

***In Situ* Adsorption Investigation of Hexadecyltrimethylammonium Chloride on Self-assembled Monolayers by Surface Plasmon Resonance and Surface Enhanced Infrared Absorption Spectroscopy**

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In situ adsorption kinetics of hexadecyltrimethylammonium chloride (C₁₆TAC) on 1-dodecanethiol and 3-mercapto-1-propanol self-assembled monolayers (SAM) was investigated by surface plasmon resonance and surface enhanced infrared absorption spectroscopy. Adsorption from a dilute solution on 1-dodecanethiol SAM proceeded slow after initial fast increase. Adsorption from solutions at medium concentrations converged to a constant value through a maximum at the initial stage. Adsorption at a high concentration above critical micelle concentration became constant without through a maximum. These behaviors indicate the existence of two types of adsorption; one is faster bulk adsorption (physisorption), where excess accumulation sometimes occurs, and another is slower adsorption (chemisorption) being accompanied with rearrangement. Adsorption on 3-mercapto-1-propanol SAM was always slow over the wide C₁₆TAC concentration regions. This implies that the adsorption mechanism of C₁₆TAC depends on chemical structure of thiol.

1. INTRODUCTION

Adsorption and desorption kinetics of molecules on solid substrates is important concerns in many applications and has been explored experimentally and theoretically [1,2]. High attention was for kinetic control of the preparation of self-assembled monolayer (SAM) with high quality, which is one of typical thin films with high ordered array and prepared by the spontaneous chemisorption of molecules onto the metal surface. The kinetics investigations of SAM were carried out by a quartz crystal microbalance (QCM) monitor method, surface plasmon resonance (SPR) spectroscopy, atomic force microscopy, ellipsometry, and attenuated total reflection-surface enhanced infrared absorption spectroscopy (ATR-SEIRA) [1,3,4]. These techniques are applicable to *in situ* investigation of not only general adsorption and desorption kinetics of molecules on solid substrates but also chemical reaction kinetics of molecules with SAM or of antigen-antibody on substrate [1,2,5,6].

One of authors (T. I.) and her collaborator [1] performed the adsorption investigation of 3-mercaptopropionic acid (MPA) on Au surface and of hexadecyltrimethylammonium chloride (C₁₆TAC) on MPA SAM by using ATR-SEIRA. In the present work, *in situ* adsorption kinetics of C₁₆TAC on 1-dodecanethiol and 3-mercapto-1-propanol SAMs are investigated by SPR and ATR-SEIRA. The results are compared with the previous system.

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2. EXPERIMENTAL SECTION

1-Dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$), 3-mercapto-1-propanol ($\text{HS}(\text{CH}_2)_3\text{OH}$), ethanol, and chloroform-d are commercial products. C_{16}TAC ($\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Cl}^-$) was recrystallized from ethanol-acetone mixture.

SPR spectroscopic examination was performed at 30°C on a Biosensor Analytical System (Nippon Laser & Electronics Lab.) [2]. A SAM-coated Au substrate used was prepared from a Au-evaporated glass substrate by treating with ethanol solutions (1 mM) of thiols.

Infrared spectra were recorded at room temperature ($\sim 25^\circ\text{C}$) on a Bio-Rad FTS 575C FT-IR Spectrometer. SAM was prepared from a chloroform-d solution (7 mM) of 1-dodecanethiol, and infrared reflection absorption spectrum (IRAS), time-resolved ATR-SEIRAS, and ATR-SEIRAS were measured according to the procedure reported before [1]. Time resolved ATR-SEIRAS were also measured for an aqueous solution (0.1 wt %, 3 mM) of C_{16}TAC on 1-dodecanethiol SAM and Au surface. Interferograms were accumulated 256 or 512 times (except time resolution experiment) at 4 cm^{-1} resolution.

3. RESULTS

SPR reflectance angle shifts as a function of adsorption time on 1-dodecanethiol and 3-mercapto-1-propanol SAMs are shown in Fig. 1 for aqueous solutions with different C_{16}TAC concentrations. The adsorption for a 10^{-4} wt% solution proceeded with initial fast and successive slow increases. The equilibrium reached after ~ 5000 sec. On the other hand, the angle shift values for 0.5×10^{-3} and 5×10^{-3} wt% solutions converged to a constant value through a maximum. The maximum was reached at shorter time with larger shift value with increasing the concentration up to 10^{-2} wt%. The angle shift for a solution of 10^{-1} wt%, which is larger than critical micelle concentration (cmc), reached to a constant value (~ 0.06 degree) without through a maximum after the initial increase. The angle shift values at the adsorption equilibrium are consistent with each other for solutions above 0.5×10^{-3} wt%, indicating the saturated adsorption or the Langmuir monolayer adsorption. As seen in Fig. 1(b), angle shifts for aqueous solutions with $(5.0 - 100) \times 10^{-3}$ wt% C_{16}TAC concentrations on 3-mercapto-1-propanol SAM continued to increase even after ~ 5000 sec, although the shift value was highest for a 10^{-2} wt% solution. This indicates that the adsorption equilibrium is not accomplished even after ~ 5000 sec.

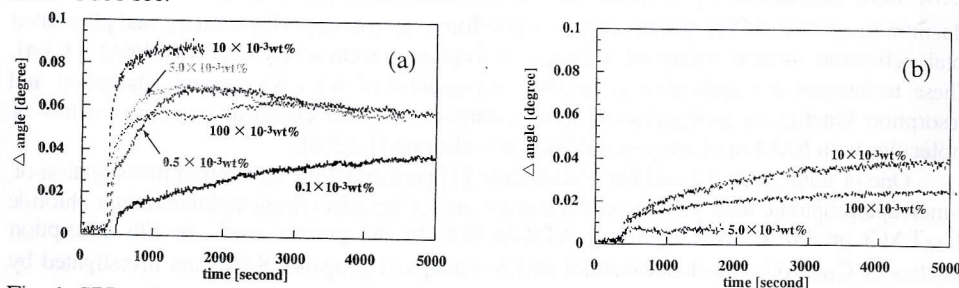


Fig. 1. SPR reflectance angle shifts as a function of time for adsorption from aqueous solutions with various C_{16}TAC concentrations on 1-dodecanethiol (a) and 3-mercapto-1-propanol (b) SAMs.

IRAS was measured for a 1-dodecanethiol SAM on Au surface. Since a SH stretching band around 2580 cm^{-1} disappeared, all observed bands are ascribed to SAM. Four bands were found around $3000 - 2800\text{ cm}^{-1}$ and their wavenumbers and assignments are listed in Table 1. It is suggested from positions of the CH_2 stretching vibration bands that alkyl chains of 1-dodecanethiol in SAM take trans-zigzag configuration. A time-resolved ATR-SEIRA was measured for 1-dodecanethiol adsorption from a chloroform-d solution on Au surface. Absorbance rapidly increased in the initial adsorption and reached to the equilibrium value. Band positions in spectra in equilibrium with solution and of dried SAM were consistent with those of IRAS, as seen in Table 1, indicating no configurational change of molecules in SAM. It should be noted that the absorbance of ATR-SEIRA was 100 time stronger than that of IRAS, suggesting the advantage of ATR-SEIRA for the detection of tiny amount of adsorbed molecules.

Figure 2(a) shows a time-resolved ATR-SEIRAS for C_{16}TAC adsorption from an aqueous 10^{-1} wt% solution on 1-dodecanethiol SAM. The equilibrium was reached at early stage of adsorption. It was estimated from the comparison between spectra before and after adsorption of C_{16}TAC that the contribution of SAM on absorption bands of CH_3 and CH_2 stretching vibration modes is about $1/4 - 1/3$ of total absorbance, indicating the effective adsorption of C_{16}TAC on SAM. Measurement was carried out even on Au surface without SAM. Although both time-resolved profiles were similar to each other, absorbances of CH_3 and CH_2 stretching vibration bands on SAM were 3 times larger than those on Au surface. This indicates the efficiency of the SAM on adsorption of C_{16}TAC . As seen in Table 1, alkyl chains of adsorbed C_{16}TAC have trans-zigzag configuration as well as those of 1-dodecanethiol.

Table 1 Observed IR band positions (cm^{-1})^{a)} and their assignments.

1-dodecanethiol in chloroform-d		C_{16}TAC in H_2O			assignment
IRAS	ATR-SEIRAS	ATR-SEIRAS, with solu.	ATR-SEIRAS, with solu.	ATR-SEIRAS, with solu.	
without solu. ^{b)}	with solu. ^{c)}	without solu. ^{b)}	on SAM ^{b)}	on Au ^{b)}	
2965m	2963m	2961w	2955w	2954w	CH_3 asymmetric stretching
2920s	2914s	2920s	2915s	2917s	CH_2 antisymmetric stretching
2879m	2871m	2873w	2871w	sh	CH_3 symmetric stretching
2850w	2846vw	2852m	2847m	2847m	CH_2 symmetric stretching

a) vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

b) Background is Au substrate. c) Background is chloroform-d.

4. DISCUSSION

The adsorption of C_{16}TAC on thiol SAM depends on molecular species of SAM and C_{16}TAC concentration. It is noticed from SPR reflectance angle shift values that the adsorption of C_{16}TAC proceeds more abundant for 1-dodecanethiol SAM than for 3-mercapto-1-propanol SAM. Since 3-mercapto-1-propanol SAM does not have any specific interaction site with C_{16}TAC , C_{16}TAC on the SAM must be physisorbed. Then the adsorption is less and slow.

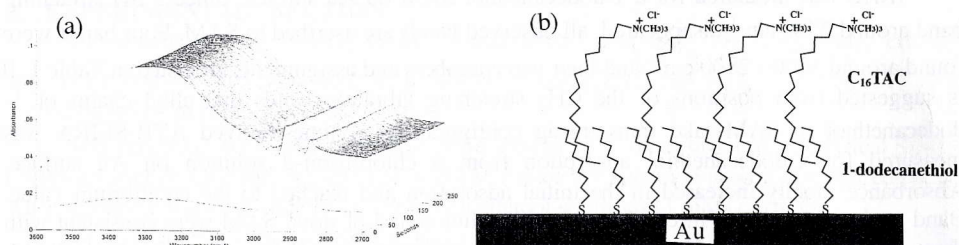


Fig. 2. $C_{16}TAC$ adsorption from an aqueous solution (0.1 wt%) on 1-dodecanethiol SAM. (a) A time-resolved ATR-SEIRAS (125 sets of 4 times accumulation). (b) Schematic presentation of adsorption model at equilibrium.

$C_{16}TAC$ adsorption on 1-dodecanethiol SAM obeys Langmuir monolayer isotherm but not the kinetics. The adsorption mechanism through maximum for the $C_{16}TAC$ adsorption from aqueous 0.5×10^{-3} and 5.0×10^{-3} wt% solutions on 1-dodecanethiol SAM implies the coexistence of chemisorption and physisorption. Physisorption happens at short term (within ~ 1200 second). Then excess physisorbed molecules are desorbed with rearrangement to chemisorption. The schematic adsorption model at equilibrium is shown in Fig. 2(b). 1-Dodecanethiol SAM interacts hydrophobically with $C_{16}TAC$. The equilibrium is accomplished when the monolayer of $C_{16}TAC$ covered hydrophobic SAM surface. $C_{16}TAC$ molecules in the monolayer on SAM have trans-zigzag configuration but do not orient normal to the surface, as estimated from the comparison of CH_2 and CH_3 stretching vibration band intensities.

For $C_{16}TAC$ adsorption on MPA SAM, the fast adsorption at early stage was followed by the slow adsorption [1]. This adsorption accompanied with the transition of MPA SAM to the carboxylate SAM and the ion-pairing of carboxylate SAM and $C_{16}TAC$ by the electrostatic interaction, different from the case of $C_{16}TAC$ adsorption on 1-dodecanethiol SAM.

Kinetics and mechanism of adsorption of hexadecyltrimethylammonium bromide at the interface of negatively charged silica and water were investigated by Pagac et al. [7]. They demonstrated that monomeric surfactants adsorb on silica with a defective bilayer structure at concentrations below cmc, while a close-packed monolayer of micelles is formed on the surface at concentrations above cmc. This is not the present case, because the surface of 1-dodecanethiol SAM is not hydrophilic, and no bilayers and no micelles of $C_{16}TAC$ adsorb.

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