

Surface Mass Titrations of Self-Assembled Monolayers of ω -Mercaptoalkanoic Acids on Gold

Katsuaki Shimazu,* Tadashi Teranishi, Kouki Sugihara, and Kohei Uosaki[†]

Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810

[†] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

(Received March 30, 1998; CL-980235)

The acid/base properties of self-assembled monolayers of ω -mercaptopalcanoic acids on Au are evaluated by measuring the mass change during the titration of the monolayers using a quartz crystal microbalance (QCM). This novel surface mass titration method by QCM determined the acid dissociation constants of the monolayers to be 6.4-5.8 in pKa, slightly dependent on the chain length of the molecule. The capability for the present method to measure acid density is also demonstrated.

Quantitative evaluation of the physico-chemical properties of surface-immobilized molecules has recently become one of the most important topics. This trend is synchronized with the abrupt increase in number of studies in the field of the self-assembled monolayer (SAM),^{1,2} since the design of a surface with SAM is based on the properties of the molecules immobilized, and precise control of the surface function becomes very important as the assembly technique is improved. The surface properties of SAMs are not necessarily the same as those of precursor molecules in the bulk phase; lateral interactions between the immobilized molecules and electronic effect by adsorption may modify the intrinsic properties of the molecules. In this paper, we propose a new technique for evaluating the acid/base properties of SAMs with a quartz crystal microbalance (QCM). The mass of the electrode surface is measured during the titration of SAMs. We term this technique "surface mass titration." The surface mass titration is comparable when evaluating the acid dissociation constant, with and is superior when evaluating the acid density on the surface, to other techniques based on contact angle,³⁻⁵ interfacial force⁶⁻⁹ and capacitance,¹⁰ as will be described.

6-Mercaptohexanoic acid, 11-mercaptopundecanoic acid and 16-hexadecanoic acid were synthesized according to the procedure reported in the literature.¹¹ Reagent grade 3-mercaptopropionic acid was purchased from Kanto Chemicals. All other chemicals were of reagent grade or better and were used as received. All solutions were prepared with Milli-Q water and were sufficiently deoxygenated with argon of 5N purity prior to use. The substrate of the self-assembled monolayers was a 200 nm gold thin film evaporated in vacuo onto a 5 MHz, AT-cut quartz crystal wafer held at 300°C. The gold film thus prepared shows typical characteristics of a Au(111) surface for the underpotential deposition of Cu²⁺. The predominant growth of Au(111) on the quartz crystal has been also reported in the literature.¹²⁻¹⁴ The self-assembled monolayers (SAMs) of thiols were constructed by immersing the substrate in ethanolic solution of the thiols for 3 h.

The electrolyte solution used for the surface mass titration experiments was 0.1 M NaCl whose pH was initially adjusted to 4.0 with HCl. A NaOH aqueous solution was added at a constant rate to the solution in which the QCM sensor head (MAXTEK model PS550) and pH electrode were immersed. During the titration, the solution was stirred and constantly

purged by argon.

From resonance frequency, f and pH recorded simultaneously, surface mass titration curves (frequency change, Δf versus pH plots; Δf is defined as $\Delta f = f(\text{pH}) - f(\text{pH}=4)$) were obtained. The results are summarized in Figure 1. For all the mercaptoalkanoic acids used, the frequency decreased or mass increased¹⁵ with the increase in pH of the solution, independent of chain length (Figures 1 a-d). Such changes were never obtained for the alkanethiol monolayers of various chain lengths from C6 to C12 (Figure 1e shows the result for the decanethiol monolayer) and for bare Au (Figure 1f). Therefore, the mass increase observed for mercaptoalkanoic acid monolayers is clearly related to the dissociation of carboxylic acid. We attribute this increase to the conversion of the surface carboxylic acid to the carboxylate anion associated with a sodium cation. Such ion association at monolayer/electrolyte solution interfaces is often observed; for example, the ferrocenium cation and perchlorate ion at a 11-ferrocenylundecanethiol SAM,¹⁶⁻¹⁸ and the phenolate ion and alkaline metal cations at a 2,5-dihydroxythiophenol SAM.¹⁹ The frequency change through the titration, Δf_t , therefore, corresponds to the total number of carboxylates formed or carboxylic acids initially present. Table 1 lists the average Δf_t 's for several independently prepared samples. Assuming that sodium ion is not hydrated upon the association, the number of cations was calculated from Δf_t to be $8.7-10.7 \times 10^{14}$ molecules/cm² using Sauerbrey's equation.²⁰ These values are within the range expected for a monolayer, but are somewhat

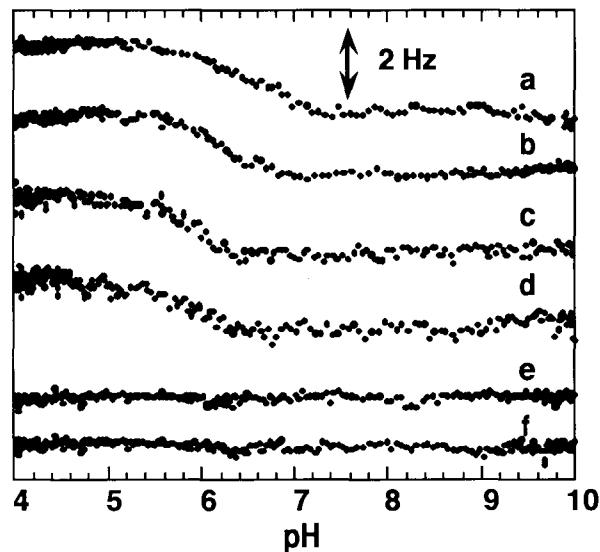


Figure 1. Surface mass titration curves for (a-e) SAMs of thiols and (f) bare Au. (a) 16-mercaptopoctadecanoic acid, (b) 11-mercaptopundecanoic acid, (c) 6-mercaptophexanoic acid, (d) 3-mercaptopropionic acid, (e) mercaptodecanethiol.

Table 1. Total frequency changes (Δf_t 's) and pKa's for mercaptoalkanoic acid SAMs on Au

SAM	Δf_t / Hz	pKa
mercaptohexadecanoic acid	2.2 \pm 0.3	6.4 \pm 0.2
mercaptoundecanoic acid	2.1 \pm 0.2	6.1 \pm 0.1
mercaptohexanoic acid	1.9 \pm 0.2	6.0 \pm 0.2
mercaptopropionic acid	1.8 \pm 0.2	5.8 \pm 0.1

higher if taking into account the size of the carboxyl group. It is suggested from the number of adsorbed thiols independently estimated by the electrochemical desorption²¹ and cation dependence of Δf_t that transport of sodium ion occurs in the hydrated state with 2-4 water molecules. Accurate estimation of the hydration number will allow one more precisely to determine the surface acid density from Δf_t .

Since the frequency change is proportional to the number of carboxylate ion formed, an apparent pKa value is given by the pH at half the total frequency change. The average values of pKa's for several independent experiments are listed in Table 1. The pKa is slightly dependent on the chain length of the thiol; the longer chain mercaptoalkanoic acid gives a larger surface pKa. The bulk-phase pKa for mercaptopropionic acid is reported to be 4.16,²² and those for the other longer chain mercaptoalkanoic acids are approximately estimated to be 4.6-5.0.²³ Therefore, it is concluded that the surface pKa's are larger than those in the bulk phase. Such positive shifts have been obtained using other techniques: pKa's for the mixed SAMs of mercaptoundecanoic acid/alkanethiols by contact angle measurements are in the range of 6.2-11.5 depending on the surface density and chain length of the methyl-terminated alkanethiols,^{3,5} and the pKa of mercaptopropionic acid by double-layer force measurements is 8.0.⁸ Some others have reported nearly identical pKa values with bulk phase values: pKa of mercaptoundecanoic acid SAM is determined from adhesion force measurements to be 4.8-5.5.^{6,7} Although the real reason for the discrepancy in pKa is presently unclear, the fact that our data are within those reported demonstrates the usefulness of the surface mass titration.

In summary, it is evident that the surface mass titration proposed in the present study has the capability of evaluating both the pKa and acid density of SAMs. Although several other approaches have been developed to evaluate the acid/base properties of SAMs, none of them show such dual capability. The pKa values obtained here agree with those reported using other techniques, and therefore, reliability of the surface mass titration is confirmed. Further examination as to the reason for the pKa shift is under way. At the end of the paper, we should

mention that experiments which seem to be based on a similar idea have been conducted by Wong et al.²⁴ However, they observed over a thousand hertz frequency increase during the titration of 16-mercaptophexadecanoic acid SAM. They concluded from the impedance analysis of the quartz crystal that the shift is due to changes in the viscoelastic properties of the hydrodynamic layer in contact with the QCM. As a result, titration based on mass measurements was not achieved. We are now conducting a detailed examination to understand the discrepancy between their and our data.

This work is partially supported by Grant-in-Aid for Scientific Research (09640711) and for Priority Area Research of "Electrochemistry of Ordered Interfaces" (09237101, 09237204, 10131203) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1. A. Ulman, "An Introduction To Ultrathin Organic Films: From Langmuir-Blodgett To Self-Assembly," Academic Press, Boston, MA(1991).
2. H. O. Finklea, in "Electroanalytical Chemistry," ed by A. J. Bard and I. Rubinstein, Marcel Dekker, New York(1990), Vol. 19, p109.
3. S. E. Creager and J. Clarke, *Langmuir*, **10**, 3675 (1994).
4. M. A. Bryant and R. M. Crooks, *Langmuir*, **9**, 385 (1993).
5. T. R. Lee, R. I. Carey, H. A. Biebuyck, and M. Whitesides, *Langmuir*, **10**, 741 (1994).
6. D. V. Vezenov, A. Noy, L. F. Rozsnyai, and C. M. Lieber, *J. Am. Chem. Soc.*, **119**, 2006 (1997).
7. E. W. van der Vegt and G. Hadzioannou, *Langmuir*, **13**, 4357 (1997).
8. K. Hu and A. J. Bard, *Langmuir*, **13**, 5114 (1997).
9. H. X. He, C. Z. Li, J. Q. Song, T. Mu, L. Wang, H. L. Zhang, and Z. F. Liu, *Mol. Cryst. Liq. Cryst.*, **294**, 99 (1997).
10. M. A. Bryant and R. M. Crooks, *Langmuir*, **9**, 385 (1993).
11. E. B. Troughton, C. D. Bain, G. M. Whitesides, R. G. Nuzzo, D. L. Allara, and M. D. Porter, *Langmuir*, **4**, 364 (1988).
12. G. L. Borges, K. K. Kanazawa, J. G. Gordon II, K. Ashley, and J. Richer, *J. Electroanal. Chem.*, **364**, 281 (1994).
13. M. Watanabe, H. Uchida, M. Miura, N. Ikeda, *J. Electroanal. Chem.*, **384**, 191 (1995).
14. K. Uosaki, S. Ye, H. Naohara, Y. Oda, T. Haba, and T. Kondo, *J. Phys. Chem.*, **101**, 7566 (1997).
15. Impedance analysis of quartz crystals during the titration did not show any evidence that the frequency was influenced by factors other than mass.
16. K. Shimazu, I. Yagi, Y. Sato, and K. Uosaki, *Langmuir*, **8**, 1385 (1992).
17. K. Shimazu, Y. Sato, I. Yagi, and K. Uosaki, *Bull. Chem. Soc. Jpn.*, **67**, 863 (1994).
18. K. Shimazu, I. Yagi, Y. Sato, and K. Uosaki, *J. Electroanal. Chem.*, **372**, 117 (1994).
19. K. Shimazu, Y. Ohtomo, Y. Sato, and K. Uosaki, in preparation.
20. D. A. Buttry and M. D. Ward, *Chem. Rev.*, **92**, 1355 (1992).
21. M. M. Walczak, D. D. Popeno, R. S. Deinhammer, B. D. Lamp, C. Chung, and M. D. Porter, *Langmuir*, **7**, 2687 (1991).
22. "Ionization Constants of Organic Acids in Aqueous Solution," ed by E. P. Serjeant and B. Dempsey, IUPAC Chemical Data Series, Pergamon Press, Oxford, New York(1978).
23. These pKa values are taken from those of corresponding SH-free carboxylic acids, since the effect of introducing SH seems to be negligible for long-chain molecules.
24. J. Wang, L. M. Frostman, and M. D. Ward, *J. Phys. Chem.*, **96**, 5224 (1992).