

Miscibility in two phase-separated binary self-assembled monolayers composed of hydrophilic components on Au(111)

Pham Hong Phong

Institute of Chemistry, Vietnam Academy of Science and Technology

Received 16 September 2016; Accepted for publication 11 April 2017

Abstract

The typical characteristic of two binary self-assembled monolayer (SAMs) composed of 11-aminoundecanethiol hydrochloride (AUT), and 10-carboxy-1-decanethiol (MUA) in each and the other was 2-hydroxyethanethiol (MeOH) was investigated. The dependence of charges (Q), estimated from the peak areas in cyclic voltammograms on the mixing ratios of components ($\chi^{\text{sol}}_{\text{MeOH}}$) indicated that $Q_{\text{MUA}} = Q_{\text{MeOH}}$ at $\chi^{\text{sol}}_{\text{MeOH}} = 0.8$, meanwhile $Q_{\text{AUT}} = Q_{\text{MeOH}}$ at $\chi^{\text{sol}}_{\text{MeOH}} = 0.5$, suggesting that adsorbed MUA molecules prevented the adsorption of MeOH molecules. Fourier transform infrared spectrometry (FTIR) showed the increase of band at 2855 cm^{-1} and 2965 cm^{-1} , assigned to symmetric and asymmetric of CH_2 , respectively, of SAM of AUT, indicating the more perpendicular orientation of AUT molecules compared with MUA molecules on the Au(111) surface. This result interpreted the degree of phase separation in binary SAMs of AUT-MeOH compared with binary SAMs of MUA-MeOH.

Keywords. Binary self-assembled monolayers, miscibility, hydrophilic components.

1. INTRODUCTION

Self-assembled monolayers (SAMs) are nanostructured materials that have been attractive to many studies because they provide a convenient, flexible and simple system to tailor the interfacial properties of metals, metal oxides, and semiconductors [1]. The most extensively studied class of SAMs is derived from the adsorption of alkanethiols on substrates such as gold, silver, copper, and mercury. The high affinity of thiols for the surfaces of noble and coinage metals makes it possible to generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at exposed interfaces. In order to tailor the surface properties, two or more components having different chemical functionalities have been used to provide more possibilities in modification. Thus, studies of characteristics of multi-component SAMs are essential to understand fundamentals of these types of nanostructured materials. Such as, studies of characteristics of various combination of two alkanethiols by co-adsorption onto Au(111) from a mixing solution: domain structures of binary SAMs composed of 3-mercapto-1-propanol and 1-tetradecanethiol on Au(111) [2], miscibility of 1-undecanethiol and 11-mercaptopundecanoic acid on Au(111) [3], phase separation of 2-

mercaptoethanesulfonic acid and 1-octadecanethiol on Au(111) [4], or ideal nonideality in adsorption of 2-aminoethanethiol and 2-mercaptoethane sulfonic acid on Au(111) [5]. These results provide basics for further investigations of many studies on SAMs and their applications [6-10].

In this context, we recently reported that a binary SAMs of AUT and MeOH (AUT-MeOH) was employed as an initial binary SAM for preparing the phase-separated binary SAMs composed of AUT and MUA by electrochemically selective replacement technique [11]. Particularly, co-adsorption of both AUT and MUA components from a mixing solution forms a homogenous binary SAMs [12]. Thus, in order to obtain a phase separation between these components, it is needed to use another technique as reported. However, in the previous work, the combination of two alkanethiols: AUT and MeOH was employed to prepare the initial phase-separated binary SAMs, the researchers did not further focus on investigations to interpret why this binary SAMs was used instead a binary SAMs of MUA and MeOH (MUA-MeOH). This is due to that it requires further systematic investigations, and thus, is reported in this paper. Here, the electrochemical behaviors of these binary SAMs were focused to explain that a combination of AUT and MeOH has more advantages than that of MUA and MeOH to employ as an initial binary SAMs.

Simultaneously, the obtained results were presented to provide characteristics of these hydrophilic binary SAMs to support for studies in molecular engineering in nanostructured materials.

2. EXPERIMENTAL

2.1. Reagents

11-aminoundecanethiol hydrochloride (AUT), 10-carboxy-1-decanethiol (MUA) was purchased from Donjindo, and 2-hydroxylethanethiol (MeOH) was purchased from TIC Co. These chemicals were used without further purification.

Water was purified through a Mili-Q system (Millipore Co.). All other chemical were of reagent grade and used without further purification. Au(111) substrates were prepared by vapor deposition of gold (99.99 % purity) onto freshly cleaved mica sheets (Nilaco, Japan) which were baked at 580 °C prior to the desorption and maintained at 580 °C during the deposition.

2.2. Preparation of the binary SAMs of AUT-MeOH and MUA-MeOH

Binary SAMs of AUT-MeOH and MUA-MeOH were prepared by immersing Au(111) substrates for 24±5 h in ethanol solution of these thiols where the total concentration of thiols was kept at 1 mM. The composition of these SAMs was controlled by varying the molar ratio of MeOH, $\chi^{\text{sol}}_{\text{MeOH}}$, keeping C_{total} constant. Here, $\chi^{\text{sol}}_{\text{MeOH}}$ was defined by $\chi^{\text{sol}}_{\text{MeOH}} = C^{\text{s}}_{\text{MeOH}} / C^{\text{s}}_{\text{total}}$, and $C^{\text{s}}_{\text{total}} = (C^{\text{s}}_{\text{MeOH}} + C^{\text{s}}_{\text{AUT}})$ for binary SAMs of AUT-MeOH, and $C^{\text{s}}_{\text{total}} = (C^{\text{s}}_{\text{MeOH}} + C^{\text{s}}_{\text{MUA}})$ for binary SAMs of MUA-MeOH. Binary SAMs were then rinsed with ethanol and dried in air.

2.3. Apparatus

Cyclic voltammetry for the reductive desorption of adsorbed thiols was used to examine a surface composition at each process of the replacement. The voltammograms were recorded in a deaerated 0.5 mol dm⁻³ KOH aqueous solution at scan rate of 20 mV/s at 25 °C. A Au(111) deposited mica coated with the SAM was mounted at the bottom of a cone-shape cell using an elastic O-ring. The surface area of the electrode was estimated to be 0.126 cm². The potential was referred to an Ag/AgCl (saturated KCl) electrode.

Fourier transform infrared spectra (FTIR) were recorded with a Thermo-Matton Infinity spectrometer equipped with a HgCdTe detector and a photoelastic modulator (Hinds, PEM-90). The

signal was demodulated with a synchronous sampling demodulator (GWC Instruments). The differential reflectance was numerically converted to absorbance.

3. RESULTS AND DISCUSSION

The characteristics of binary SAMs of AUT-MeOH and MUA-MeOH were studied by voltammetry for reductive desorption as presented representatively in Fig. 1. In order to emphasize the behaviors, voltammograms recorded for single SAMs of AUT, MUA and MeOH were also depicted. It is well known that the peak potential in voltammograms reflects the Gibbs energy for reductive desorption of thiolate SAMs [13]. Hence, among these single SAMs, the desorption of SAM of MeOH requires the lowest energy due to weak Van Der Waals interactions between the molecules on Au(111) surface, giving the appearance of a peak at -0.60 V. Both SAMs of MUA and AUT possess stronger Van Der Waals interactions due to having longer alkyl chains (*n*), giving more negative peak potentials, at -0.95 V and -0.97 V, respectively. A difference of 20 mV between two peaks of SAMs of AUT and MUA is due to one ethylene unit longer in SAM of AUT, leading to the requirement of a little more energy for reductive desorption [14]. Contrarily, voltammograms recorded for binary SAMs of AUT-MeOH and MUA-MeOH show two peaks corresponding to the desorption of domains containing a rich component in each binary SAMs. As seen in these curves, there is a shift of peaks at -0.60 V of SAM of MeOH to the negative direction, meanwhile peaks at -0.95 V and -0.97 V shifts to the positive direction. These peak shifts clearly indicate the mutual solubility of components during adsorption [3, 15].

In order to know reasons for this phenomenon, it is noted that the adsorption of alkanethiols from mixing solution on the substrates takes place through various steps, as briefly described as following: (i) diffusion from solution phase to the substrate surface; (ii) binding to atoms on the substrate under lying down state; (iii) standing up for stabilization [16]. Hence, in the cases of hydrophilic binary SAMs of AUT-MeOH and MUA-MeOH, the formation of domains can be suggested as following: after diffusion from solution to the Au(111) surface for adsorption, like-molecules tend to aggregate together to stabilize domains of AUT or MUA separated from MeOH domains. This tends to prevent a mix of unlike-molecules within domains. Particularly, the peak shifts shown in Fig. 1 reveal that there is a miscibility of AUT or MUA into

MeOH domains. This is due to adsorbed AUT and MUA molecules are more surface active than MeOH molecules because of higher value of methylene units (n), leading to a surface diffusion into domains of MeOH. But interestingly, adsorbed MeOH molecules, having short alkyl chain, can also exist in AUT or MUA domains, in which Van Der Waals interactions between AUT or MUA molecules much stronger than MeOH molecules. This behavior can be interpreted by repulsive interactions between deprotonated carboxyl ($-\text{COO}^-$) and protonated amino ($-\text{NH}_3^+$) functional groups existing in MUA and AUT domains, respectively [12], resulting in vacant sites on the surface for the adsorption of MeOH molecules. This is a typical characteristic of this type of hydrophilic binary SAMs. And this is different from those reported by other authors, in which binary SAMs composed of a hydrophilic component having short alkyl chain length and a hydrophobic one with very long alkyl chain length forms a clear-cut phase separation between two components [2, 4, 15].

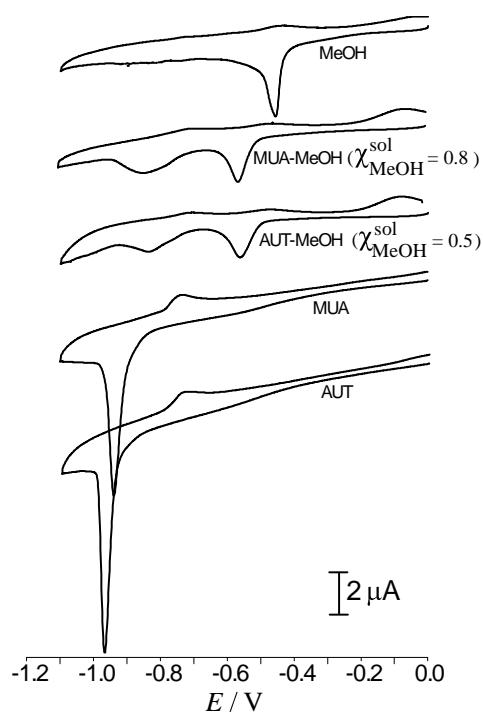


Figure 1: Cyclic voltammograms for reductive desorption of single and binary SAMs, recorded in KOH 0.5 M solution, $v = 0.1 \text{ V/s}$

Obviously, the formation of separated domains of each component in hydrophilic binary SAMs significantly depends on the interactions between like-molecules and unlike-molecules, which are affected by number of molecules diffused from solution phase. Therefore, the influence of domain formation on the solution compositions ($\chi_{\text{MeOH}}^{\text{sol}}$)

was studied as shown in Fig.2.

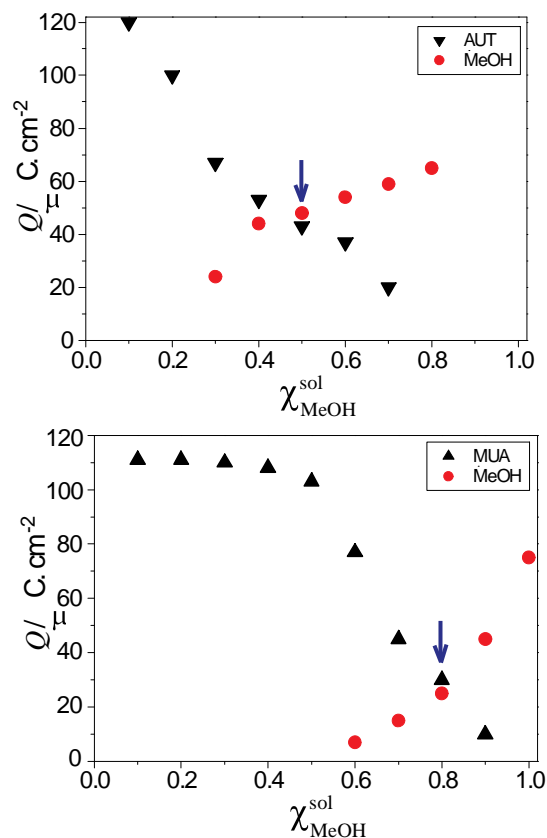


Figure 2: Dependence of charges of: AUT; MUA; MeOH domains on $\chi_{\text{MeOH}}^{\text{sol}}$ in binary SAMs of AUT-MeOH (A) and MUA-MeOH (B). Arrows denote the specific value of $\chi_{\text{MeOH}}^{\text{sol}}$ at which $Q_{\text{AUT}} = Q_{\text{MeOH}}$ and $Q_{\text{MUA}} = Q_{\text{MeOH}}$

As seen in this figure, where the charge (Q) was estimated from the peak areas on the cyclic voltammograms recorded for binary SAMs prepared at various $\chi_{\text{MeOH}}^{\text{sol}}$. The formation of AUT domains separated from MeOH domains can be clearly seen at $\chi_{\text{MeOH}}^{\text{sol}} \approx 0.3$ (Fig. 3a), whereas the formation of MUA domain separated from MeOH domain can be obtained at $\chi_{\text{MeOH}}^{\text{sol}} \approx 0.6$ (Fig. 3b). Furthermore, it is interesting to see that the value of $\chi_{\text{MeOH}}^{\text{sol}}$ at which $Q_{\text{AUT}} = Q_{\text{MeOH}}$ and $Q_{\text{MUA}} = Q_{\text{MeOH}}$ is 0.5 and 0.8, respectively (denoted by arrows in figures 2a and 2b). The difference in this value of $\chi_{\text{MeOH}}^{\text{sol}}$ suggests that the formation of MUA domains prevents the adsorption of MeOH molecules from solution phase compared with that of AUT. In order to interpret this phenomenon, Fourier transform infrared spectroscopy (FTIR) technique was used to study the structure of single SAMs of AUT and MUA, as shown in Fig. 3. In this figure, the increase of bands

at 2855 cm^{-1} and 2965 cm^{-1} , assigned to symmetric and asymmetric stretching vibrations of CH_2 , respectively, of AUT SAM can be clearly seen. This indicates that the orientation of AUT molecules is more perpendicular to the Au(111) surface than that of MUA molecules. Particularly, the kinetic adsorption of SAMs composed of multi-components of alkanethiols has been investigated previously [16], indicating that alkanethiol molecules adsorb on the surface by initially lying on the flat before gradually standing up to form tightly packed SAMs. Thus, in the cases of single SAMs of AUT and MUA, the standing up of MUA molecules to self-assembly induces less vacant sites on the surface than that of AUT molecules. This makes a reduction of possibility for MeOH molecules to adsorb on the surface in binary SAMs of MUA-MeOH compared with in binary SAMs of AUT-MeOH. This means that the value of $\chi_{\text{MeOH}}^{\text{sol}}$ employed for preparation of binary SAMs of MUA-MeOH should be higher than that to form binary SAMs of AUT-MeOH, as obtained results depicted in Fig. 2.

A more evidence reflects the higher degree of phase separation in binary SAMs of AUT-MeOH compared with binary SAMs of MUA-MeOH, that is the peak at $E = -0.85$ V in the curve recorded for MUA-MeOH is not sharp like the peak of AUT-MUA, its top broads about 100 mV as seen in Fig. 1.

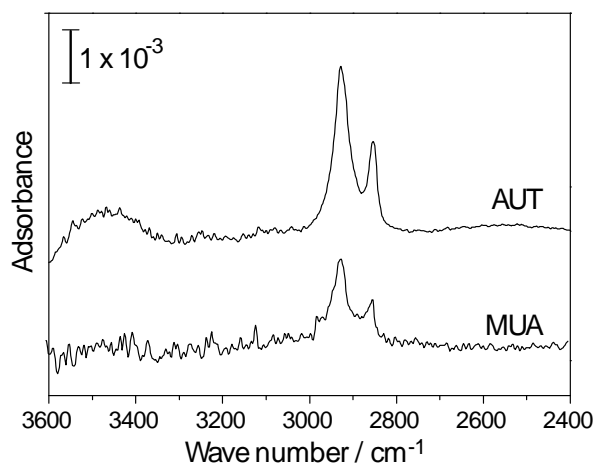


Figure 3: FTIR spectra of single SAMs of AUT and MUA

These clear evidences suggest that the miscibility of MeOH into AUT domains should be lower than MeOH into MUA domains. This is a real advantage of binary SAMs of AUT-MeOH compared with SAMs of MUA-MeOH in degree of phase separation. The obtained result, thus, provided more fundamental knowledge to interpret the reasons of using binary SAMs of AUT-MeOH as an

initial binary SAMs for selective replacement technique as we reported in previous works [11].

4. CONCLUSION

In this study, the formation of separated domains in binary SAMs of AUT-MeOH and MUA-MeOH was investigated and compared to emphasize the role of intermolecular interactions in the formation of domains containing hydrophilic components. The obtained results are fundamental to interpret the advantage of binary SAMs of AUT-MeOH used as an initial SAMs to prepare phase-separated binary SAMs composed of oppositely charged components having similar alkyl chains that tends to form homogenous by adsorption from mixing solution, for instant, binary SAMs of AUT-MUA as reported.

REFERENCES

1. J. C. Love, L. A. Estroff, J. K. Jenah et al. *Self-assembled monolayers of thiolates on Metal as a form of nanotechnology*, Chem. Rev., **105**, 1103-1169 (2005).
2. D. Hobara, T. Kakiuchi. *Domain structure of binary self-assembled monolayers composed of 3-mercaptopropanol and 1-tetradecanethiol on Au(111) prepared by coadsorption*, Electrochem. Commun., **3**, 154-157 (2001).
3. T. Kakiuchi, M. Iida, N. Gon, D. Hobara, S. Imabayashi, K. Niki. *Miscibility of adsorbed 1-undecanethiol and 11-mercaptoundecanoic acid species in binary self-assembled monolayers on Au(111)*, Langmuir., **17**, 1599-1603 (2001).
4. D. Hobara, K. Ueda, S. Imabayashi, M. Yamamoto, T. Kakiuchi. *Phase separation of binary self-assembled thiol monolayers of 2-mercaptopropanesulfonic acid and 1-octadecanethiol on Au(111)*, Electrochem., **67**, 1218-1220 (1999).
5. Y. Ooi, D. Hobara, M. Yamamoto, T. Kakiuchi. *Ideal nonideality in adsorption of 2-aminoethanethiol and 2-mercaptopropane sulfonic acid to form electrostatically stabilized binary self-assembled monolayers on Au(111)*, Langmuir, **21**, 11185-11189 (2005).
6. D. Capitao, R. Sahli, N. Raouafi, B. Limoges et al. *Electro-assisted of binary self-assembled 1,2-dithiolane monolayers on gold with predictable composition*, Chem. ElectroChem., **3**, 1422-1428 (2016).
7. D. Bu, S. Riechers, J. Liang, G. Liu. *Impact of nanografting on the local structure of ternary self-assembled monolayers*, Nano Res., **8**, 2102-2114 (2015).
8. A. Oliver, F. Meyer, J. -M. Raquez et al. *Surface-initiated controlled polymerisation as a convenient*

- method for designing functional polymer brushes: From self-assembled monolayers to patented surfaces*, Prog. Polym. Sci., **37**, 157-181 (2012).
9. L. J. C. Jeuken, N. N. Daskalakis, X. Han et al. *Phase separation in mixed self-assembled monolayers and its effect on biomimetic membranes*, Sen. Act. B, **124**, 501-509 (2007).
 10. M. K. Strulson, D. M. Johnson, J. A. Maurer. *Increase stability of glycol-terminated self-assembled monolayers for long term patterned cell culture*, Langmuir, **28**, 4318-4324 (2012).
 11. P. H. Phong. *Artificially phase separated ternary self-assembled monolayers composed of 11-amino-1-undecanethiol and 1-dodecanethiol and 10-carboxy-1-decanethiol on Au(111) prepared by electrochemically selective replacement technique*, J. Chem., **53**, 166-169 (2015).
 12. P. H. Phong. *Oppositely charged state formation of the homogenous binary self-assembled monolayers composed of 10-carboxy-1-decanethiol and 11-amino-1-undecanethiol on Au(111)*, J. Adv. Nat. Sci., **9**, 289-298 (2008).
 13. C. A. Widrig, C. Chung, M. D. Porter. *The electrochemical desorption of n-alkanethiol monolayers from polycrystalline Au and Ag electrodes*, J. Electroanal. Chem., **310**, 335- 359 (1991).
 14. S. Imabayashi, M. Iida, D. Hobara et al. *Reductive desorption of carboxylic-acid-terminated alkanethiol monolayers from Au(111) surfaces*, J. Electroanal. Chem., **428**, 33-38 (1997).
 15. D. Hobara, M. Ota, S. Imbayashi. *Phase separation of binary self-assembled thiol monolayers composed of 1-hexadecanethiol and 3-mercaptopropionic acid on Au(111) studies by scanning tunneling microscopy and cyclic voltammetry*, J. Electroanal. Chem., **444**, 113-119 (1998).
 16. P. H. Phong, V. V. Sokolov, N. Nishi, M. Yamamoto, T. Kakiuchi. *Concentration-dependent switching of the mode of phase separation in ternary self-assembled monolayers of 2-mercaptoethanethiol sulfonic acid, 2-aminoethanethiol and 1-dodecanethiol on Au(111)*, J. Electroanal. Chem., **600**, 35-44 (2007).

Corresponding author: **Pham Hong Phong**

Institute of Chemistry

Viet Nam Academy of Science and Technology

No. 18, Hoang Quoc Viet, Cau Giay District, Hanoi

E-mail: phphong@ich.vast.vn; Telephone number: (84) 4 38362008.