Preparation and Characterization of Self-Assembled Multilayers of Octadecylamine on Mica from Ethanol Solutions

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Films of octadecylamine molecules on mica have been prepared from ethanol solutions and characterized by atomic force microscopy. Multilayer films are formed exposing terraces with alternating frictional and wear properties, which are assigned to methyl and amino group terminations. Micellar formation in the ethanol solution and subsequent deposition onto the mica is the proposed growth mechanism. By addition of acid, the ratio between protonated and unprotonated molecules was changed. The influence of this parameter on the structure of the terraces is also reported.

1. Introduction

The preparation of self-assembled monolayers (SAMs) and their study using atomic force microscopy (AFM) have received much attention in the past few years.[1] The vast majority of theses studies are devoted to alkyl molecules with thiol or silane functional groups that provide strong binding to supports such as gold, mica, and glass.

We have prepared octadecylamine self-assembled monolayers on mica with the motivation of expanding this field to systems with weaker molecule−support bonding. In a previous paper[2] we described AFM studies of the self-assembled monolayers formed using chloroform solutions. With this solution only incomplete monolayers or islands were produced. This was explained by the hydrophobic character of the solvent and by the fact that interfacial water was needed for the growth of the amine films.

We now report on the formation of multilayers of octadecylamine molecules on mica from ethanol solutions. As we shall see, ethanol solutions favor the formation of multilayers stacked with alternate methyl and amine terminations, as opposed to the partial monolayers obtained from the chloroform solutions. We discuss the effect of preparation conditions on the quality and size of the terraces as well as their stability under mechanical stress (scanning with the AFM tip under load) and under chemical influences such as rinsing with pure solvent.

Well-defined multilayered systems are interesting because terraces of alternating chemical termination can provide models for synthesis of nanoscale structures with properties that vary in the z-direction (perpendicular to the surface) in addition to the $x−y$ in-plane structuring achieved by microfabrication techniques such as microprinting. They also provide excellent models for in situ studies of the tribological, chemical, and electrostatic properties of functional groups.

2. Experimental Section

Octadecylamine (Fluka, >99% purity) was used as received and dissolved in ethanol (Aldrich, HPLC grade) to obtain 15 mM solutions. Samples (3 × 1 cm) of muscovite mica ($KAl_2(Si_3AlO_{10})(OH)_2$, Mica New York Corp.) were cleaved on both sides at ambient conditions (typically 20 °C and 40−50% relative humidity) and within seconds immersed in the solution for periods of 15−30 s. The samples were subsequently rinsed by dipping in pure ethanol. Rinsing redissolves material to an extent that is determined by number and duration of dipping cycles. Specimens were later dried under a N_2 stream for several minutes and kept in a test tube until analyzed (usually after overnight ripening). To study the effect of protonation of the amine groups in the morphology of the layers, controlled amounts of HCl were added from 1 M aqueous solutions. The ratio between protonated and unprotonated ($R−NH_3^+$:$R−NH_2$) amine molecules is calculated using the formula $a/(c − a)$, where a is the number of HCl molecules added and c is the original amount of octadecylamine molecules dissolved.

The atomic force microscope (AFM) scanner head is home-built and operates inside a box that provides sound isolation and humidity control. It is operated by an RHK Technology (Troy, Michigan) electronic unit. Si_3N_4 cantilevers (NanoProbes, Digital Instruments, Santa Barbara, CA) with 0.12 N/m nominal force constant were employed. The z-distance scale (normal to the surface) was calibrated using a test silicon grating (TGZ01, Silicon-MDT, Moscow) with nominal step heights of 25.5 nm. Smaller scale calibration was done in situ by generating 1 nm deep holes on the mica surface by scanning under a large load.[3]

3. Results

3.1. Multilayer Formation. In contrast to the sub-monolayer islands obtained by using hydrophobic chloroform solvent,[2] deposition from concentrated solutions in ethanol produced multilayer structures with well-defined flat terraces. A comparison of the films obtained using these two solvents is shown in Figure 1. Some of the terraces have widths of more than 1 μm. The step height between terraces is 4.5−5 nm or multiples thereof.

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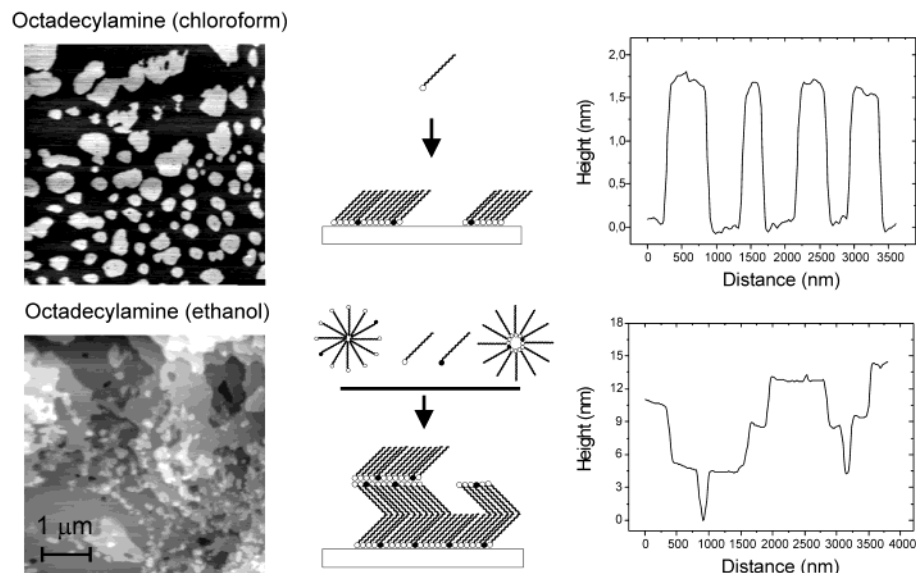(3) Kopta, S.; Salmeron, M. *J. Chem. Phys.* **2000**, *13* (18), 8249.

Figure 1. Topographic (5 × 5 μm) AFM images and line profiles of the structures formed by octadecylamine adsorption on mica. The octadecylamine was deposited from 15 mM solutions in chloroform (top) and ethanol (bottom), in this latter case with no HCl added. Experimental conditions were room temperature and 30 s immersion time in both cases. The schematic models illustrate the proposed mechanism of formation: single molecules (top) and micelles (bottom). Unprotonated and protonated amino groups are respectively indicated by white and dark circles.
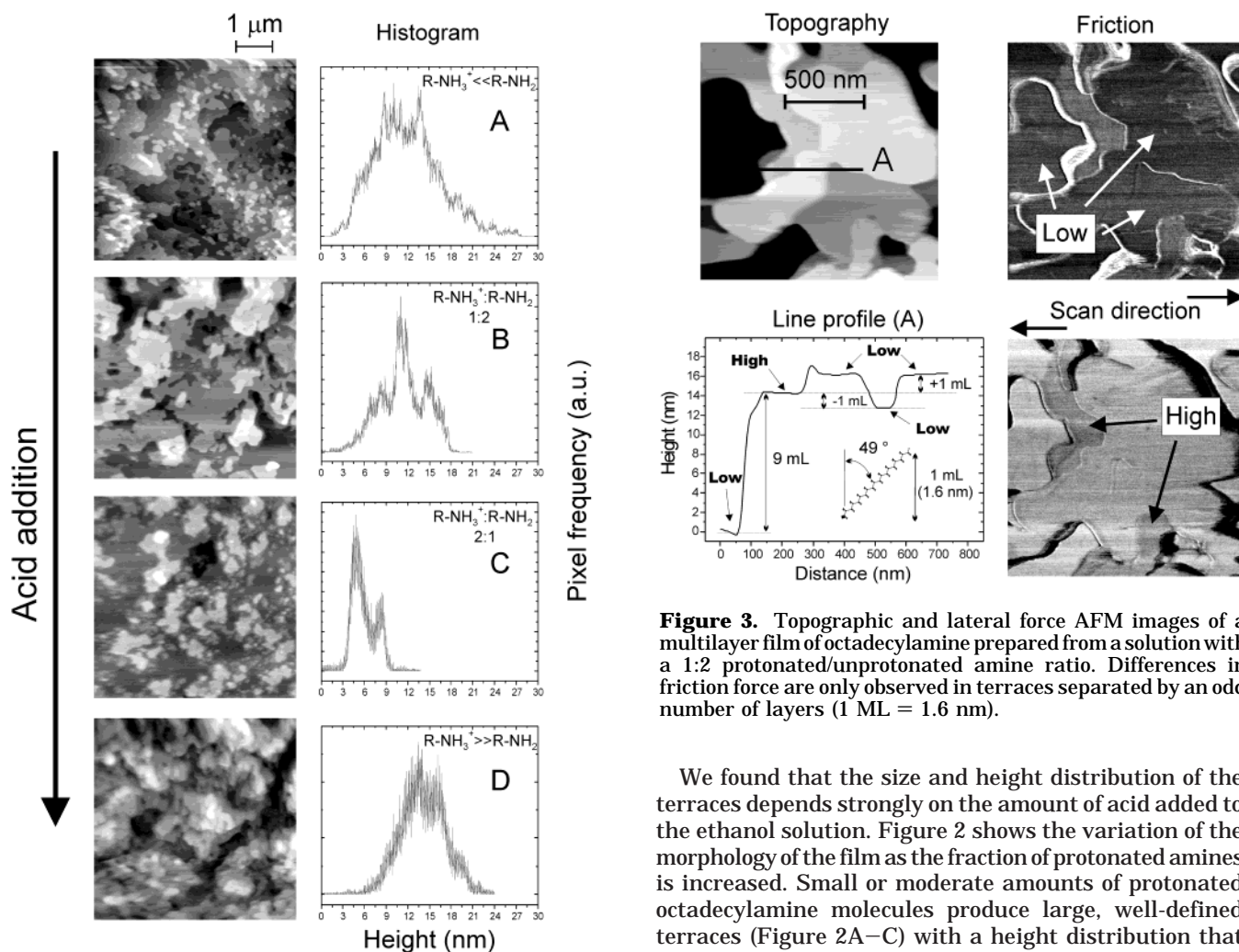

Figure 2. Influence of addition of acid to ethanol solution (15 mM) on the topography of films of octadecylamine. Image size is 5 × 5 μm. Adsorption time is 30 s followed by gentle rinsing in clean ethanol. Histograms showing terrace height distribution are included.

Figure 3. Topographic and lateral force AFM images of a multilayer film of octadecylamine prepared from a solution with a 1:2 protonated/unprotonated amine ratio. Differences in friction force are only observed in terraces separated by an odd number of layers (1 ML = 1.6 nm).

We found that the size and height distribution of the terraces depends strongly on the amount of acid added to the ethanol solution. Figure 2 shows the variation of the morphology of the film as the fraction of protonated amines is increased. Small or moderate amounts of protonated octadecylamine molecules produce large, well-defined terraces (Figure 2A−C) with a height distribution that progressively narrows as HCl is added. At the same time, the height of the step separating terraces evolves from 1 to 3 ML (1 monolayer (ML) = 1.6 nm). On the other hand, the terrace size is reduced in the case of fully protonated octadecylamine solutions (Figure 2D).
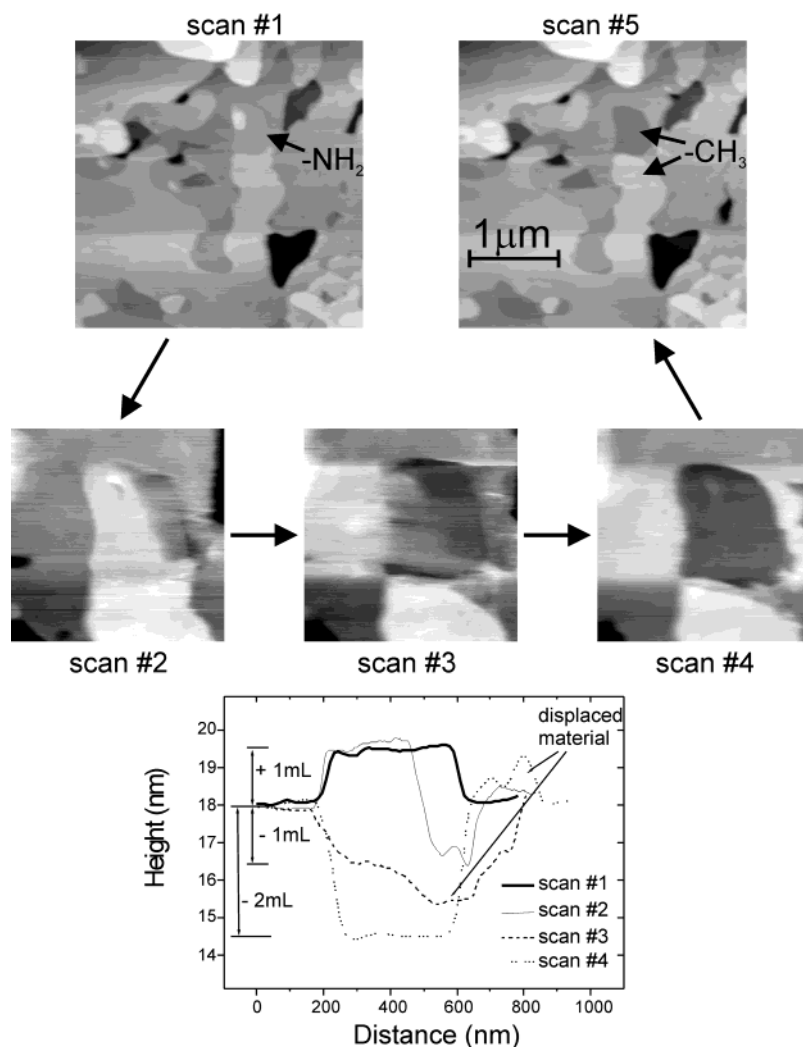
Figure 4. Selective wear by removal of octadecylamine monolayers upon successive scans at 0 nN applied force (i.e, with only the adhesive force of 46 nN). The removal proceeds by elimination of first two and then one layer, as shown in the central magnified images. Line profiles showing the modifications in topography are shown at the bottom. No HCl was added in the preparation of the multilayer film.

3.2. Friction Properties. It has been established[4-9] that the chemical identity of the terminal group has a strong influence on the frictional properties of SAMs. We thus expect that the frictional contrast of the terraces will be determined by whether the molecular termination is either methyl ($-CH_3$) or amine ($-NH_2$). Such a contrast change is indeed observed in terraces separated by an odd number of monolayers, as shown in Figure 3. In contrast, no frictional differences are detected in terraces separated by even multiples of the monolayer height.

3.3. Mechanical Stability (Wear). In addition to differences in the friction properties of alternating terraces, we observed a selective removal of layers upon repeated scanning over the same area, as shown in Figure 4. Interestingly the wear characteristic depends on whether the exposed group is $-NH_2$ or $-CH_3$. Wear of terraces exhibiting high friction (presumably $-NH_2$

terminated) stops when the original surface termination is replaced by one of low friction characteristics ($-CH_3$). It is also interesting (and unexpected) that layer removal proceeds by elimination of a bilayer followed by a single monolayer. This was observed using either Si_3N_4 or boron doped silicon tips.

3.4. Chemical Stability. Removal of molecular layers can also be achieved by chemical means, by rinsing with the pure ethanol solvent. Such layer removal was performed as a way to purposely expose patches of bare mica that would serve as reference planes for topographic and friction measurements. Figure 5 shows the evolution of a multilayer film upon successive cycles of rinsing by dipping in ethanol. In general, a first cycle of rinsing is always applied to remove weakly adsorbed molecules, Figure 5A,B. This produces well-defined terraces with a narrow height distribution, typically with 8.5−9 nm (6 ML) difference between the highest and the lowest points of an image. Furthermore, the vast majority of steps are 4.5−5 nm (=3 ML) high, as shown in Figures 5 and 6. Further rinsing creates holes on terraces that were initially flat. The holes are 4.5−5 nm deep, i.e., 3 ML, as shown in Figure 5C. The terrace height distribution changes in such a way that the area of the 6 ML peak progressively decreases while that of the 3 ML peak remains or decreases

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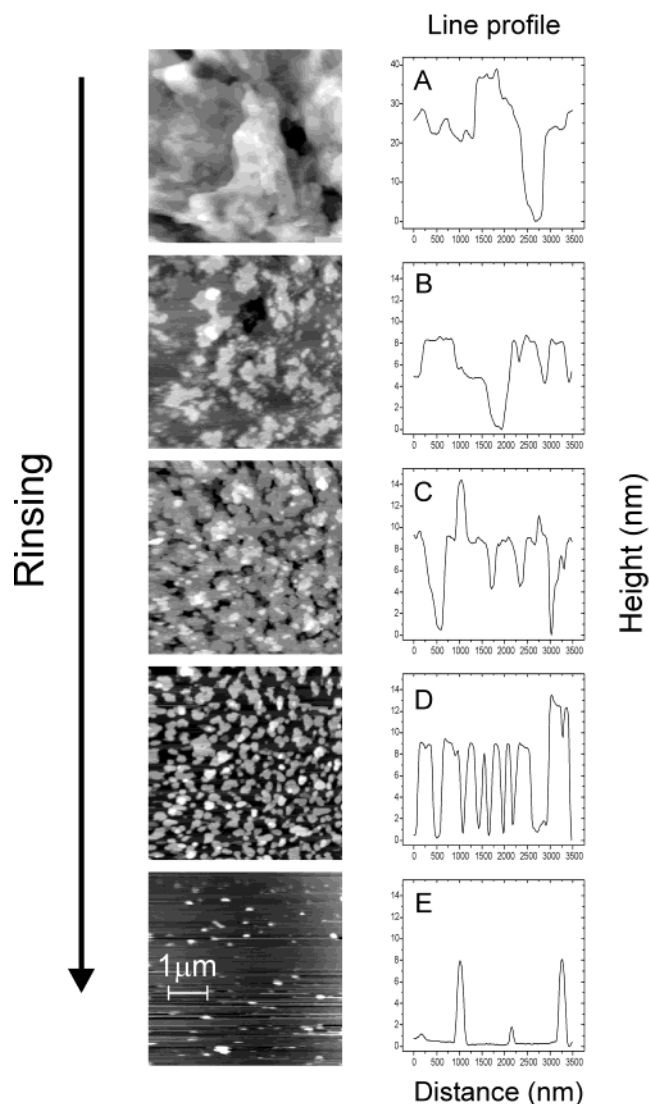
Figure 5. Effect of rinsing with pure ethanol on the structure of an octadecylamine multilayer film grown on mica from a 2:1 protonated/unprotonated amine solution. Line profiles are shown on the right. Progressive rinsing (A−D) leaves a distribution of 3, 6, and 9 ML islands.

Figure 6. Histograms showing the height distribution for images B, C, and D in Figure 5. Image B shows a narrow height distribution in which terraces are separated by 3 ML. The dissolution process starts by removing 3 ML units from amino-terminated 6 ML terraces (C) followed by additional 3 ML removals as solvent accessibility to deeper layers is improved and finally leaving 6 ML islands (D).

slightly (Figure 6C,D). It is possible that the large holes develop from small preexisting pinholes invisible in the initial images because their diameters are less than the contact diameter of the tip (a few nanometers). Unfortunately, attempts to resolve the structure of layers always ended in damage to terraces. Rinsing eventually exposes patches of bare mica (Figure 5D,E), coexisting with islands 8.5−9 nm high (6 ML). Further rinsing leads to samples with few and nearly exclusively islands of 6 ML height. Finally, extensively rinsed specimens show no features.

3.5. Influence of Acid Addition. We found that the structure of the islands obtained after rinsing strongly depends on the amount of acid added to the ethanol solution used during film preparation. Figure 7A shows that loosely packed 1 ML islands are the result of rinsing multilayered films prepared without the addition of acid (Figure 2A). On the other hand, if sufficient HCl is added to the solution to fully protonate the octadecylamine molecules, elongated islands 2 ML high (i.e., a bilayer) with sharp, interconnected edges appear after the rinsing cycle (Figure 7D). Some areas showing a double bilayer were detected as well (bright regions in this figure), together with a few small 3 ML islands. If the concentration
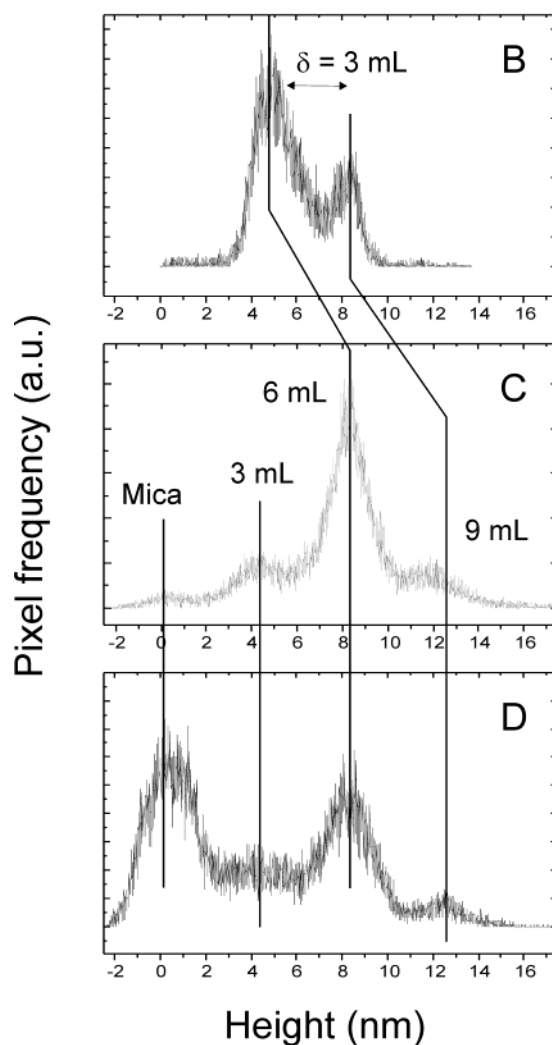
of protonated and unprotonated molecules is similar, 6 ML islands develop as already described. This is shown in Figure 7B,C. The percentage of these islands increases as the number of protonated molecules increases (R−NH$_3^+$:R−NH$_2$ 2:1), as shown in Figure 7C. When this ratio is 1:2 (Figure 7B), the island size and height distribution is more heterogeneous, with many islands consisting of 3, 6, and 9 ML.

4. Discussion

We have shown in Figure 1 how the hydrophobicity of the solvent used in the preparation of the octadecylamine solutions affects the structure of the films. Our explanation for this effect is based on the high solubility of octadecylamine in the hydrophobic chloroform. In this solvent multilayer formation is unfavorable because the cohesive van der Waals energy gain from successive layers in contact through their methyl groups is not large enough to compete with the solution energy. On the other hand, a solvent like ethanol, especially in concentrated solutions, seems to favor the formation of micellar solutions, with both methyl- and amino-terminated units (see schematic drawings in Figure 1). Although we have found no data
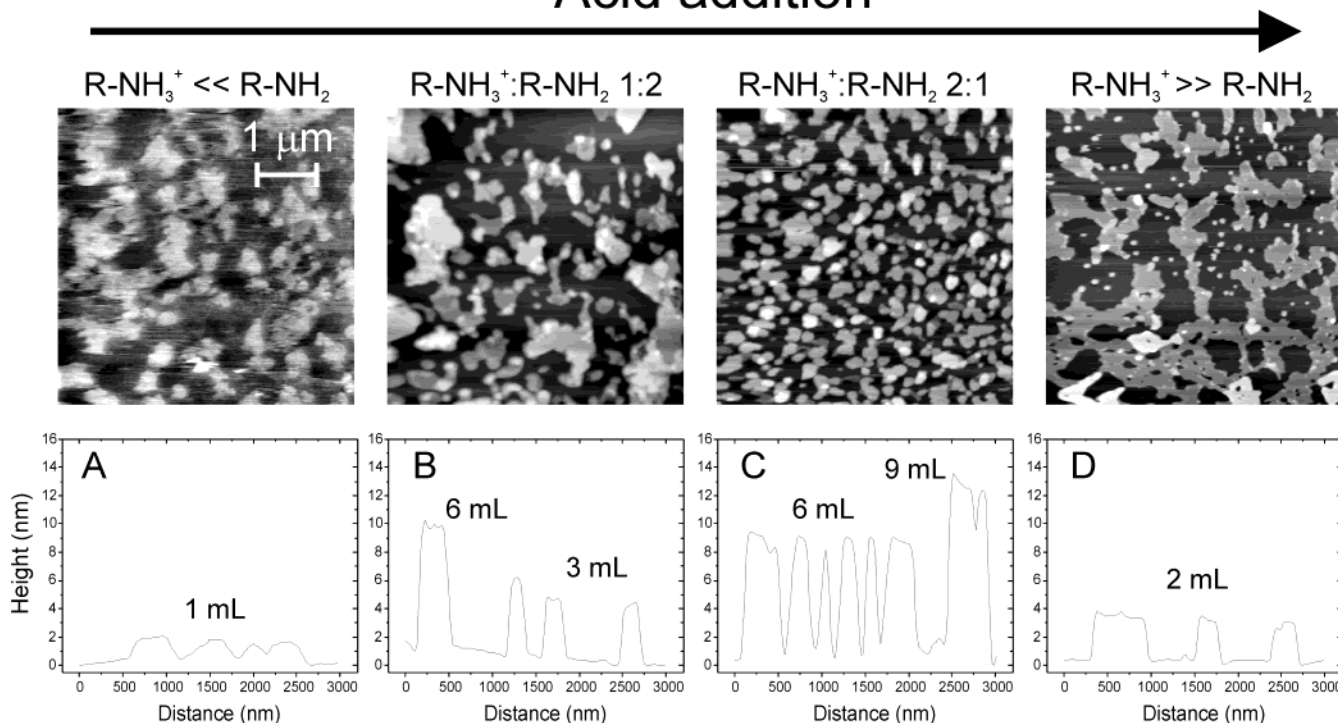
Acid addition

Figure 7. Structure of islands obtained after terrace rinsing with ethanol as a function of the amount of HCl added (A−D) to the preparation solution. Multilayered islands (3, 6, and 9 ML) are obtained when the amount of protonated and unprotonated amine molecules are comparable (B and C). Fully protonated solutions produce 2 ML islands (D), while no acid addition leaves 1 ML islands (A).

in the literature about micelle formation in this particular case, we propose that the adsorption of such micellar units is responsible for the multilayer growth and for the alternation of terminations, with terraces exposing amino or methyl end groups. Because of electrostatic repulsions between protonated amine groups, we expect that the number of micelles exposing amine groups will increase with acid addition, while micelles exposing methyl groups would form when no acid is added. The relative abundance of these two types of micelles will determine the layering structure of the films.

The different chemical nature of the terrace termination (amino or methyl) is clearly the reason for the observed differences in friction when the terraces are separated by an odd number of monolayers. Low friction should be associated with the chemically inert methyl termination, while high friction to the more reactive amino group termination.

The observed differences in mechanical stability can also be ascribed to the different chemical reactivity of these two terminations. The higher reactivity of the amine groups will also result in higher adhesion between tip and surface and to preferential wear of layers with this termination. Interestingly, this is not achieved by removing just one, but three monolayers. Intuitively, one would expect the removal to proceed by first removal of a single amino-terminated layer since this exposes a low energy methyl surface. If the load is sufficient, removal of pairs of layers should follow. The present observations may indicate that the lowest applied load is already too large. More experiments, with varying the applied force, should be performed to better understand the wear behavior. Other variables that might influence wear are water content (humidity) and degree of protonation. Such experiments are in preparation in our laboratory.

A similar layer removal pattern occurs during chemical attack with ethanol. Amino-terminated islands are pref-

erentially eroded, while methyl-terminated ones are dissolved at a lower rate (Figure 5). The amino-terminated terraces are first attacked, creating 3 ML deep holes that expose a $-CH_3$ termination. Once holes are formed, solvent accessibility is improved and the process is amplified by the removal of material in groups of 3 and 6 ML. As in the case of mechanical wear discussed above, preferential attack of the amino-terminated terraces is expected based on their higher reactivity. Here also the observed removal of material in units of 3 ML is not yet understood.

It is also interesting to analyze the influence of the amine protonation ratio on the stability of the films obtained after rinsing in ethanol (Figures 7 and 8). As we have discussed, the degree of protonation should determine the relative abundance of micelles exposing methyl or amino groups and this in turn will affect the topography and chemical termination of the islands. In the absence of protonated amine molecules (except for a small number formed by reaction with the solvent), the film is easily washed by ethanol leaving only methyl-terminated 1 ML islands, similar to those obtained from chloroform[2] solutions. At the other extreme, films formed from fully protonated solutions are also easily dissolved, but leaving in this case amino-terminated 2 ML (bilayer) islands. This bilayer arrangement should decrease the electrostatic repulsion between the charged amino groups. A balance between the concentrations of protonated and unprotonated molecules appears to be necessary to produce multilayers with better chemical resistance toward redissolution in ethanol. When the concentrations of protonated and unprotonated molecules are comparable, multilayer islands can then be obtained. Within this range, a low protonation ratio favors the presence of 3 ML units (methyl terminated), while a high ratio leads to films dominated by amino-terminated 6 ML layers. Thus, as the amount of acid is increased, the terrace termination
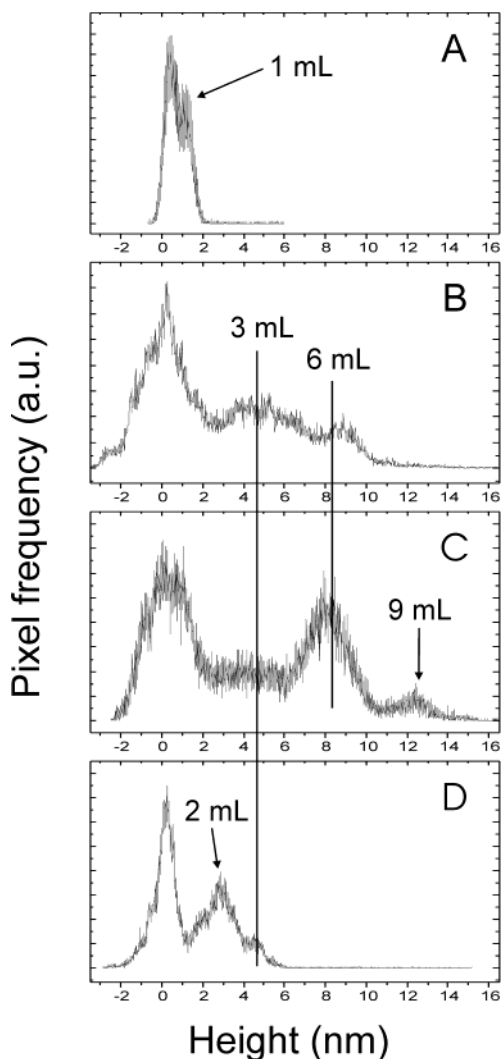
Figure 8. Histograms showing the height distribution corresponding to the images in Figure 7. Progressive addition of HCl in the solution favors the evolution from methyl-terminated islands (1 and 3 ML) to amino-terminated (6 and 2 ML) ones after rinsing with pure ethanol.

is transformed from methyl (odd number of layers) to amino (even), Figure 8.

5. Conclusions

We have shown that multilayers of octadecylamine can be prepared on the surface of mica when using solutions of the molecule in ethanol. Each layer has a height of 1.6 nm, consistent with a closely packed arrangement of molecules with straight, parallel alkane chains, tilted at an angle of 49° away from the normal. The formation of multilayers is in contrast with the single monolayers produced when using hydrophobic chloroform solutions. We have also shown that the stacking of these layers is such that the terraces expose methyl and amino groups when separated by an odd number of layers. Micellar formation in the solution is the proposed mechanism of the multilayer formation. The mechanical (friction, wear) and chemical properties (attack by ethanol) are strongly dependent on the termination, with low friction being associated with the chemically inert methyl groups and high friction with the amine termination. The structure and topology of the layering after chemical attack with ethanol was observed to depend on the degree of protonation of the original amine preparation solution. Low protonation ratios favor methyl-terminated multilayered islands, while high protonation ratios leave amino-terminated residues. We have proposed that the mechanism that drives this topological structuring is the degree of electrostatic charging associated with protonation. To minimize electrostatic energy, amino-terminated micelles should form preferentially at high protonation ratios, which in turn favors this termination in the exposed terraces. An interesting effect is the removal, through both mechanical and chemical wear, of units of 3 ML, an observation for which no explanation is available at present.