# Force titration of amino group-terminated self-assembled monolayers of 4-aminothiophenol on gold using chemical force microscopy

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## Abstract

Chemical force microscopy (CFM) was used to measure the adhesion force between $NH_2$-terminated probe tip and gold substrate modified with self-assembled monolayers (SAMs) of 4-aminothiophenol (4-ATP). The curve of adhesion force as a function of solution pH value (force titration curve) was obtained. The $pK_{1/2}$ of surface $NH_2$ group of 4-ATP SAMs obtained from the force titration curve is 5.3, comparable with $pK_{1/2} = 4.9$ determined by the conventional contact angle titration.

*Keywords:* Force titration; Adhesion force; Self-assembled monolayer; Chemical force microscopy; Contact angle titration; Surface $pK_{1/2}$ value

## 1. Introduction

Chemical force microscopy (CFM) [1–4], which uses a chemically modified tip as the force probe, is a new variant of atomic force microscopy (AFM) [5]. By CFM, one can investigate the intermolecular interactions on a nanometer scale and map a chemically inhomogeneous surface. It has demonstrated great capabilities in chemical specification and identification. Force titration, a new titration concept recently proposed by us [6,7] and Vezenov et al. [8] independently, is a novel use of CFM for characterizing the dissociation properties of surface functional groups like COOH, $NH_2$, etc. Previously, we have studied the COOH-terminated self-assembled monolayers (SAMs) on gold using this force titration technique, and obtained the surface $pK_{1/2}$ value[1] of COOH groups [6,7]. Similar results have also been reported by Vezenov et al. [8]. Herein, comparative studies using both force titration and contact angle titration are conducted on the surface $NH_2$ groups of 4-aminothiophenol SAMs on gold.

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[1] The surface $pK_{1/2}$ value we obtained from the force titration or contact angle titration is the apparent surface $pK$ value, which is expressed by the corresponding bulk solution pH value at which the functional groups at the interface are half-ionized. For comparison, the surface $pK$ values we used from the quoted literature are also the apparent $pK$ values.

## 2. Experiment

4-Aminothiophenol (4-ATP) (Aldrich) and other reagents were analytical grade and used as received. Ultrapure water with a resistance of above 16.8 MΩ cm was used throughout the experiments. The ionic strength of phosphate buffer solution was kept 0.01 M.

Si(111) substrate and commercial $Si_3N_4$ tip (Digital Instruments (DI), Santa Barbara, CA) were sputter-coated sequentially with a 10-nm Ti adhesion layer and a 100-nm Au layer. The spring constant of such modified tip-cantilever was calibrated using the described method [9]. The Au-coated Si substrate and tip were then immersed in 1 mM 4-ATP ethanol solution for 24 h to form SAMs. Before use, the modified substrate and tip were rinsed with ethanol, ultrapure water, and dried with high-purity Ar gas sequentially. Adhesion measurements were conducted with a Nanoscope E System equipped with a fluid cell (DI). Contact angle measurements were done with a JJC-2 goniometer (The Fifth Optical Instrument Factory of Changchun, China).

## 3. Results and discussion

The adhesive interaction between $NH_2$-terminated tip and sample of 4-ATP SAMs was measured in a fluid cell filled with phosphate buffer solution. The force curve, which represents the variation of tip-cantilever deflection, is recorded as the sample approaches, contacts and separates from the tip. The point on the force curve at which the sample just separates from the tip is called the pull-off point. The pull-off force at the pull-off point corresponds to the adhesion force between tip and sample, which can be derived from the tip-cantilever deflection by multiplying the tip-cantilever spring constant. By systematically changing the pH value of buffer solution, a plot of adhesion force versus pH value, which is called the force titration curve, was obtained. To ensure the comparativity of data obtained at different pH solutions, one tip was used throughout one set of force titration experiments.

Fig. 1 shows the typical force curves obtained at different pH solutions. When the sample is gradually approaching to the probe tip, an attractive interaction is observed when $pH \leq 5.4$ and a repulsive interaction appears when $pH \geq 6.2$. Fig. 2A gives the force titration curve of surface $NH_2$ groups on gold, where each data point was a statistical average of more than 400 individual adhesive force measurements using Gaussian fit [2]. It shows that the adhesion force decreases when pH value increases. The sharp decrease of adhesion force occurred from pH 4, and when $pH > 8$, the adhesion force reached a minimum value (nearly zero), suggesting the appearance of a repulsive interaction between tip and sample. Towards acid pH region, the adhesion force becomes gradually increased and reaches a maximum, indicating the appearance of an attractive interaction. From Fig. 2A, we estimated the $pK_{1/2}$ value of surface $NH_2$ groups of 4-ATP SAMs to be 5.3.

For comparison, we also titrated the 4-ATP SAMs on gold by contact angle measurement. 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 $NH_2$ groups of 4-ATP SAMs was estimated to be 4.9, comparable with the force titration result. It should be pointed out that throughout the pH range examined, the contact angle change was only 9 ° and there is a large dispersion of the data points as seen from Fig. 2B, which apparently leads to a large error in determining the $pK_{1/2}$ value. Contrastingly, the remarkable change in adhesion force allows a precise evaluation of surface $pK_{1/2}$ value. Bryant and Crooks [10] used an in situ electrochemical method to obtain the surface $pK_{1/2}$ of 4-ATP SAMs, which was 5.9. It is noted that force titration, contact angle titration and electrochemical approaches give the difference $pK_{1/2}$ values, 5.3, 4.9 and 5.9, which, we believe, arises from the different spatial resolution of the methods employed. The 4-ATP molecule cannot form a close packing SAM on gold, and a lot of defects and pinholes may exit in the SAMs. Therefore the contact angle and electrochemical measurements can only give an average value of surface contributions. However, the $pK_{1/2}$ value obtained by force titration technique may reflect the local dissociation properties of the examined molecules, because the CFM tip is very sharp and only a very small region of the sample surface beneath the tip is characterized.

It is very interesting to compare Fig. 2A with the force titration curve of (3-aminopropyl)triethoxysilane (APTES) SAMs on silicon [8,11]. In Fig. 2A, the adhesion force decreases with the increase of pH value. There is an attractive force in low pH and a repulsive force in high pH. This is completely different with that of APTES SAMs, where there is a repulsive force in low pH and an attractive force in high pH [8,11]. The force titration behavior of APTES SAMs can be briefly interpreted as follows: the repulsive interaction at low pH value may arise from the long-range electrostatic interaction between the protonated $NH_2$ groups of tip and sample surface, while the attractive interaction may originate from the Van der Waals interaction between neutral surface $NH_2$ groups [8]. Obviously the force titration behavior of 4-ATP SAMs cannot be explained in such a straightforward way. We believe that different force titration behaviors may arise from the different molecular structures. At low pH, the unconjugated APTES molecule may keep the positive charge localized on the SAM surface, while the conjugated structure of 4-ATP may disperse the positive charge to the whole molecule, leading to the difference of electrostatic surface potentials (ESP). This has been proved by quantum mechanics (ab initio calculation). The largest ESP value of 4-ATP SAM is 18.1 $e\text{Å}^{-1}$/molecule ($e$ is an electronic charge) in neutral form, and 8.8 $e\text{Å}^{-1}$/molecule in protonated form. Comparing the largest ESP values mentioned above, 18.1 $e\text{Å}^{-1}$/molecule leads to the repulsive force at high pH (neutral form) and 8.8 $e\text{Å}^{-1}$/ molecule results in the attractive force at low pH (protonated form) [12].

## 4. Conclusion

We have titrated $NH_2$-terminated 4-aminothiophenol SAMs on gold surface using the force titration technique, and have obtained the $pK_{1/2}$ value of the surface amino groups of 5.3, which is comparable with the contact angle titration result ($pK_{1/2} = 4.9$). The direct comparative study clearly shows that force titration is a sensitive and accurate method to measure the $pK_{1/2}$ value of surface acid/basic groups. It also shows that the conjugated structure of the titrated molecule may strongly influence the force titration behavior.

## Acknowledgements

The authors gratefully acknowledge the financial support from the State Science and Technology Committee, the State Education Committee and the National Natural Science Foundation of China.

## References

[1] C.D. Frisbie, L.F. Rozsnyai, A. Noy, M.S. Wrighton, C.M. Lieber, Science 265 (1994) 2071.

[2] A. Noy, C.D. Frisbie, L.F. Rozsnyai, M.S. Wrighton, C.M. Lieber, J. Am. Chem. Soc. 117 (1995) 7943.

[3] S. Akari, D. Horn, H. Keller, W. Schrepp, Adv. Mater. 7 (1995) 549.

[4] J.-B.D. Gree, M.T. McDermott, M.D. Porter, J. Phys. Chem. 99 (1995) 10960.

[5] G. Binnig, C.F. Quate, C. Gerber, Phys. Rev. Lett. 56 (1986) 930.

[6] H.X. He, C.Z. Li, J.Q. Song, T. Mu, L. Wang, H.L. Zhang, Z.F. Liu, Mol. Cryst. Liq. Cryst. A 294/295 (1997) 99.

[7] H.X. He, C.Z. Li, J.M. Wang, X.J. Xu, Z.F. Liu, Acta Phys. Chim. Sin. 13 (1997) 293.

[8] D.V. Vezenov, A. Noy, L.F. Rozsnyai, C.M. Lieber, J. Am. Chem. Soc. 119 (1997) 2006.

[9] J.E. Sader, I. Larson, P. Mulvaney, L.R. White, Rev. Sci. Instrum. 66 (1995) 3789.

[10] M.A. Bryant, R.M. Crooks, Langmuir 9 (1993) 385.

[11] H. Zhang, H.X. He, J. Wang, T. Mu, Z.F. Liu, Appl. Phys. A 66 (1998) S269.

[12] J.M. Wang, H. Zhang, H.X. He, T.J. Hou, Z.F. Liu, X.J. Xu, J. Mol. Struct. (Theochem.) (1998) in press.

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Fig. 1. Representative force curves for $NH_2$-terminated tip and sample modified with 4-ATP SAMs in different pH solutions.

Fig. 2. (A) Force titration curve for $NH_2$-terminated tip and sample modified with 4-ATP SAMs. (B) Contact angle titration curve of 4-ATP SAMs on gold.

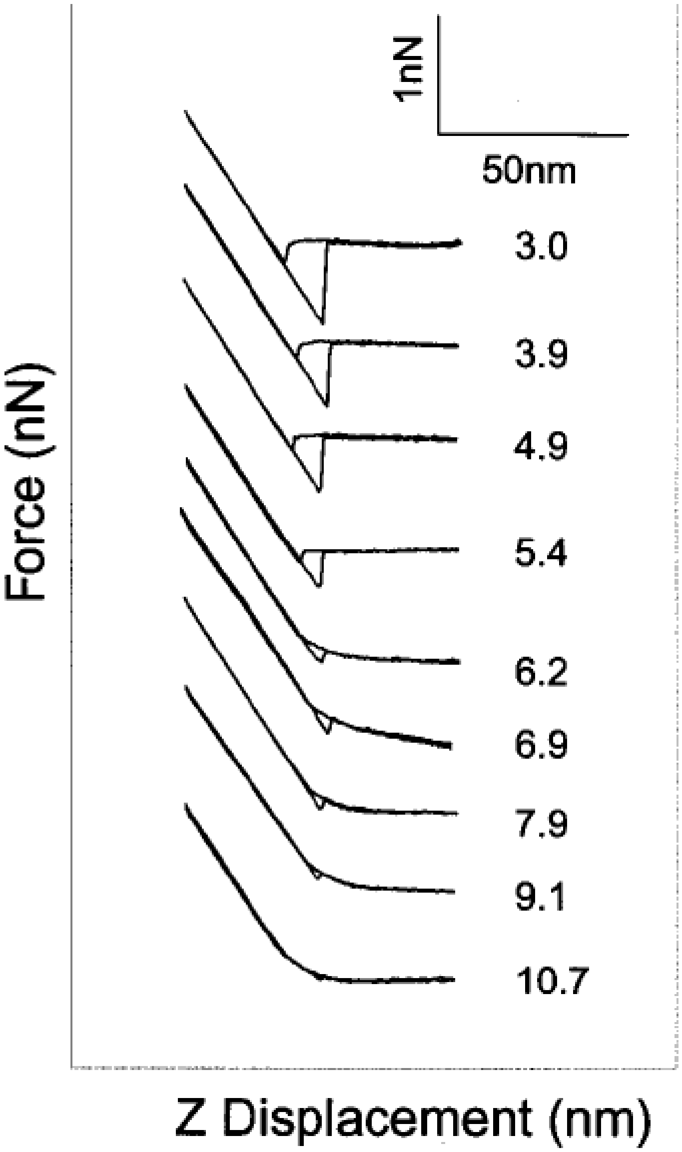

Fig. 1.

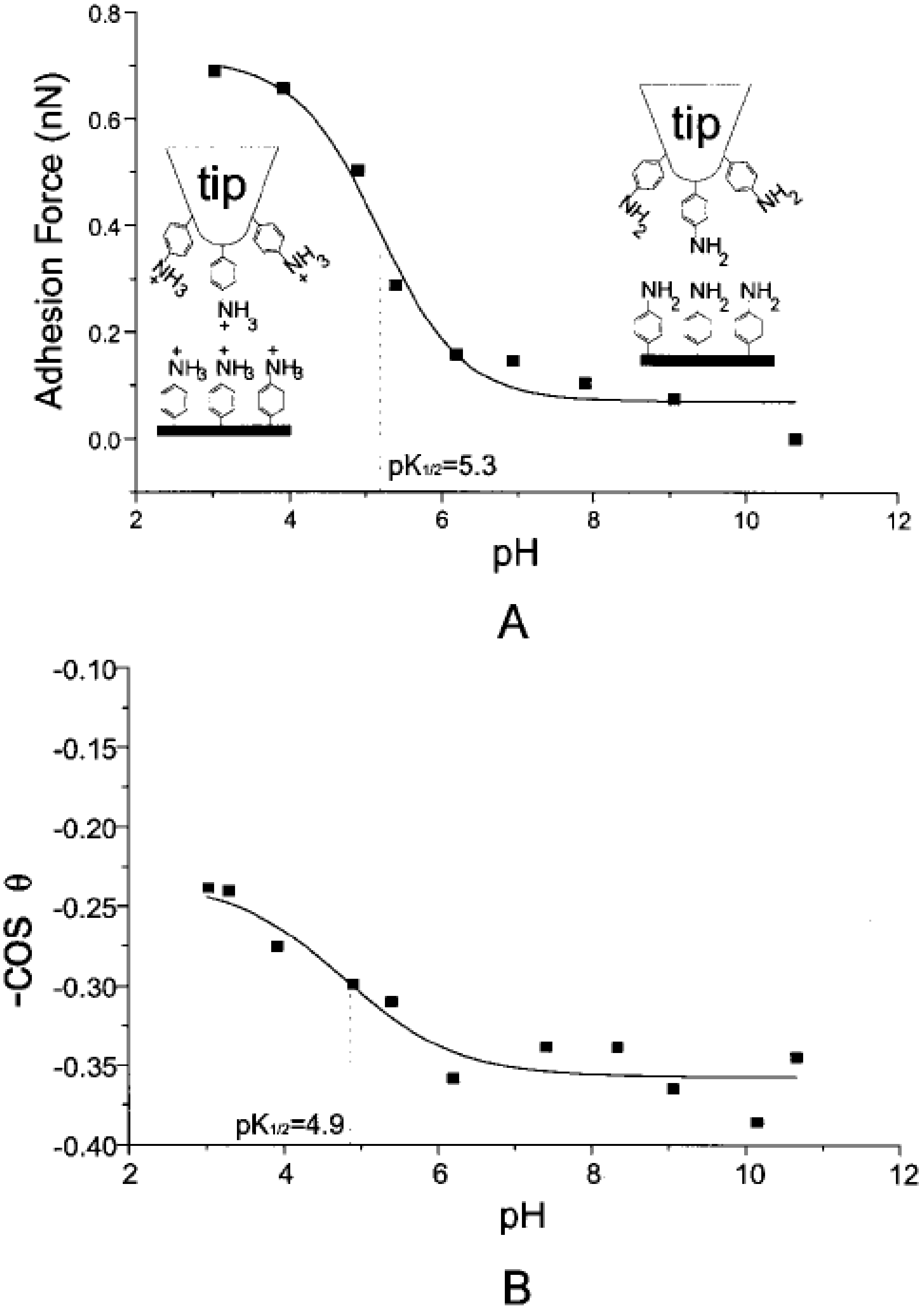
0.8
0.6
0.4
0.2
0.0
Adhesion Force (nN)
tip
NH3
NH3
NH3
NH3 NH3 NH3
tip
NH2
NH2
NH2
NH2 NH2 NH2
pK1/2=5.3
2
4
6
8
10
12
pH
A
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
-COS θ
pK1/2=4.9
2
4
6
8
10
12
pH
B

**Fig. 2.**