement method was confirmed by probing the Langmuir-Blodgett films as well as PEM surfaces. The possible applications of the optical setup at soft matter interface in near future have been also addressed.