

Surface wettability and spectroscopic studies on miscibility and ion adsorption of binary biomimetic self-assembled monolayers on gold surfaces

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Abstract—Binary self-assembled monolayers (SAMs) have been much studied due to their high applicable potential as a model of biomimetic surfaces. However, the research about miscibility of binary SAMs has not much been investigated yet. In this work, we focused on analyzing the binary SAMs composed of mercaptohexadecanoic acid (MHA)-hexadecanethiol (HDT) on gold surfaces with Cassie equation, Israelachvili equation, and FTIR spectroscopy to confirm that the binary SAMs are well mixed. As a result, MHA-HDT binary SAMs are considered miscible because the result obtained from FTIR spectra is in good agreement with that calculated by Israelachvili equation for the case that two different molecules are well mixed on the surface. Also, the adsorption of cadmium ions on binary SAMs was confirmed by the appearance of carboxylate stretching bands.

Key words: Self-assembled Monolayers, Binary Miscibility, FTIR Spectroscopy, Surface Wettability

INTRODUCTION

Surface reactivity is known to be highly sensitive to the details of structural and compositional distribution of reactive materials as well as impurities [1-3]. Controlling nano-scale surface properties, including the abundance and the spatial distribution of functional group sites, will give a chance to develop biocompatible biomaterials, biosensors, protein adsorption, and molecular electronics [4,5]. Generally in materials aspects, investigation of chemical properties at the heterogeneous surfaces is more relevant to catalytic systems than that at the homogeneous ones [6,7].

Mixing phenomena at air/water interfaces have been much studied about patch or domain formation when two kinds of materials are mixed because the degree of domain formation is a key factor to control the mechanism for membrane receptor and enzyme activity such as protein patching for cell-cell recognition, ligand binding, transport, catalysis, and transmembrane signaling [8-10]. Meanwhile, fabrication of mixed self-assembled monolayers (SAMs) is another method for making a multicomponent system on a solid substrate. Recently, mixed SAMs have been attracting attention due to their high applicable potential as a model of biomimetic surfaces [11-13].

To investigate lateral steric effects, Lahiri et al. [14] studied the binding of carbonic anhydrase to mixed SAMs composed of benzenesulfonamide as a binding ligand and ethylene glycol groups as a surface matrix. However, they did not demonstrate whether the mixed monolayers are well-mixed or not. Riepel et al. [15] controlled the mixing conditions that lead to optimum binding capacity of streptavidin. Mixed SAMs prepared from loading solutions containing 75-95% of the biotinylated alkanethiol resulted in high

immobilization level of functional streptavidin. Although an addition of inert to original pure surface plays an important role to change the properties of the surface reactivity, the mechanism has not been found because it is very difficult to make a mixed template and analyze up to the molecular level [16,17]. Therefore, many researchers have tried to describe the mixed surface by using molecular simulations [18-20].

In this work, we analyzed the binary SAMs composed of MHA-HDT on gold surfaces with surface wettability (Cassie equation and Israelachvili equation) and FTIR spectroscopic studies. External-reflection (ER) FTIR spectroscopy was used to calculate the composition of monolayer on the mixed SAMs composed of MHA-HDT molecules. Also, the adsorption of cadmium ions to mixed SAMs was confirmed by the appearance of carboxylate stretching bands.

EXPERIMENTAL SECTION

1. Materials

16-Mercaptohexadecanoic acid (MHA; $\text{HS}(\text{CH}_2)_{15}\text{COOH}$; 90%), 1-hexadecanethiol (HDT; $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$; 92%), and cadmium chloride (CdCl_2 ; 99.9%) were obtained from Aldrich and used without further purification. Ethanol used as a solvent was purchased from Fluka (99.8%) and filtered with 0.20 μm (Millipore; millex-FG). Water used in experiments was first distilled and then purified with a Millipore-Q purifying system. The resistivity of final deionized water (DI) was 18.2 $\text{M}\Omega\cdot\text{cm}$.

2. Preparation of SAMs

A thermal evaporator operation at $\sim 10^{-6}$ torr was used to deposit ~ 500 Å of titanium and ~ 100 Å of gold (99.99%) onto silicon wafers (LG siltion; (111) plane). The wafers were stored at room temperature and cut into smaller size (20 mm $\times$ 20 mm) before use. Evaporated gold substrates (Au/Ti/Si) can be cleaned by a brief (5 min) exposure to $\text{H}_2\text{SO}_4/\text{KCr}_2\text{O}_7$ solution (10 : 1 v/v) and washed with DI water for enough time. Binary solutions (MHA and HDT) for self-assembly are prepared in concentration of 1 mM with varying

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composition from 100 : 0 to 40 : 60. Gold substrates were cleaned with filtered ethanol and immersed in the prepared solutions for 2–4 h. Fabricated binary SAMs were immersed into cadmium chloride solution (1 mM) to react. After 30 min, the reacted SAMs were washed with filtered ethanol instead of DI water to avoid sweeping the cadmium ion from binding.

3. Contact Angles and FTIR Spectroscopy

Contact angles were used to study the surface wettability of the binary SAMs on gold surfaces. Contact angles were obtained with a face contact anglemeter CA-DT (Japan, FACE) by a droplet method at room temperature with DI water. All data were averaged by gauging five times. Grazing ER-FTIR spectra were obtained on the FTIR spectrometer, an ambient atmosphere bench (Perkin-Elmer, Spec-

trum GX). All spectra are reported as $\log(R/R_0)$ (i.e., absorbance) vs. wavenumber (cm^{-1}), where R_0 is the reflectivity of a bare gold background substrate and R is the reflectivity of the monolayer/gold sample. The resolution of spectra equipped with liquid nitrogen cooled MCT (mercury cadmium tellurium) was adapted as 8 cm^{-1} ; 256 scans were co-added for good signal-to-noise ratio.

RESULTS AND DISCUSSION

1. Analysis on ER-FTIR Spectroscopic Methodology

Prior to optimizing the conditions of ER-FTIR measurement, it is necessary to understand the incidence direction, the plane of incidence, polarization, and electric field of infrared beam (Fig. 1). Fig. 1(a, b) shows schematically the sort of vibrations that take place. Vibration of plane-polarized light takes place in only one of these possible planes. When the IR beam is irradiated to gold or SAMs on the gold substrates with the normal direction of surface, the angle of incidence is 0° . The incidence plane is defined as the plane composed of incidence direction and reflectance direction. The electric component of the incident field is the perpendicular direction of beam propagation. When the direction of molecular vibration is harmonized with the direction of the electric vector, IR absorption occurs. When plane-polarized light is parallel to the incidence plane, it is called as p-polarized beam (0°). Conversely, when plane-polarized light is perpendicular to the incidence plane, it is called as s-polarized beam (90°) (Fig. 1(c)).

To find the optimum condition, fundamental experiments were operated as follows. First, FTIR spectra of pure MHA SAMs with no-polarization were obtained from varying incidence angles such as Fig. 2(a). As the incidence angle was increased, the intensity of methylene band for MHA SAMs increased at over than 50° . When the incidence direction was near normal, the polarized beam controlled from 0° to 90° was irradiated at near-normal to ensure the effect of electrical field direction. There are not any peaks except the water peak around $3,000\text{--}3,500 \text{ cm}^{-1}$ (Fig. 2(b)). FTIR spectra in case that the incidence beam with grazing angle (75°) is polarized from 0° to 90° are shown in Fig. 2(c). As the angle of polarization (change from p-pol. to s-pol.) increased, the intensity of methylene band decreased. This result is in good agreement with the theoretical one [21]. Therefore, grazing angles over than 75° with p-polarization were chosen to analyze as optimal condition for ER-FTIR measurement.

2. Compositional Analyses of Binary SAMs

2-1. Wettability Analysis Based on Cassie Equation [22] and Israelachvili Equation [23]

In the case of the Cassie equation, heterogeneous surfaces including impurities or polycrystallinity over small length scales can be modeled. Especially, it is presumed that the surface is composed of well-separated and distinct patches or domains. For a liquid droplet on a surface, the Young-Dupré equation [24] is

$$\gamma_L (1 + \cos \theta) = W \quad (1)$$

where γ_L is the surface tension of the liquid and W is the work of cohesion of the liquid with the surface. For two homogeneous surfaces,

$$\gamma_L (1 + \cos \theta_1) = W_1 \quad (2)$$

$$\gamma_L (1 + \cos \theta_2) = W_2 \quad (3)$$

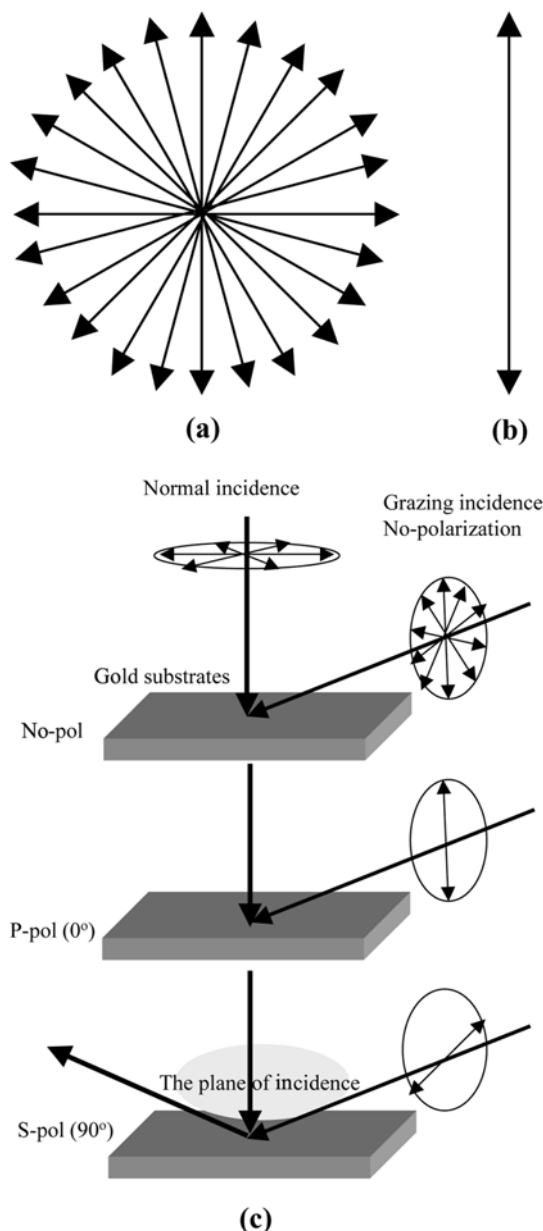


Fig. 1. Schematic cartoons of (a) ordinary light and (b) plane-polarized light, and (c) geometry of incidence plane and polarized light.

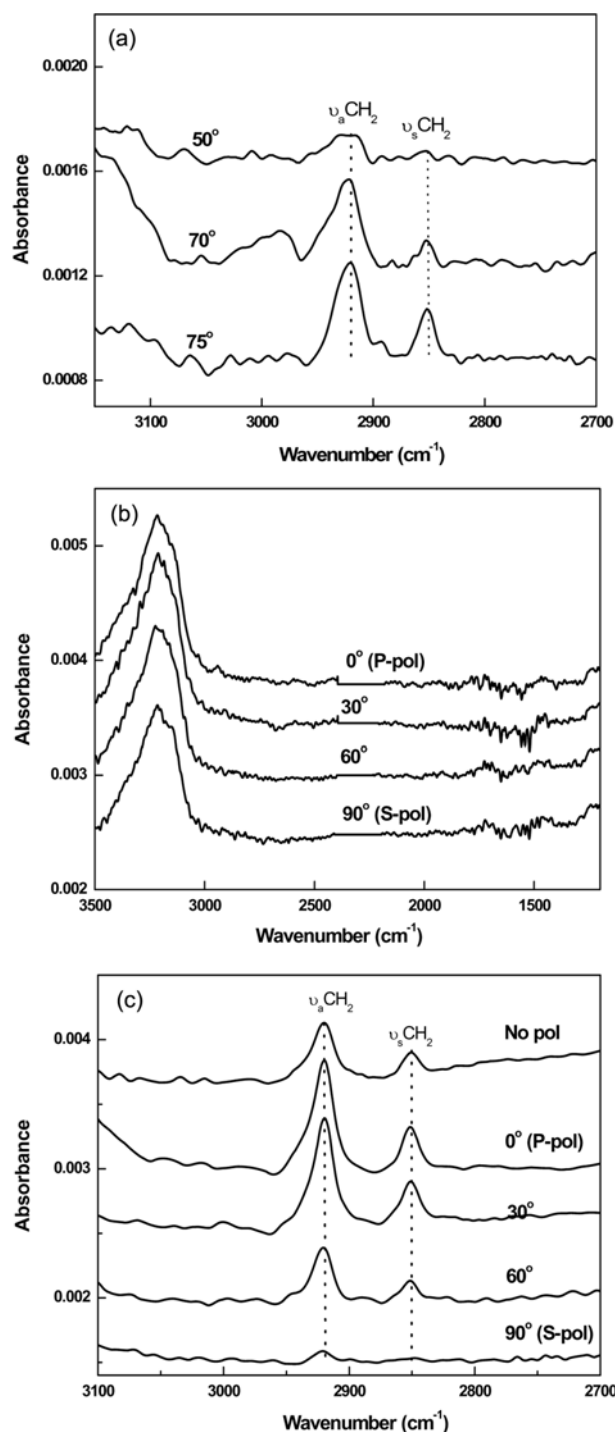


Fig. 2. Optimization of ER-FTIR measurement of MHA SAMs on the gold substrate. (a) Spectra according to varying incidence angle with no-polarization, (b) spectra according to varying angle of polarization at near normal direction, (c) spectra according to varying angle of polarization at grazing angle at 75°.

For a heterogeneous surface composed of patches of 1 and 2,

$$\gamma_L (1 + \cos \theta) = W = f_1 W_1 + f_2 W_2 \quad (4)$$

Where θ is the contact angle of binary monolayers, f_1 and f_2 are the fractional areas of the patches, and W_1 and W_2 are the mean cohe-

sion energies in the patches. When Eqs. (1)-(4) are combined, the Cassie equation can be obtained as follows:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (f_1 + f_2 = 1) \quad (5)$$

Eq. (5) can be adopted only when the binary system forms discrete patches [25].

When the binary system is not in the form of discrete patches, what should be averaged is not the cohesion energy, but rather the polarizabilities, dipole moments, and surface charge from theories of van der Waals and electrostatic forces [23]. For the two homogeneous surfaces and the liquid, these quantities (i.e., polarization, dipole moment, etc.) are denoted by w_1 , w_2 , and w_L , respectively.

$$\gamma_L (1 + \cos \theta) = W_1 \propto \{w_1 w_L\}^{1/2} \quad (6)$$

$$\gamma_L (1 + \cos \theta_2) = W_2 \propto \{w_2 w_L\}^{1/2} \quad (7)$$

$$\gamma_L (1 + \cos \theta) = W = \{(f_1 w_1 + f_2 w_2) w_L\}^{1/2} \quad (8)$$

By combining Eqs. (6)-(8), the final equation is presented as follows:

$$(1 + \cos \theta)^2 = f_1 (1 + \cos \theta_1)^2 + f_2 (1 + \cos \theta_2)^2 \quad (9)$$

This equation is called the Israelachvili and Gee equation [23].

2-2. Spectroscopic Analysis of Binary SAMs Composed of MHA and HDT

Binary SAMs formed by coadsorption of two different thiols (MHA and HDT), which have the same chain length but have different

Table 1. Quantitative results on binary SAMs by various methods

MHA fraction in the sol'n	Ave. contact angle	Calculated MHA composition on the binary SAMs		
		Cassie eq'n	Israelachvili eq'n	FTIR deconvolution
100	13.4°	1	1	1
80	42.6°	0.81	0.74	0.66
60	62.0°	0.60	0.49	0.51
40	79.0°	0.38	0.27	0.33
0	107°	0	0	0

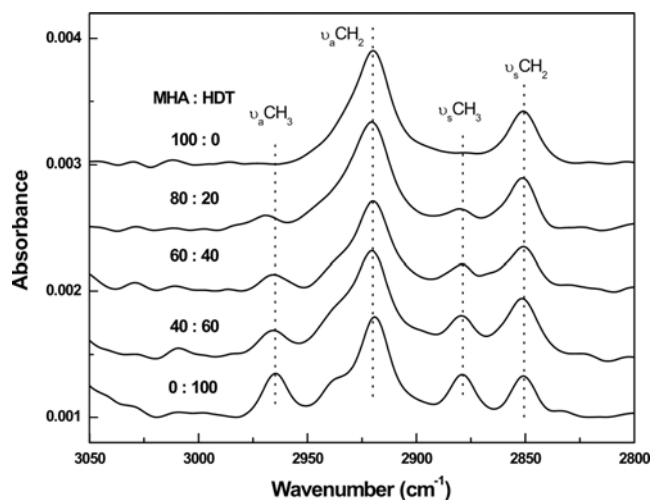


Fig. 3. ER-FTIR results of binary SAMs on the gold substrates according to the composition of MHA and HDT.

head group, were analyzed. Generally, the composition at the binary SAMs after self-assembly is not identical with one in the binary

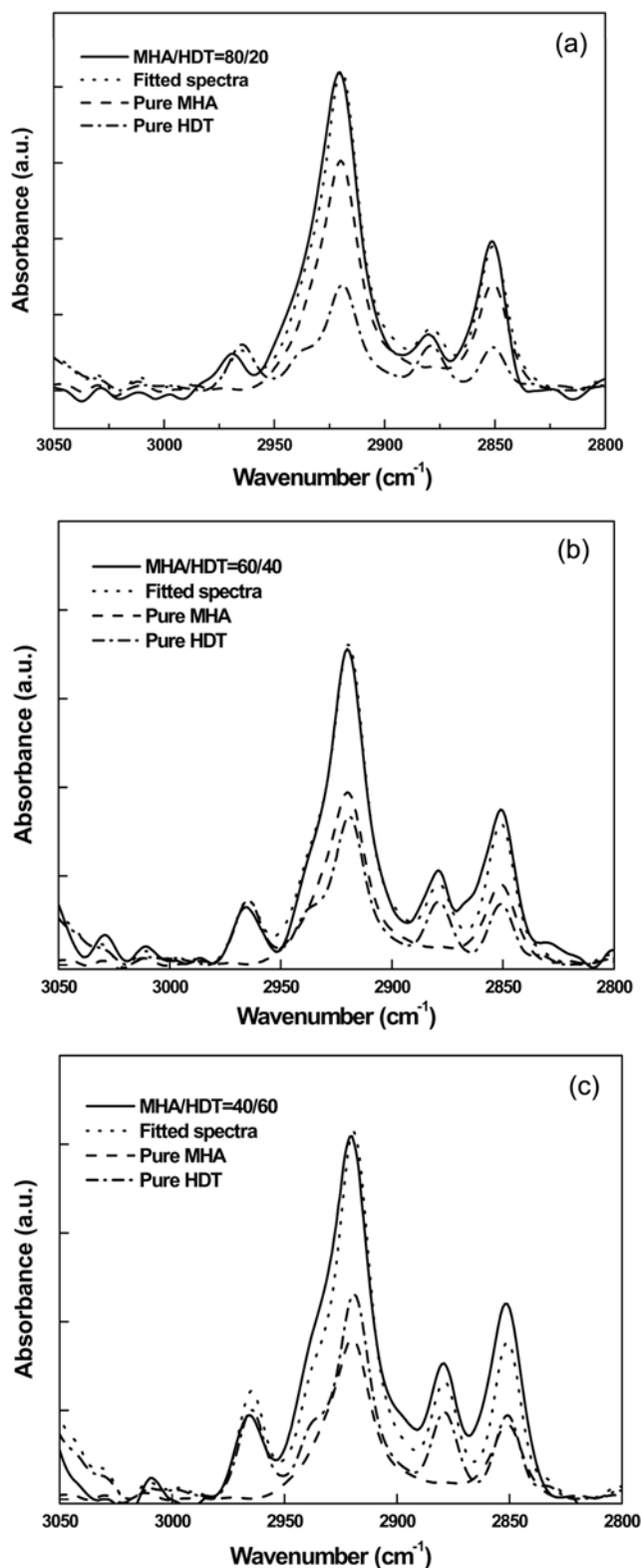


Fig. 4. Peak combination with pure MHA and pure HDT to fit the binary spectra. (a) MHA/HDT=80/20 (molar ratio in the mixed solution), (b) MHA/HDT=60/40, (c) MHA/HDT=40/60.

solution. Therefore, it is necessary to analyze the composition at the binary SAMs. Contact angle SAMs was measured to study surface wettability of the binary SAMs. Surface composition at the binary SAMs was calculated by using the Cassie equation and Israelachvili equation from contact angles. Then these results were compared with those of FTIR deconvolution (Table 1). MHA has a hydrophilic headgroup ($-\text{COOH}$), while HDT has a hydrophobic headgroup ($-\text{CH}_3$). The average contact angles of pure MHA and pure HDT show 13.4° and 107° , respectively [26]. As increasing the moieties of HDT, the contact angle goes up to 107° . C-H stretching region of the grazing ER-FTIR spectra of HDT is different from that of MHA because HDT has methyl stretching band ($-\text{CH}_3$). The composition of the binary SAMs can be analyzed by FTIR deconvolution. There are asymmetric methyl stretching band ($\nu_a\text{CH}_3$, 2964 cm^{-1}), asymmetric methylene stretching band ($\nu_a\text{CH}_2$, 2919 cm^{-1}), symmetric methyl stretching band ($\nu_s\text{CH}_3$, 2879 cm^{-1}), and symmetric methylene stretching band ($\nu_s\text{CH}_2$, 2850 cm^{-1}) in the HDT spectra, while MHA has two peaks, $\nu_a\text{CH}_2$ at 2919 cm^{-1} and $\nu_s\text{CH}_2$ at 2850 cm^{-1} (Fig. 3). As the composition of HDT in the binary solution increases, the intensity of asymmetric and symmetric methyl stretching band appears and gradually increases but the other two peaks maintain original states.

The spectra of FTIR of binary SAMs on gold surface can be decomposed with two FTIR spectra of pure MHA and HDT. The combined spectra were well fitted to the original mixed spectra, as shown in the Fig. 4. Here, CH_2 stretching band for pure MHA or HDT was used as an internal reference for the calibration because immobilized MHA and HDT molecules formed the binary SAMs on the gold substrates. The relative composition (Φ) equation was introduced [27].

$$\Phi_i = \frac{\frac{A_i}{A_{i,P}}}{\frac{A_i}{A_{i,P}} + \frac{A_j}{A_{j,P}}} \quad (10)$$

Where A_i and A_j are denoted as the area of i or j component in the

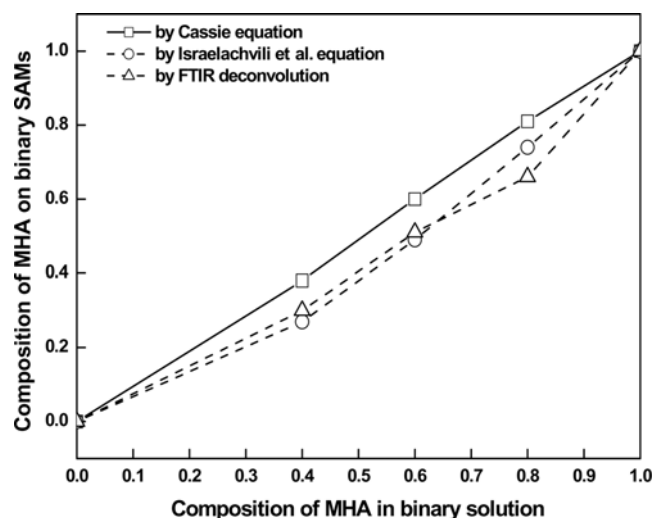


Fig. 5. The results of compositional analysis by surface wettability and FTIR spectroscopy.

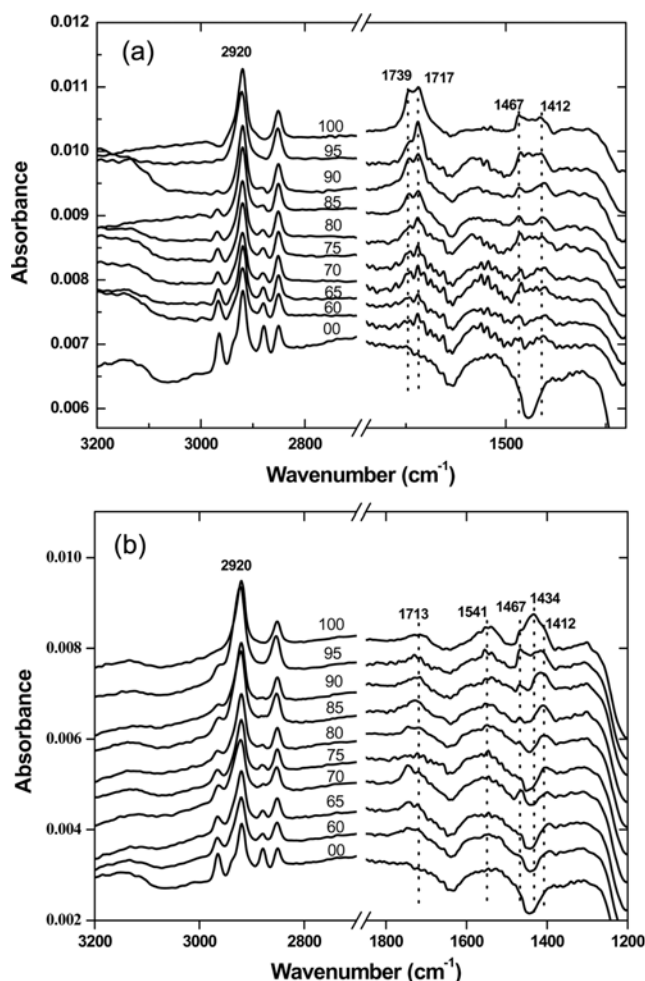


Fig. 6. (a) The results of ER-FTIR of binary SAMs composed of MHA and HDT ($C_{\text{MHA+HDT}}=1$ mM), (b) The results of ER-FTIR of reaction between the binary SAMs and cadmium ion ($C_{\text{Cd}}=1$ mM, pH=5.5, reaction time=0.5 h).

binary SAMs, respectively. $A_{i,P}$ and $A_{j,P}$ are denoted as the area of i or j component in the pure SAMs, respectively. The results of compositional analysis by surface wettability and FTIR spectroscopy are plotted in Fig. 5. The MHA composition at the binary SAMs obtained from the Cassie equation is in agreement with one in mixed solution, while the other two cases show that the MHA composition on the binary SAMs is smaller than that on the binary solution. Meanwhile, the Israelachvili equation can be used for the mixed surface where two different molecules are well mixed on the surface. Therefore, it is considered that MHA-HDT binary SAMs are miscible.

3. Surface Reaction Analysis of Binary SAMs against Metal Ion Adsorption

The results of ER-FTIR of binary SAMs (MHA : HDT) are shown in Fig. 6(a). The spectrum of pure MHA SAM not only has $\nu_{\text{a}}\text{CH}_2$ at 2919 cm^{-1} , $\nu_{\text{s}}\text{CH}_2$ at 2850 cm^{-1} but also carbonyl stretching bands ($\nu_{\text{C=O}}$, 1739 and 1717 cm^{-1}) and methylene scissoring band (δCH_2 , 1467 cm^{-1}). Especially, carbonyl stretching bands stand for two kinds of carboxylic acid. The band at 1739 cm^{-1} arises from free carboxylic acid, and the one at 1717 cm^{-1} arises from the hydro-

gen bonded carboxylic acid [28]. It indicates that there are some non close-packed monolayers. If the surface of substrates is flat, hydrogen bonding interactions among the carboxylic acid groups occur homogeneously, indicative of showing only one carbonyl stretching. But on rough substrates, hydrogen-bonding degenerates, and then the peak of carboxylic acid splits into two peaks [29]. As the addition of HDT increases, the carbonyl peak decreases and asymmetric methyl stretching band ($\nu_{\text{a}}\text{CH}_3$, 2964 cm^{-1}) symmetric methyl stretching band ($\nu_{\text{s}}\text{CH}_3$, 2879 cm^{-1}) band starts to appear and increases. The intensity of the carbonyl stretching band linearly decreases with the surface composition. The binary SAMs reacted with cadmium ion solution (1 mM, pH=5.5) for 30 min. As compared to Fig. 6(a), the carbonyl stretching band decreases and the asymmetric carboxylate stretching band ($\nu_{\text{a}}\text{COO}^-$) at 1541 cm^{-1} and symmetric carboxylate stretching band ($\nu_{\text{s}}\text{COO}^-$) at 1434 cm^{-1} appear, an indication of binding MHA with cadmium ion, as shown in Fig. 6(b). The intensity of $\nu_{\text{a}}\text{COO}^-$ is smaller than that of $\nu_{\text{s}}\text{COO}^-$ in case of pure MHA SAMs because the dipole-moment of symmetric stretching is the normal direction to the surface and that of asymmetric stretching is parallel to the surface. As the amount of HDT increases, water noise interferes around the head group region ($1500\text{--}1700\text{ cm}^{-1}$). Fortunately, the intensity of the symmetric carboxylate stretching at 1434 cm^{-1} decreases, indicating the decrease of cadmium adsorption. As a result, it was possible to identify the metal adsorption on SAMs, but it was difficult to analyze quantitatively with compositional analysis of FTIR due to unstable FTIR spectra and water noise. FTIR spectra after metal adsorption on the binary SAMs showed the possibility of study about heterogeneity on the binary SAMs.

CONCLUSIONS

We analyzed the composition of the binary SAMs composed of MHA-HDT on gold surfaces by means of ER-FTIR spectroscopic results and surface wettability measurements correlated with the Cassie equation and Israelachvili equation, which confirmed that the binary SAMs are well mixed. The MHA composition at the binary SAMs obtained from the Cassie equation is in agreement with that in mixed bulk solution. However, the results of the ER-FTIR and Israelachvili equation show that the MHA composition on the binary SAMs is smaller than one on the mixed solution. Therefore, MHA-HDT binary SAMs on gold surfaces are considered to be miscible because the result obtained from FTIR spectra is in good agreement with that calculated by the Israelachvili equation for the case that two different molecules are well mixed on the surface. Also, the adsorption of cadmium ions on binary SAMs was confirmed by the appearance of carboxylate stretching bands.

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NOMENCLATURE

HDT : hexadecanethiol

MHA : mercaptohexadecanoic acid

ER-FTIR : external-reflection FTIR

SAMs : self-assembled monolayers

W : the work of cohesion of the liquid with the surface

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