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Interfacial kinetic enhancement of metal ion adsorption on binary mixed self-assembled monolayers

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Abstract

The adsorption of metal ions, a type of surface reaction on binary mixed self-assembled monolayers (SAMs) on a gold surface composed of 1,6-hexanedithiol (HDT) with 11-mercaptoundecanoic acid (MUA), was monitored by *in situ* surface plasmon resonance (SPR) measurements. The differential SPR reflectance (ΔR) enables the kinetics of adsorption of Pt^{2+} on the mixed SAMs to be investigated. Unlike single HDT SAM, kinetic analyses of the mixed SAMs showed that the rate of adsorption of Pt^{2+} was enhanced and that it was highly dependent on the fraction of MUA present. These SPR measurements suggest that the adsorption rate of metal ions can be readily manipulated simply by using mixed SAMs.
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Keywords: Self-assembled monolayers; Mixed SAM; Surface plasmon resonance; Kinetics; Adsorption

1. Introduction

Self-assembled monolayers (SAMs) have been the subject of recent studies because of their potential for scientific and technological applications, which include chemical and biological sensing, the fabrication of molecular devices, and surface patterning [1–3]. Other advantages include their ease of preparation, well-defined structure, and capacity to permit a wide range of functional groups to be incorporated into their constituent molecules. Fine tuning the functionality of SAMs is important for realistically modeling a large variety of interfacial phenomena that are often difficult to study on a bare surface [2,3]. Mixed SAMs, composed of ω-functionalized alkanthiols with different chain lengths and functionalities can be exploited to tune the functionality of SAMs. By adjusting the concentration, type, and spatial distribution of the terminal group of mixed SAMs, the physical/chemical properties of SAMs can be directly regulated [4–7]. Accurate kinetic studies on surfaces require the careful control of surface properties, which is now feasible, because of the availability of mixed SAMs techniques.

The adsorption of heavy metal ions to a functionalized substrate have been extensively studied from the start point of both fundamental interest and applications, such as a hazard assessments of biomaterials in organisms and effective adsorbents for heavy metal ions [8–12]. The nature of adsorbent–adsorbate interactions, adsorption kinetics and thermodynamics form the basis for a broad range of applications. However, the kinetics of adsorption are difficult to qualitatively interpret, due to the complexity of the components, such as the pore geometry of the adsorbent, and the difficulty in devising model systems that permit good kinetic measurements of the reactions [11–13].

Surface plasmon resonance (SPR) spectroscopy, an evanescent wave technique; possessing maximum sensitivity on a surface, which decays exponentially with distance from the metal surface, has been utilized to collect *in situ* adsorption kinetics data because the adsorption of a metal ion on a surface would lead to a change in the local dielectric constant [14–23].

The adsorption of a metal ion to a thiolated surface has been reported to follow a cooperative adsorption mechanism [12,20,21]. This phenomenon is explained by the change induced in the hydrophilictiy of the surface as result of the adsorption. Therefore, in this study, mixed SAMs of 1,6-hexanedithiol (HDT) with 11-mercaptoundecanoic acid (MUA) were fabricated on a gold substrate, in an attempt to

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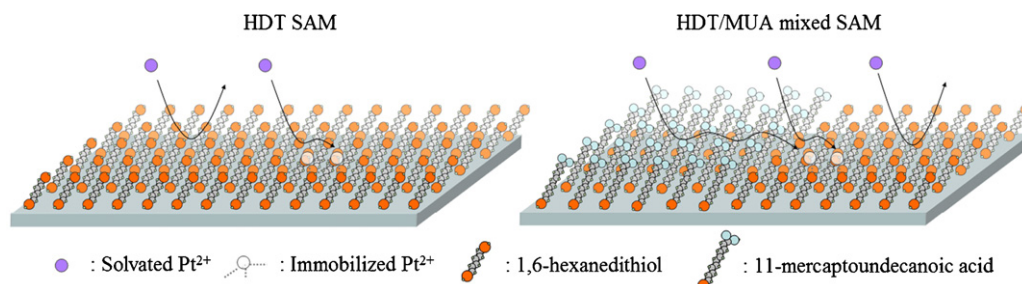 *E-mail address:* jyi@snu.ac.kr (J. Yi).

Fig. 1. Schematic illustration of the proposed mechanism for the adsorption of Pt^{2+} ions to an HDT SAM immobilized surface (left side) and an HDT/MUA mixed SAMs immobilized surface (right side). The thiolated surface is initially hydrophobic, and the approach of a solvated Pt^{2+} ion to the HDT surface is difficult. After the thiolated surface becomes hydrophilic due to the formation of charged $-S^-Pt^{2+}$ moieties, the approach of solvated Pt^{2+} ions to the HDT surface is facilitated. In HDT/MUA mixed SAMs (right side), the surface is partially covered by carboxyl groups at the initial stage. As a result, the surface is initially hydrophilic and attracts positive metal ions via the electric static charge of the carboxyl groups of MUA. Pt^{2+} ions which are attracted by the MUA-rich region on the surface can be readily adsorbed by the thiol functionality of the HDT rich region.

change the properties of the surface into a more attractive moiety for metal ions. The experimental procedures are summarized in Fig. 1, carboxyl groups of MUA on the surface attract metal ions while the inner thiol group of HDT adsorbs them. A thiol functionality was introduced for the adsorption of heavy metal ions and a carboxyl group was employed to attract the metal ions from the solution to the surface.

We observed the adsorption kinetic of metal ions on the surface of binary mixed SAMs immobilized using SPR spectroscopy. Binary mixed SAMs of HDT with MUA were fabricated on a gold substrate, on which the adsorption kinetics could be measured by SPR spectroscopy. Binary mixed SAMs composed of alkanethiols containing different chemical functionalities offer a chemically bi-functional environment for metal ion adsorption [4,5,13,21], and the influence of the surface constituent on the adsorption kinetics of metal ions to the surface were investigated. The surface properties of the mixed SAMs could be controlled by adjusting of the ratios of the individual components in solution, and they induced an enhancement in the kinetics of metal ion adsorption on the surface. This approach can be used to readily control the surface properties and enhance the interfacial kinetics using a mixed self-assembly method.

2. Experimental

1,6-Hexanedithiol (HDT) and 11-mercaptoundecanoic acid (MUA) were purchased from Aldrich and were used without further purification. The water used was purified to above 18 MΩ using a Milli-QTM water system (Millipore). Microscopic slide glasses (1 in. × 1 in. SF10) were used as substrates for further modification and were first cleaned by immersion in a piranha solution ($H_2SO_4:H_2O_2 = 7:3$, v/v). The glass substrates were rinsed several times with the copious amounts of DI water and ethanol and, then, dried under N_2. A 50 nm thin gold film was deposited by a thermal evaporation with a 5 nm Cr adhesion layer.

Binary SAMs of HDT and MUA were prepared by immersing the gold substrates for 15 h in an ethanolic solution of the two thiols, in which the total thiol concentration was maintained at 1 mM (χ is the molar concentration of one

molecule in solution, $\chi_{HDT} + \chi_{MUA} = 1$) The substrates were then rinsed with ethanol and dried in air. The composition of the binary SAMs was controlled by changing the mixing ratios of two thiols in the solution [24].

The prepared binary mixed SAM immobilized substrates were attached to an SF10 prism with index matching oil ($n = 1.730 \pm 0.0005$). A Teflon cell was attached to the substrate, and a prepared metal ion solution allowed to flow into it. A 635 nm He–Ne diode laser (Power Technology Inc.) was p-polarized and collimated with a lens through the prism onto the gold substrate. Both the prism and the gold substrate were mounted on a rotating plate, to permit the angle of incident light to be controlled. Reflectance was measured with a photo-power meter (Oriel). A 0.1 mM aqueous solution of potassium tetrachloroplatinate (K_2PtCl_4, Aldrich) was prepared for the target metal ion (Pt^{2+}). The pH of the aqueous solutions was controlled at 7.

3. Results and discussion

Fig. 2(A)–(C) shows AFM images of binary mixed SAMs of HDT with MUA on Au thin films with various of mole fractions of HDT in the solution (χ_{HDT}). From the AFM images of the mixed SAMs, the major difference in surface morphology between the binary mixed SAM and single SAMs is the appearance of numerous small, isolated islands. As χ_{MUA} is increased, the density of the islands on the surface, referred to as MUA-rich region, increased, as expected. It is thought that hydrogen bonding of carboxyl groups induces the segregated MUA islands on the Au surfaces. The size of the islands is comparable to those of phase-segregated mixed SAMs [4,5].

Image analyses in Fig. 2 show that the areal density of the islands is 7 μm^{-2} ($\chi_{MUA} = 0.1$), 21.75 μm^{-2} ($\chi_{MUA} = 0.5$), and 43.75 μm^{-2} ($\chi_{MUA} = 0.9$), respectively. Thus, the areal density of the MUA-rich region increases as a function of the fraction of MUA in the binary solution. This can be attributed to the similar enthalpy of adsorption of both MUA and HDT despite the differences in chain length and functionality between them. The chemisorption enthalpies of an alkanethiol on gold were reported to be independent of alkyl chain length [25]. This trend is in good agreement with Auger electron spectroscopy (AES)
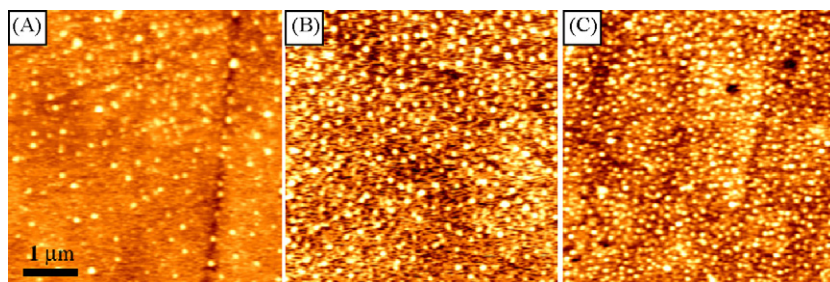
Fig. 2. Topographical AFM images of mixed HDT/MUA SAMs formed on gold substrates from (A) a $\chi_{MUA} = 0.1$ solution, (B) a $\chi_{MUA} = 0.5$ solution and (C) a $\chi_{MUA} = 0.9$ solution. The bright areas, which are the longer carbon chain rich molecular domains, increase with the mole fraction of MUA used in the solution.

analyses. The quantity of oxygen atoms on the surface increases with increasing the MUA fraction.

The change in hydrophilicity of mixed SAMs was investigated by contact angle measurements. The thiol (–SH) in HDT is relatively more hydrophobic than the carboxyl group (–COOH) in MUA. When in contact with a drop of water, the contact angle of the HDT SAM was 86.1°. As expected, when the MUA fraction in the binary solutions was increased, the contact angle decreased to 81.4° ($\chi_{HDT} = 0.9$) and 70.8° ($\chi_{HDT} = 0.1$) [26]. The above results suggest that the surface hydrophilicity changes because the surface composition of the two thiols is controlled by the mixing ratios of HDT and MUA in the solution.

Fig. 3 shows SPR measurements for the adsorption kinetic of Pt^{2+} ions on the prepared SAMs with various mixing ratios. The initial concentration of Pt^{2+} was fixed at 0.1 mM. The kinetics data were collected after the Pt^{2+} solution was allowed to flow in the cell and make contact with the SAM surfaces. It was confirmed that the SPR signal corresponds to the Pt^{2+} ion coverage on the surface [20,21]. From these results, it is clear that the adsorption kinetics of mixed SAMs was significantly enhanced compared with a single SAM. For the case of single SAMs, there are noticeable delays in the adsorption kinetics, compared to that for the mixed SAMs. The degree of enhancement depends on the MUA fraction in the solution. The data in Fig. 3 suggests that the adsorption profile can be distinctively divided into two steps, B and C. In step B, the rate of adsorption increases with time, after which, the adsorption behavior follows the Langmuir type (step C). In step C, a decaying trend in adsorption rate can be seen for the mixed SAMs as well as single SAMs, however, the initial rate of adsorption is different in each case.

It is also clear that, the coverage with time, shown in Fig. 3(C), follows first-order Langmuir adsorption kinetics, and that the adsorption kinetic data can be fit to the following equation [20,21,27]:

$$\frac{d\Gamma(t)}{dt} = k_a C_0 \left(1 - \frac{\Gamma(t)}{\Gamma_{max}}\right) \qquad (2)$$

where $\Gamma(t)$ is the time-dependent surface coverage of the adsorbed Pt^{2+}, Γ_{max} the coverage of adsorbed Pt^{2+} when the adsorption reaches equilibrium, which is assumed to be unity, C_0 the initial concentration of Pt^{2+} in the bulk solution, and k_a is the adsorption constant of Pt^{2+} on a thiolated surface. Fig. 3(C)

shows that the fit of the equation to the experimental data and k_a for each case are as follows: 6×10^{-2} ($\chi_{HDT} = 0.9$), 5.5×10^{-2} ($\chi_{HDT} = 0.1$), 3×10^{-2} ($\chi_{HDT} = 1$) and 2.5×10^{-2} ($\chi_{HDT} = 0$). Assuming that the concentration of Pt^{2+} near the surfaces is the same, the adsorption constants (k_a) for the mixed SAMs are nearly two-fold higher than that for the single SAMs.

The initial adsorption rate, the slope of coverage with time in Fig. 3(B), was calculated to be 4.5×10^{-3} ($\chi_{HDT} = 0.9$), 5.0×10^{-4} ($\chi_{HDT} = 0.1$ and $\chi_{HDT} = 0$), and 2.5×10^{-3} ($\chi_{HDT} = 1$). The initial adsorption rate can be simplified using the equation below, assuming that all of the initial conditions are static:

$$r_{ads} = k_a C_{Pt} S_{surface} \qquad (3)$$

where r_{ads} is the initial rate of adsorption of Pt^{2+} on the surface, C_{Pt} the concentration of Pt^{2+} near the surfaces, and $S_{surface}$ is an area of initially exposed site for Pt^{2+} adsorption.

Using the adsorption constants from Fig. 3(C), the $S_{surface}$, can be estimated from above equation. The calculated adsorption constant, initial adsorption rate and surface of adsorption site are listed in Table 1. The adsorption constants (k_a) of the mixed SAMs ($\chi_{HDT} = 0.1$ and 0.9) are higher than single SAMs ($\chi_{HDT} = 0$ and 1). This indicates that the bi-functionality of mixed SAMs is more attractive for metal ion adsorption. The initial adsorption rates (r_{ads}) of HDT dominant SAMs ($\chi_{HDT} = 0.9$ and 1) are also higher than the other SAMs ($\chi_{HDT} = 0$ and 0.1), indicating that the initial adsorption rate is dependent on the initially exposed HDT composition on the surface. The reason for this is that the thiol end group of HDT works as strong adsorption site for Pt^{2+}. From the results, assuming that the initial C_{Pt} is the same in all cases, the calculated area of an adsorption site is proportional to the molar concentration of HDT (χ_{HDT}) except for the case of MUA. This is well consistent with the results of the AFM image analyses.

The thiol group (–SH) has a high affinity for Pt^{2+} compared with other functionalities, and the adsorption of Pt^{2+} to a thiol

Table 1
Calculated adsorption constant, initial adsorption rate and area of the adsorption site for each experimental case

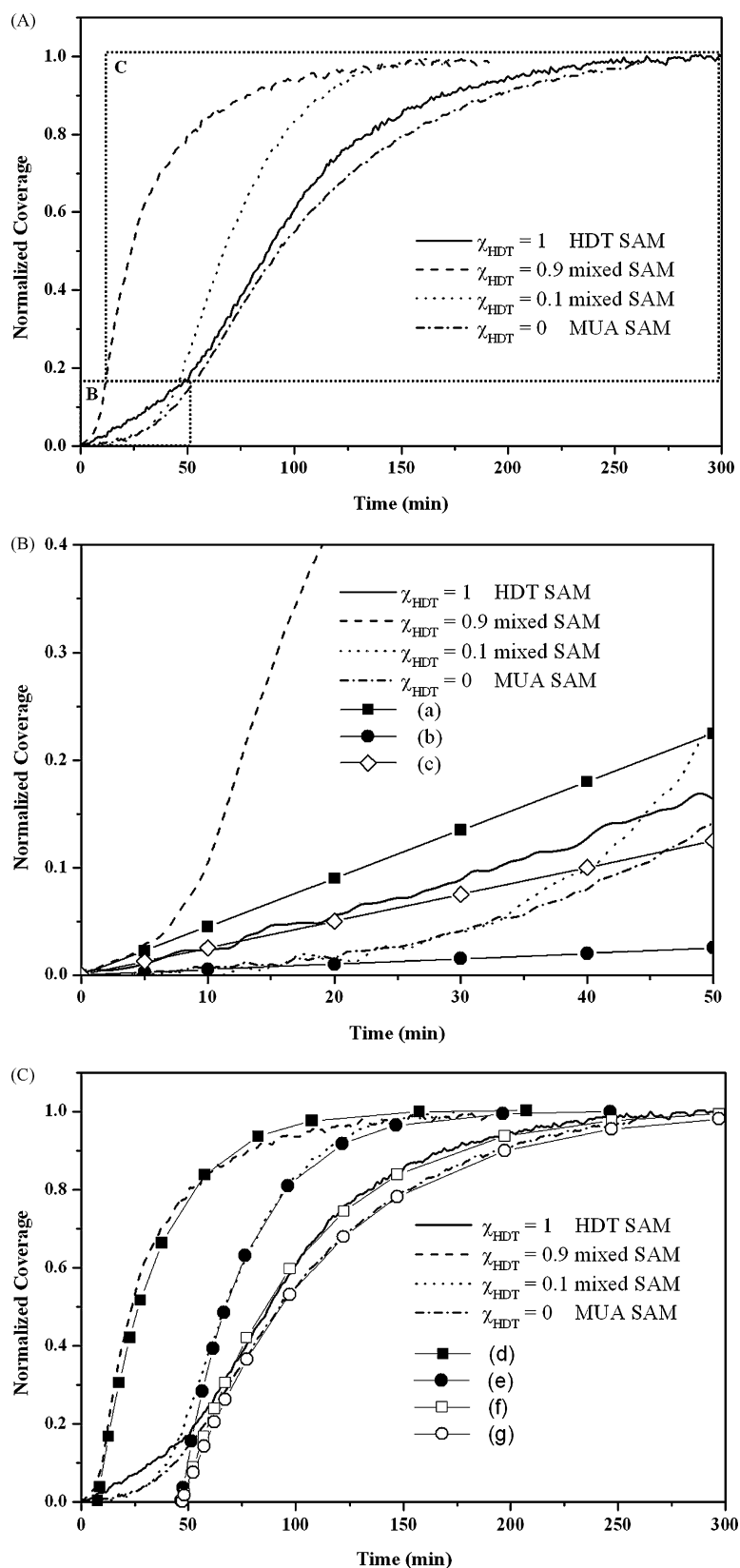| χ_{HDT}	1	0.9	0.1	0
k_a	3.0×10^{-2}	6.0×10^{-2}	5.5×10^{-2}	2.5×10^{-2}
r_{ads}	2.5×10^{-3}	4.5×10^{-3}	5.0×10^{-4}	5.0×10^{-4}
$C_{pt}S_{surface}$	8.3×10^{-2}	7.5×10^{-2}	9.1×10^{-3}	2.0×10^{-2}

Fig. 3. The *in situ* SPR measurements of the adsorption kinetics of Pt^{2+} on an HDT/MUA mixed SAM and single SAM on a gold substrate in an aqueous 0.1 mM Pt^{2+} solution. (A) The adsorption kinetics can be divided into B, in which the initial adsorption rate accelerates with coverage, and C, Langmuirian behavior adsorption. (B) Comparison of *in situ* adsorption data with linear kinetics as a function of initial adsorption rate, r_{ads} of (a) 4.5×10^{-3} ($\chi_{HDT} = 0.9$ mixed SAM), (b) 5.0×10^{-4} ($\chi_{HDT} = 0.1$ mixed SAM and MUA SAM) and (c) 2.5×10^{-3} (HDT SAM), respectively. (C) Comparison of *in situ* adsorption data with first-order Langmuir kinetics as a function of rate constant, k_a of (d) 6.0×10^{-2} ($\chi_{HDT} = 0.9$ mixed SAM), (e) 5.5×10^{-2} ($\chi_{HDT} = 0.1$ mixed SAM), (f) 3.0×10^{-2} (HDT SAM), and (g) 2.5×10^{-2} (MUA SAM), respectively. The adsorption constant for the mixed SAMs is higher than that for single SAMs.

group is known to be a very strong and fast reaction [11,12]. Thus, it is thought that the main adsorption site is the thiol functionality of HDT rather than the carboxyl functionality of MUA in the mixed SAMs.

In case of the MUA SAM, the adsorption capacity for Pt^{2+} was also shown. However, the adsorption ability of MUA for Pt^{2+} is weaker than that for an HDT SAM, and the adsorption kinetics are correspondingly slow.

The enhancement in adsorption kinetics by the binary mixed SAMs can be explained by the adsorption of Pt^{2+} to a thiolated surface. Previous studies reported that the adsorption of Pt^{2+} to a thiolated surface follows a cooperative adsorption mechanism and S-type adsorption behavior [20,21]. The rate of adsorption is accelerated by the hydrophilicity of the Pt^{2+} ion complexed with a thiol group until the surface becomes sufficiently hydrophilic to permit the facile approach of Pt^{2+} to the surface. The kinetics then follows Langmurian behavior because the affinity of metal ions to the surface is not increased after a certain coverage of Pt^{2+} ion complex on the surface. The main reason for these kinetic enhancements for the mixed SAMs is that the carboxyl group of MUA attracts Pt^{2+} ions in water. The electrostatic attraction of the negative charge and the hydrophilictiy of the carboxyl groups induce the facile approach of Pt^{2+} to the mixed SAMs surface compared to the HDT SAM. Therefore, the adsorption kinetics of Pt^{2+} on mixed SAMs is higher than that on the single HDT SAM.

4. Conclusion

In this paper, we examined the kinetic enhancement of metal ion adsorption to the binary mixed SAMs, composed by HDT and MUA, owing to the bi-functionality of the surface. The fabrication of binary mixed SAMs from solutions with a various ratios of HDT and MUA on a thin gold film was exploited. The hydrophilicities and compositions of individual molecules on the surfaces were dependent on the mixing ratios in the solution. Kinetic analyses of the Pt^{2+} adsorption onto the surfaces by SPR measurement confirmed that the adsorption kinetics could be controlled by a surface modification via the use of binary mixed SAMs, and the modified properties were consistent with the kinetics. Thus, kinetic analyses, obtained via SPR measurements are expected to be a useful procedure for understanding the factors that influence interfacial reactions.

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