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Title(English)	The Role of Hydrogen Bonding Interactions in The Interfacial Phenomena Governing Functions and Behaviors of Biomaterials
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Title of thesis:**The role of hydrogen bonding interactions in the interfacial phenomena governing functions and behaviors of biomaterials****Chapter 1: General introduction**

Responses of biological systems on artificial surfaces are often influenced by the phenomena occurring at the interfaces. The interfacial phenomena governing functions and behaviors of biomaterials were investigated by infrared spectroscopy. Self-assembled monolayer of methoxy-tri(ethylene glycol)-terminated alkanethiols (EG3-OMe SAMs) posing bioinert behavior and ureido-derivatized polymers posing thermo-responsive behavior were employed. Employing vibrational spectroscopy methods, changes in hydrogen bonding interactions can be examined. Surface-enhanced infrared absorption (SEIRA) spectroscopy is suitable for investigation of changes in hydrogen bonding interactions of water molecules in the vicinity EG3OMe SAM since it enables analysis of interfacial water and prevent spectra of bulk water. In the case of ureido-derivatized polymers, temperature-dependent attenuated total reflection infrared (ATR-IR) spectroscopy was employed to observed changes in hydrogen bonding interactions that involve functional group of PAU and surrounding water at the phase transition temperature.

Chapter 2: Principles and theoretical aspects of infrared absorption spectroscopy and hydrogen bonding interactions

The principles and theoretical aspects of infrared spectroscopy, spectra analysis, and hydrogen bonding interactions are briefly described.

Chapter 3: Hydrogen bonding interactions of water molecules governing water-induced repulsion in bioinertness of gold-supported methoxy-tri(ethylene glycol)-terminated alkanethiols monolayers

This study clarified the correlation between molecular packing density of gold- and silver-supported self-assembled monolayer of methoxy-tri(ethylene glycol)-terminated alkanethiols (EG3-OMe SAMs) and the mechanisms underlying bioinertness. The molecular packing density affected the behavior of interfacial water, in particular the hydrogen bonding states of interfacial water. The interfacial water with certain states of hydrogen bonds plays important role as a physical barrier that prevent cell adhesion and protein adsorption. EG3-OMe/Ag SAM posed high molecular packing density and exhibited low resistance to protein adsorption and cell adhesion, whereas EG3-OMe/Au SAM posed low molecular packing density and exhibited bioinertness. The analysis of the interfacial phenomena governing bioinertness conducted by surface force and surface-enhanced infrared absorption (SEIRA) measurements suggested the presence of water-induced repulsion originated from interactions between ethylene glycol moieties of the monolayer and interfacial water. SEIRA enabled analysis of hydrogen bonding states of the interfacial water, that were modulated by SAM-water interactions. The interactions were affected by the molecular packing density of EG3-OMe SAM.

These findings contribute to molecular level understanding of mechanisms underlying bioinert behavior of organic artificial materials that are widely employed in biomedical applications.

Chapter 4: Hydrogen bonding interactions of ureido group as the key factor in the phase transition mechanisms of ureido-derivatized polymer posing upper critical solution temperature (UCST) behavior in aqueous solution

In this study, attenuated total reflection infrared (ATR-IR) measurements and first principle calculations were performed to analyze the origin of phase transition of poly(allylamine)-co-poly(allylurea) (PAU) in aqueous solution. Shifts in frequency of CO stretching modes (Amide I) to higher frequency were observed in ATR-IR spectra. Results of first principle calculations employing dimers of ureido models showed that CO stretching modes of ureido without intramolecular hydrogen bonds appeared at higher frequency compared to that of having intramolecular hydrogen bonds. The breaking of intramolecular hydrogen bonds between ureido units of PAU was proposed as the key factor of entropy gain in the phase transition mechanisms. At $T < UCST$, the hydrogen bonding interactions between ureido units of PAU might contribute to the aggregation of polymer. At $T > UCST$, the breaking of the PAU-PAU hydrogen bonds gave more freedom for PAU-water interactions, allowing PAU became miscible in water solution.

Chapter 5: Summary & conclusions

Herein, methoxy-terminated oligo(ethylene glycol) monolayers (EG3OMe SAMs) were employed as the model system to clarify the role of hydrogen bonding interactions in the mechanisms underlying bioinert behavior of artificial surfaces at molecular level. Surface-enhanced infrared absorption spectroscopy (SEIRA) measurements showed that hydrogen bonding networks of the interfacial water were modulated by interactions between water molecules and ethylene glycol moieties of EG3OMe SAMs that strongly depend on the molecular packing density. Behavior of interfacial water, especially the hydrogen bonding states of interfacial water, was responsible in water-induced repulsion that govern bioinertness. The modulated hydrogen bonding interactions of water molecules in the vicinity of bioinert EG3OMe SAM plays important role as a physical barrier in the mechanisms underlying bioinertness. This study also revealed the importance of hydrogen bonding interactions in the phase transition mechanisms of poly(allylamine)-co-poly(allylurea) PAU in aqueous solution. Temperature-dependent IR spectra of PAU in aqueous solution and ab initio calculations for models of PAU showed that the breaking of hydrogen bonding interactions between ureido units of PAU was the key factor in the phase transition mechanisms PAU posing UCST behavior in aqueous solution.