

Effect of chain length on the adhesion behaviour of n-alkanethiol self-assembled monolayers on Au(1 1 1): An atomic force microscopy study

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Abstract. The effect of chain length on the adhesion behaviour of n-alkanethiols $\text{CH}_3(\text{CH}_2)_n\text{SH}$, where $n = 5, 6, 7, 9, 10, 11, 14$ and 15 has been followed by carrying out pull-off force measurement using atomic force microscopy (AFM). The self-assembled monolayers on Au(111) surface has been characterized by reflection absorption infra-red spectroscopy (RAIRS) and contact mode AFM. It is observed that the work of adhesion is independent of thiol chain length though the standard deviation is high for short chain length thiol-based monolayers. This may be attributed to the relatively more deformable nature of the short chain thiol films due to their heterogeneity in the monolayer structure than the long chain ones. This, in turn, increases the contact area/volume between the AFM tip and the monolayer, and hence the force of adhesion. However, in the presence of water, the force of adhesion is lower than that observed in air reflecting the effects of capillary forces/polar components associated with the surface energy.

Keywords. Adhesion; alkanethiols; atomic force microscopy; force.

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1. Introduction

Organic thin film-based assemblies on solid supports form excellent models for studying the fundamental aspects of adhesion wetting, friction, electron transfer etc. [1]. The close-packing associated with the self-assembled organic thin films enforce a conformational rigidity which is very important for miniaturized devices. Nanolevel adhesion and friction are important issues in the area of nanoelectronics, microelectro-mechanical devices (MEMS), thin-film transistors etc. [2]. The adhesion forces are composed of intermolecular forces that occur between the adsorbate and the adsorbent at the point of contact. This is the major component of the origin of interfacial energy. Adhesion is also associated with certain dissipative forces that are related to the viscoelastic or plastic deformation of the adsorbates.

The self-assembly technique is a very convenient method and has been extensively used to prepare surfaces of various patterns in a controlled manner [1a].

Towards this direction, self-assembled monolayers of alkanethiols on gold have received considerable attention since the interaction chemistry between the substrate and the molecules is well-understood. The surface structural properties of alkanethiol SAMs and the chemical nature of interaction between the thiols and the substrates have been studied using various techniques such as IR, FT-Raman, STM and SAXS. However, the studies on interfacial properties in terms of adhesion and friction have received only limited attention [1,3,4]. The studies on adhesion and friction have been mainly concentrated on silicon surfaces with silane monolayers since they are believed to closely mimic the tribological conditions [4a]. Additionally, it is believed that silicon substrates are smoother than the gold surfaces and are conducive to form well-ordered structures, though the self-assembly itself is a tedious vapour phase process [5].

Atomic force microscopy provides precise measurements of normal surface forces in the nanometer scale and are useful for controlling adhesion, friction and wear associated with various interfaces [4]. The adhesion force measurements have received considerable attention and serve as a sensitive probe for understanding the chemical interaction and surface energies. The pull-off force measurements in electrochemical systems reflect the changes on the surface of the electrodes. The force between the AFM tip and the adsorbate reveals information on interfacial energies of the monolayer assemblies. Towards this direction, there have been several studies on the use of chemical force microscopy to understand the interactions between functional groups on two surfaces [6]. The studies are based on functionalized tips and anchored molecules on various substrates. The chemically modified tips have been exploited to understand and quantify adhesion, friction and also to image surfaces. The studies on the use of unmodified tips to probe the tip-anchored molecule interaction is however, limited [3,4a]. Noel and co-workers have recently probed the thermodynamic surface properties of chemically modified surfaces on a nanoscale using force measurements [3b]. The terminal group of the SAM has been shown to interact with the probe mainly through van der Waal's forces and capillary forces. Previous studies show discontinuities in the force measurement as a result of capillary meniscus depending on the relative humidity [7]. Adhesion and friction forces are reported to be highly dependent on several physical factors such as chain length, packing density and phase state [8]. The use of unmodified tips offers the flexibility of retrieving separate information on the van der Waal's forces and capillary forces.

In the present study, alkanethiol monolayers on highly oriented Au(111) surface have been characterized using force measurements, both in dry and wet states. The monolayers are characterized using grazing angle reflection absorption spectroscopy to understand the structural order associated with the monolayers. The work of adhesion has been determined as a function of thiol chain length based on the pull-off force measurements.

2. Experimental section

Chemicals: Alkanethiols of varying chain lengths, $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n = 5, 6, 7, 9, 10, 11, 14$ and 15) were purchased from Aldrich, USA and used as-received. AR grade tetrahydrofuran (Ranbaxy, India) and absolute ethanol (AR grade, Les alcools de

commerce) were used without any further purification. Millipore water was used for all the experiments.

Substrate and monolayer preparation: Highly oriented single crystalline Au(111) surfaces were used for the reflectance-absorbance infra-red (RAIR) spectroscopic measurements. The substrates were prepared by vacuum evaporation of gold on glass or mica surfaces. Gold films of 1500–2000 Å thickness were deposited onto a clean glass surface that had been covered with 150 Å thick chromium layer. Prior to the deposition of the metals, the glass slides were cleaned by placing them in hot piranha solution for 20 min, taken out and thoroughly rinsed with double distilled water and dried. The deposition of metal films was carried out at a rate of 1.0 Å/s for chromium and 4.0 Å/s for gold. During deposition, the substrate temperature was maintained at 573 K (300°C) at a pressure of 2×10^{-5} mbar and the substrate was rotated at a speed of 4–6 rotations per minute. The powder XRD (X-ray diffraction) data confirmed the formation of a highly oriented $\langle 111 \rangle$ phase. The single crystalline gold surfaces were washed with ethanol for about 15 min to ensure the removal of any impurity that might have been deposited on the surface while transferring the gold slides from the coating unit to the dessicator. After the cleaning procedure, the gold surfaces were immediately used for modification with monolayers. The roughness factor given by the ratio of the real area to the geometric area, was determined using cyclic voltammetry. This is essentially the ratio of the experimental charge associated with the stripping of a monolayer of gold oxide electrochemically formed on the gold electrode to the theoretically expected charge for unit area of the surface. Roughness factor of 1.5 was reproducibly obtained for the as-prepared gold surfaces.

A replica technique involving the deposition of nickel onto the evaporated gold surface on bare mica and subsequent removal of mica sheet using tetrahydrofuran to obtain smooth Au surfaces yields a roughness factor of 1.4.

Self-assembled monolayers were formed by immersing the substrates in alcoholic solutions of 3 mM concentrations of thiols for 12 h. The slides are subsequently rinsed in absolute ethanol for 20 min to remove any physisorbed material and further annealed for 9 h in a vacuum desiccator.

Atomic force microscopy: Force measurements are carried out using an atomic force microscope (CP-R, Thermomicroscopes/Veeco, USA). Silicon nitride cantilevers coated with gold on one side, with a spring constant of 0.1 N/m and a tip of radius 30–60 nm were used. The sample is being moved by the piezoelectric ceramic with a lateral resolution of 5 μm. The force-deflection data were then converted to force-distance curves. The values of the pull-off forces given are an average of 25 data points for each measurement for a scan area of 2 μm.

Reflectance-absorbance infra-red spectroscopy: RAIR spectra were recorded on a Perkin-Elmer (Spectrum GX, Switzerland) FTIR spectrometer equipped with liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The sample chamber was purged with ultra-high pure nitrogen gas prior to the experiment. Reference spectra were obtained on freshly cleaned evaporated Au(111). The perpendicularly polarized infra-red beam (p-polarized) was reflected from the SAM-modified

surfaces at an angle 82° to the surface normal. The spectra were averaged over 1024 scans with a resolution of 4 cm^{-1} and referenced to the bare gold substrates.

3. Results and discussion

Surface characterization using RAIR and contact mode AFM: The RAIR spectra of hexanethiol and hexadecanethiol on Au(111) surface are shown in figure 1. Only the methylene stretching frequency range is shown in order to compare the crystallinity associated with the monolayers. The peaks observed at 2919 cm^{-1} and 2850 cm^{-1} for the antisymmetric and symmetric stretching modes for the hexadecanethiol monolayer (figure 1a) show the ordered and compact nature of the monolayer. The hexanethiol monolayer (figure 1b), on the other hand, shows that the peaks are shifted to 2922 cm^{-1} and 2853 cm^{-1} , revealing the disordered state associated with the short chain monolayers. It is already well-established that short chain alkane thiol monolayers (chain length below C12) are disordered while the long chain thiol-based monolayers are ordered [9]. The sharp peaks observed in the case of C_{16} thiol-based monolayer show that monolayer is free of defects and also oriented in a very uniformly packed and dense manner. In the case of hexanethiol monolayer, the peaks are broad showing the heterogeneity in the monolayer that leads to disorderness. The peak broadening also accounts for the liquid-like

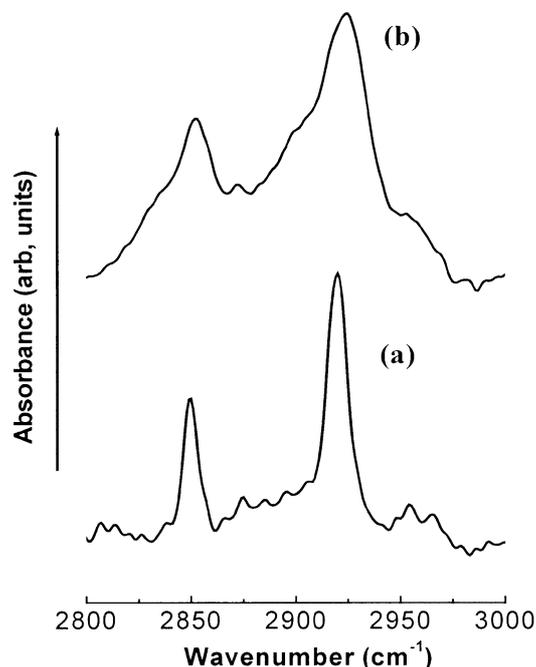


Figure 1. RAIR spectra of (a) hexanethiol and (b) hexadecanethiol monolayers on Au(111) surface.

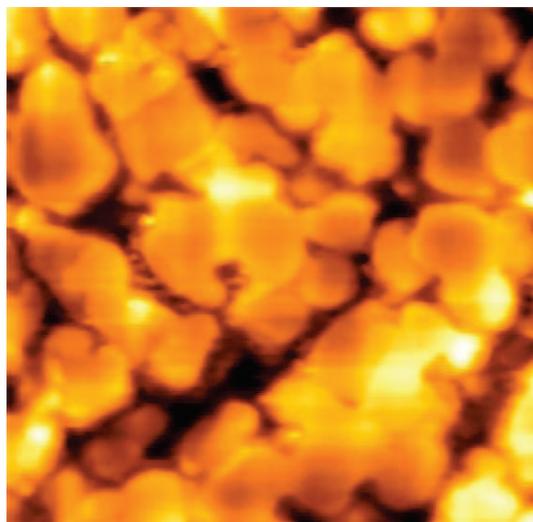


Figure 2. Contact mode AFM image obtained for dodecanethiol monolayer on Au(111) showing well-developed terraces of approximately 200 nm size. Image size is $2 \times 2 \mu$ and the scan speed is 1 Hz.

behaviour of short chain monolayers [10]. The information on order–disorder behaviour is essential to understand the adhesive forces that will be discussed later.

Figure 2 shows the topographical image for the dodecanethiol monolayer on Au(111) using contact mode AFM in air. Large, well-developed flat terraces were observed with areas ranging from 200 nm to 300 nm that are typical of thiol monolayers on gold. These surfaces are ideal for atomic level resolution emphasizing a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice periodicity [11]. Images of hexanethiol monolayers (not shown) show lack of well-developed terraces, revealing the heterogeneity and consequently the disorder in the monolayer structure. The fine grainy structure at the nanoscale level also indicates the presence of soft material.

Surface force measurements: The surface force measurements are carried out using the AFM, in the contact mode. This consists of detecting the deflection of the cantilever bearing a tip at its end while it interacts with the sample surface [12]. The deflection of the laser beam that is focused on the cantilever is detected by the four-quadrant photodiode or a photodetector. The interacting force can be calculated based on Hooke’s law using the spring constant of the cantilever. The spring constant of the cantilever used in the present study is 0.1 N/m.

Figure 3A shows a typical force–displacement curve obtained for a self-assembled monolayer of thiol on gold under ambient conditions. A jump-in to contact is observed in the approach part of the curve. This is associated with instabilities and is not discussed in the present paper. The retraction part shows a large value of force corresponding to the point where the cantilever is released from the attraction of the sample and this gives the force of adhesion or pull-off force associated with the surface. The force corresponding to the pull-off deflection when the cantilever jumps-off from the contact is measured. The large standard deviation associated

with the data may be accounted for, by the very low spring constant of the cantilever [13]. The soft levers are to be used in the present study since it is very sensitive to small changes in the adhesive force and hence the differences, if any, among the samples will be revealed quite precisely.

As observed from figure 3B, the adhesive forces observed for monolayers of different chain lengths are very similar. This is possible only when the volume of contact between the tip and the molecule is similar in all the cases. In the case of the short chain monolayers the deviation from the mean value is slightly higher than that observed for long chain thiol monolayers. This is due to the fact that short chain thiol-based monolayers have large disorder in their structure. The disorder is observed in the form of kinks, defects and chain distortions leading to decreased packing density. The packing density being low generally leads to curled and ill-defined orientations of the molecules on the surface. This is generally not

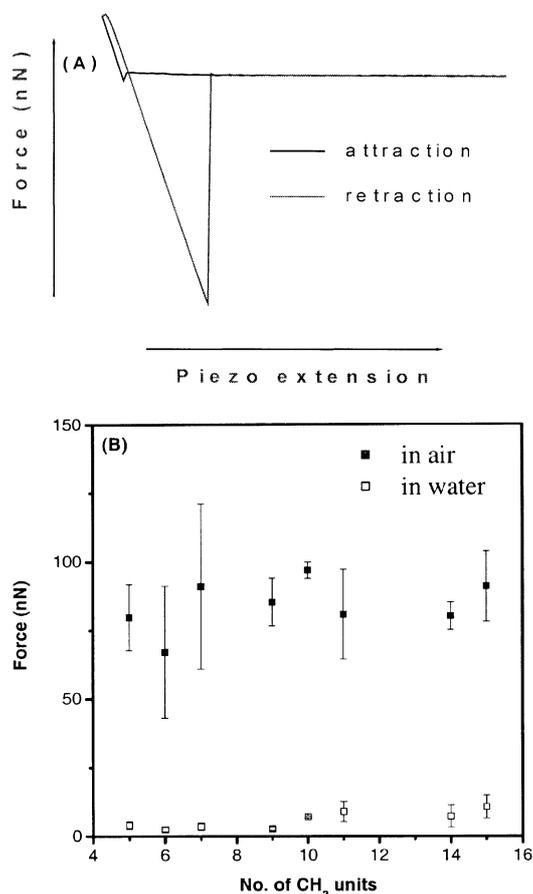


Figure 3. Pull-off force measurements on thiol SAMs. (A) Representative force–displacement curves for alkanethiol monolayers on Au(111). (B) Force of adhesion as a function of chain length of the monolayer.

very highly reproducible in terms of the relative concentrations of various defects. Hence, the short chain monolayers are prone to mechanical deformation leading to an increase in the compressibility of the monolayer. This increase in compressibility leads to high volume of contact between the tip and the molecule. Thus, the adhesion force, that depends on the volume of contact varies giving rise to large deviations in the pull-off force [14]. In spite of the large deviation from the mean value, the adhesion force is almost constant for the complete spectrum of chain lengths studied. This is likely to be due to the fact that the common CH_3 termination possibly results in similar surface energies leading to similar pull-off forces. The absolute values of force of adhesion observed is about 80 nN. This is somewhat higher than the value that would be expected for the organic thin films based on alkane thiols. This may be due to the thin layer water on the surface of the films forming a capillary bridge between the tip and the sample. It is possible that water would have condensed at the tip–monolayer junction since the experiments have been carried out at a relative humidity level of about 35%. He and co-workers have reported that relative humidity plays a large role in the condensation of water at the tip–monolayer interface [7]. In the present study, the tip is neutral and hence it may attract water molecules under ambient conditions. The possibility of the presence of intercalated solvent molecules is ruled out since the monolayers have been annealed in vacuum for about 9 h. To understand the effects of capillary forces/polar contribution to the observed adhesion force, pull-off force measurements have been carried out in water [6]. The adhesion force in air is composed of two parameters as

$$F_{\text{adhesion}} = F_{\text{cap}} + F_{\text{vdW}},$$

where F_{vdW} is the force associated with the monolayer and its structure while F_{cap} is due to the capillary forces at the interface.

Force measurements have been carried out in water for all the thiol monolayers and figure 3B shows the variation in the adhesion force as a function of chain length. The pull-off force decreases abruptly in the presence of water and is of the order of 4–7 nN. The variation with respect to chain length is, however, small. The presence of bulk water eliminates the capillary formation of water between the tip and the monolayer. Water condensation leading to capillary-based meniscus occurs when the relative humidity is above a critical level. In the present study, the neutral nature of the tip used may attract water molecules giving rise to a capillary meniscus when the measurements are carried out under ambient conditions, in air. However, the occurrence of capillary meniscus based on water condensation is avoided in the presence of bulk water and hence the force observed is totally due to the van der Waal's interactions. Another critical parameter that is to be taken into account is the long-range van der Waal's interaction between the tip and gold substrate. The ordered phases of thiol monolayers for long chain lengths probably suppresses the tip penetration into the monolayer which rules out the possibility of any tip–gold interactions. Hence, the large pull-off force obtained in air is mostly due to the capillary forces based on condensed water at the tip–monolayer interface.

Finally, the thermodynamic work of adhesion (W) (figure 4) is calculated using the following expression by applying [15]. The relationship is based on the contact between a rigid sphere and an elastic plane, which is described as, $W = F_{\text{adhesion}}/2\pi R$ where W is the work of adhesion, F is the pull-off force and R

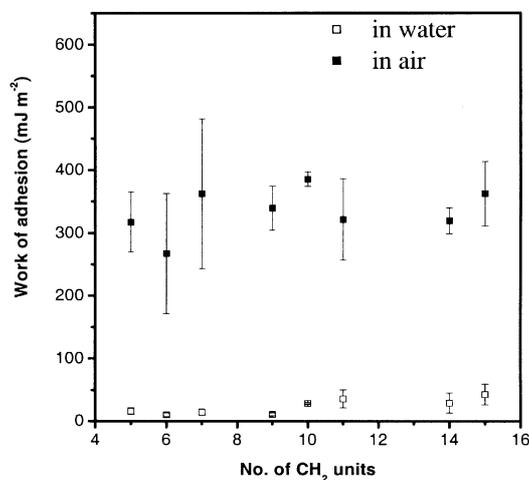


Figure 4. Work of adhesion as a function of chain length calculated from pull-off force measurements.

is the radius of the tip used (30–60 nm). Further studies are being carried out to determine the surface energy of the thiol monolayers based on contact angle and adhesive force measurements. Efforts to vary the surface energy and correlate the pull-off force to the state of the thiol monolayer are in progress.

4. Conclusions

Adhesion properties of n-alkanethiol monolayers on Au(111) have been followed as a function of chain length of thiol monolayers using atomic force microscopy. The force of adhesion is found to be independent of chain length of the thiol monolayers as observed for silane-based monolayers on silicon substrates. The frictional forces associated with the monolayers are being addressed separately.

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