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Chemical Force Titration of Conjugated Pyridyl Group-Terminated Self-Assembled Monolayers

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Chemical force microscopy (CFM) was used to follow the dissociation process of 4-mercaptopyridine (4-MP) self-assembled monolayers (SAMs) on gold. The force probe was an Au-coated Si_3N_4 tip modified with 4-MP SAM. The adhesion force between tip and substrate was found to be a function of solution pH. The $\text{pK}_{1/2}$ value of surface pyridyl groups of 4-MP SAM obtained from force titration curve was 5.4, remarkably different from the conventional contact angle titration result ($\text{pK}_{1/2}=3.3$). This difference is believed to arise from the difference in spatial resolution of two approaches. The force titration would probe the local dissociation properties of surface groups, while the contact angle titration reflects the average dissociation properties underneath the water droplet.

Keywords: chemical force titration; contact angle titration; surface $\text{pK}_{1/2}$

INTRODUCTION

In the field of surface science and interface, it is well known that the acid-base interaction plays an important role for a large number of phenomena^[1]. Now there are many techniques developed to measure the dissociation properties (the pK value) of surface acid/base groups. Representative examples are the contact angle titration technique proposed by Whitesides *et al.*^[2], the interfacial capacitance measurements by Crooks *et al.*^[3], and the approach based on second harmonic generation by Eisenthal *et al.*^[4].

Chemical force titration, a new titration technique proposed by us^[5] and Lieber *et al.*^[6] independently in 1997, is a novel use of chemical force microscopy (CFM) for characterizing the local dissociation properties of surface groups. Using this technique, we have obtained the $pK_{1/2}$ values of $-\text{COOH}$ ^[5] and $-\text{NH}_2$ ^[7,8]-terminated self-assembled monolayers (SAMs). In this paper, we report the force titration behavior of conjugated pyridyl groups on gold, which is found to be different from that of unconjugated basic groups studied before^[6,7]. Comparative studies using both force titration and contact angle titration have been done on 4-mercaptopyridine (4-MP) SAMs on gold.

Experimental

4-Mercaptopyridine (4-MP) (Aldrich) and other reagents were of analytical grade and used as received. Ultrapure water with a resistance $\geq 16.8 \text{ M}\Omega \cdot \text{cm}$ was used. The ionic strength of phosphate buffer solution was maintained at 0.01M. Si(111) substrate and commercial Si_3N_4 tip (Digital Instruments(DI), Santa Barbara, CA) were sputter-coated sequentially with a 10nm Ti adhesion layer and a 100nm Au layer. The spring constant of thus modified tip-cantilever was calibrated using the method described in the literature^[9]. The Au-coated Si substrate and tip were immersed into $1 \times 10^{-3} \text{ M}$ 4-MP ethanol solution for 24 hours to form SAMs. Adhesion force measurements were conducted with a Nanoscope E System equipped with a fluid cell (DI). Contact angle measurements were carried out with a JJC-2 goniometer (The Fifth Optical Instrument Factory of Changchun, China).

Results and discussion

The adhesive interaction between tip and sample was measured in a fluid cell filled with phosphate buffer solution. The force probe was a 4-MP SAM modified Au/ Si_3N_4 tip. Fig.1 shows the typical force curves of 4-MP SAM obtained at different pH solutions. The adhesion force gradually decreases with increasing solution pH, and reaches to zero when $\text{pH} \geq 7.4$. Plotting the adhesion force versus solution pH gives the force titration curve of surface pyridyl groups on gold (Fig.2A). Using the similar theoretical consideration done in the previous

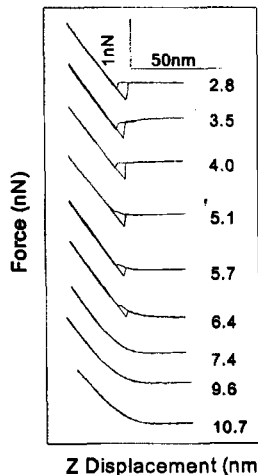


FIGURE 1 Typical force curves obtained at different pH solutions.

publications^[6,8], we estimated the $pK_{1/2}$ value of surface pyridyl groups of 4-MP SAM from Fig.2A, which was $pK_{1/2}=5.4$. For comparison, we also titrated the 4-MP SAM on gold by contact angle measurements. The result is given in Fig.2B, in which eight independent measurements were conducted for each pH value to get the average contact angle. From the contact angle titration curve, the $pK_{1/2}$ value of surface pyridyl groups of 4-MP SAM was estimated to be 3.3.

It is noted that the force titration and the contact angle titration give different $pK_{1/2}$ values over 2 pH units. This observation is believed to reflect the difference in spatial resolution of two methods. The 4-MP molecules can not form a densely-packed SAM on gold and lots of defects and pinholes may exist in the monolayer surface because of the short molecular length. Therefore the contact angle measurement can only reflect an average property of surface underneath water droplet. In contrast, since the force probe is very sharp and only a very small region of the sample surface beneath the tip contributes to force measurements, the force titration would reflect the local dissociation property of 4-MP SAM. Moreover, as evidenced by the experimental error bars shown in Fig.2, the

accuracy of force titration is obviously better than that of contact angle titration. Throughout the pH range examined, the average contact angles at different pH changed only 5°, leading to a large error in determining the $pK_{1/2}$ value as well, while the remarkable change in adhesion force allows a precise evaluation of surface $pK_{1/2}$ value (see Fig.2A).

It is very interesting to compare the force titration curves of conjugated and unconjugated basic groups. The force titration curve of 4-MP SAM is similar to that of 4-aminothiophenol (4-ATP) SAM⁽⁸⁾ but greatly different from that of (3-aminopropyl)triethoxysilane (APTES) SAM on silicon^[6,7]. The unconjugated APTES SAM shows a repulsive

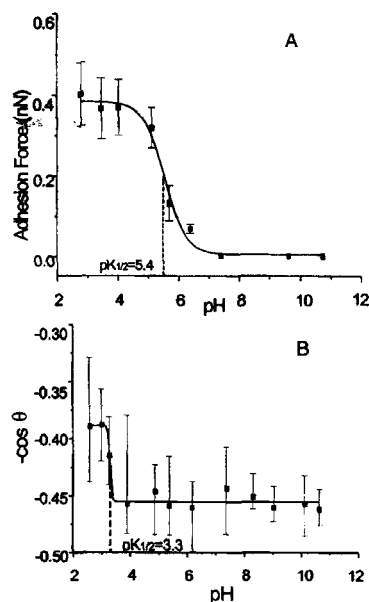


FIGURE 2 Force titration (A) and contact angle titration (B) curves of 4-MP SAMs.

force at low pH, originating from the long-range electrostatic interaction between the $-\text{NH}_3^+$ groups, and an attractive force at high pH, arising from the van der Waals interaction between the $-\text{NH}_2$ groups^[6]. However, the conjugated pyridyl and amino groups^[8] exhibit an attractive force at low pH and a repulsive force at high pH, completely opposite to the unconjugated SAMs. This can be reasonably explained by considering the charge distribution in different molecular structures. The unconjugated APTES molecule will keep its positive charge being localized on the SAM surface at low pH, while the conjugated structures of 4-MP and 4-ATP may disperse the positive charge to whole molecules, leading to the complete difference in tip-sample interactions. Quantum mechanics (*ab initio* calculation), which gives the surface charge, the electrostatic surface potential and the interaction energy versus distance curve, has supported this line of explanation^[10].

Conclusion

The 4-mercaptopyridine SAM on gold was titrated. The $\text{pK}_{1/2}$ value of the surface pyridyl groups was estimated to be 5.4 from force titration and 3.3 from contact angle titration, reflecting the difference in spatial resolution of two techniques. Direct comparative study clearly demonstrates that the force titration is a sensitive and accurate technique for determination of surface $\text{pK}_{1/2}$ values. It also shows that the conjugated nature of the titrated molecules strongly influences the force titration behavior.

References

- [1] X. -Y. Lin, F. Creuzet, and H. Arribart, *J. Phys. Chem.*, **97**, 7272 (1993).
- [2] S. R. Holmes-Farley, R. H. Reamey, T. J. McCarthy, J. Deutch, and G. M. Whitesides, *Langmuir*, **1**, 725 (1985).
- [3] M. A. Bryant, and R. M. Crooks, *Langmuir*, **9**, 385 (1993).
- [4] X. Zhao, S. Subrahmanyam, and K. B. Eisenthal, *Chem. Phys. Lett.*, **171**, 558 (1990).
- [5] 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).
- [6] D. V. Vezhenov, A. Noy, L. F. Rozsnyai, and C. M. Lieber, *J. Am. Chem. Soc.*, **119**, 2006 (1997).
- [7] H. Zhang, H. X. He, J. Wang, T. Mu, and Z. F. Liu, *Appl. Phys.*, **A 66**, S269 (1998).
- [8] H. Zhang, H. X. He, T. Mu, and Z. F. Liu, *Thin Solid Films*, **327–329**, 778 (1998).
- [9] J. E. Sader, I. Larson, P. Mulvaney, and L. R. White, *Rev. Sci. Instrum.*, **66**, 3789 (1995).
- [10] J. M. Wang, H. Zhang, H. X. He, T. J. Hou, Z. F. Liu, and X. J. Xu, *J. Mol. Struct. (Theor. Chem.)*, **451**, 295 (1998).