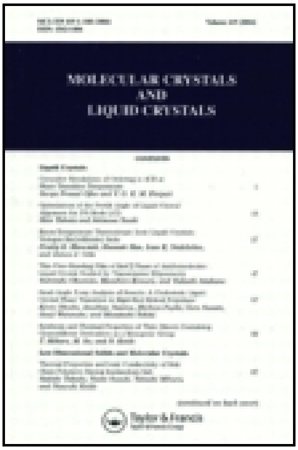

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FORCE TITRATION OF A CARBOXYLIC ACID TERMINATED SELF-ASSEMBLED MONOLAYER USING CHEMICAL FORCE MICROSCOPY

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Abstract: ω-Mercaptoundecanoic acid self-assembled monolayer (SAM) on gold was titrated with buffered water and chemical force microscopy (CFM) was used to follow the titration process by measuring the adhesion force between the SAM-modified substrate and probe tip. The adhesion force vs pH curve thus obtained, which can be named as *force titration curve,* was found to show a big hump around pH 5. Taking the contact-angle titration result together, an interpretation on this unique force titration behavior is made in terms of the rearrangement of the surface carboxylic acid groups when the probe tip and the substrate come into contact.

INTRODUCTION

After the invention of atomic force microscopy (AFM),[1] a variety of scanning force microscopy (SFM) have been developed, which detect magnetic force,[2] electrostatic force,[3] friction force,[4] etc between SFM probes and substrates. Especially, the newly developed chemical force microscopy (CFM) has made the chemical specification and identification possible.[5] With a chemically modified probe tip, CFM has been successfully used to identify and/or map different functional groups immobilized on the substrate surface.[5-6] In this paper, we report our systematic investigation of the adhesive forces between -COOH terminated self-assembled monolayer (SAM) surfaces in different pH solutions. Since the carboxylic surface groups are titrated with the buffered solution, such an experimental approach can be termed as *force titration.* The adhesive force vs pH value, i.e., *the force titration curve,* will be compared with the conventional contact angle titration data.

EXPERIMENTAL SECTION

ω-Mercaptoundecanoic acid was synthesized in our laboratory. All other reagents were analytical grade and commercially available. The silicon substrate (Si(111)) and Si_3N_4 probe (Digital Instruments (DI), Santa Barbara, CA) were sputter-coated sequentially with a 10nm Ti adhesion layer and a 100nm Au layer. SAMs of $HS(CH_2)_{10}COOH$ was formed by immersing the Au-coated substrates and probes into 1mM ethanol solutions for 24h. Before characterization, the samples and tips were rinsed in ethanol and dried with a stream of dry N_2.

Adhesion measurements were made with a DI Nanoscope E AFM equipped with a fluid cell. The buffer solutions used for the measurements were KCl+HCl for pH 3-5, phosphate buffer for pH 5-9 and KOH for pH 10-11, where the ionic strength was kept constant. Contact angle titration was performed with a contact angle goniometer (Model JJC-2, the fifth Optical Instrument Factory of Changchun, China) in terms of nonreactive spreading protocol.[7]

RESULTS AND DISCUSSION

The adhesive interaction between -COOH groups of tip and sample was measured in a fluid cell filled with different pH solutions. To ensure the validity of obtained force data, the very end of the probe tip was always imaged by scanning electron microscope (SEM) before and after titration experiments to avoid incomplete gold coating and unpredictable tip crashing. A force vs distance curve was obtained by recording the deflection signal of the cantilever as the sample approaches, contacts and then withdraws from the tip. The total time for one cycle of measurement was ca. 1 sec., long enough for avoiding oscillation at the pull-off point and hysteresis in the non-contact region. The deflection signal is equivalent to the interaction force, which can be interconverted using the cantilever spring constant. Except where noted, the systematic measurements of the adhesion forces for one set of pH titrants were made with the same

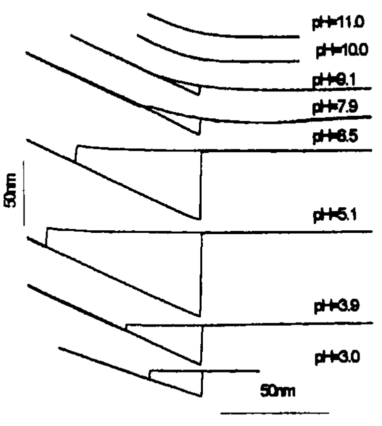

FIGURE 1. Representative cantilever deflection vs Z displacement curves taken for $HS(CH_2)_{10}COOH$ modified tip/sample system under different pH solutions.

probe tip.

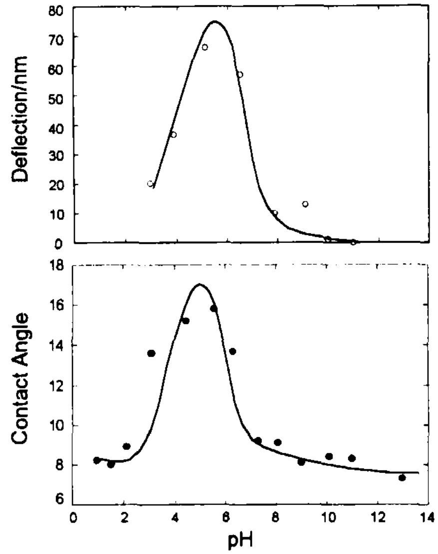

FIGURE 2. The force titration(A) and contact angle titration (B) curves of -COOH terminated SAM.

Figure 1 shows a series of typical cantilever deflection vs Z displacement curves measured in different pH solutions for $HS(CH_2)_{10}COOH$ modified tip/sample system. The adhesion force between functional groups on the tip and sample surface, corresponding to the hysteresis value in the force displacement curve(i.e., approach vs withdrawal), was statistically determined for each pH value from a huge number of force curves (≥400) taken at the same condition.[6] In Fig.2A is given the dependence on titrant pH of the adhesion force, represented here by its equivalence, cantilever deflection, which can be called as *the force titration curve* as mentioned before. Interestingly the force titration curve is unique and there exists a big hump around pH 5. To understand the origin of the hump, a series of experiments have been designed, involving changing the composition and ionic strength of the buffer, changing the -COOH terminated SAM to the untitratable $-CH_3$ terminated SAM, using different tips, etc. All the results suggested that the peak-shaped titration curve is characteristic of the -COOH system. For comparison, we also made the contact angle titration of the same system as shown in Fig. 2B. Again there exists a hump around pH 5, in nice accord with Whitesides et al's result.[8]

The unique peak-shaped force titration behavior is possibly interpreted in terms of a *chemical hysteresis*, a phenomenon occurred at the interacting surfaces that the chemical groups at the surfaces are different on separation from on approach, which usually enhances the adhesion or cohesion of the contacting surfaces.[9] At low pH, the surface groups are dominated by the uncharged -COOH, and the adhesion force may originate from the out-plane hydrogen bonding formed between -COOH groups of tip and sample when they are effectively contacting. Since the -OH group of -COOH would be preferentially exposed to the surface in this case as evidenced by the very small contact angle data, such kind of adhesive hydrogen bonding will be relatively easily created and does not require much orientational changes of surface groups. On the other hand, at high pH region, the tip and sample have the same negatively charged surface, thus the interaction between tip and sample is dominated by the long range electrostatic repulsive force. As a result, the adhesive interaction becomes very weak in alkaline solution as we have observed. At intermediate values of pH, however, the surface -COOH groups are partially ionized, leading to COO^- and -COOH coexisting on the surfaces. Taking account of the high contact angle values in this region, stable in-plane hydrogen bonding may be formed between these differently charged groups, which results in the exposure at the surface of -C=O groups or $-CH_2$ groups rather than the more hydrophilic -COOH or -COO^- groups, as was pointed out by Whitesides et al.[8] When the tip and sample come into contact, the in-plane hydrogen bonding is destroyed and instead the out-plane hydrogen bonding will be created as is the case at low pH. Apparantly this requires the remarkable rearrangement of surface groups: the -C=O groups swing away from the top surface and the -OH groups come to the surface. When the tip is withdrawn from the sample, the reverse process happens. Therefore a chemical hysteresis has occurred during the approach-separation cycle of tip and sample in this intermediate pH region, which results in the great increase of adhesion force between -COOH terminated tip and sample surfaces. More detailed studies on this system and other titratable SAMs are now in progress.

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