The influence of chain length and ripening time on the self-assembly of alkylamines on mica

J. J. Benítez[a)]
Instituto de Ciencia de Materiales de Sevilla, Centro Mixto CSIC-Universidad de Sevilla, Avenida Americo Vespuccio 49, Isla de la Cartuja, Sevilla 41092, Spain

M. Salmeron[b)]
Materials Science Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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The influence of chain length and ripening time on the self-assembly of tetradecyl (C_{14}), hexadecyl (C_{16}), and octadecylamine (C_{16}) on mica has been studied by atomic force microscopy. The overall process can be described in three stages characterized by different time scales. First, alkylamine molecules adsorb in a process controlled by water mediated interactions of the NH_2 head groups and mica. Second, surface diffusion and aggregation into islands takes place, driven by energy interactions between alkyl chains. The third stage consists of a progressive tilt of the self-assembled molecules towards the surface, driven by relaxation of the electrostatic repulsion between protonated amino groups due to water uptake from atmosphere. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2221692]

I. INTRODUCTION

Self-assembly of molecules containing alkyl chains is usually driven by the van der Waals attraction that favors formation of compact arrays of molecules with maximum contact between chains. A large amount of research has been conducted with thiols and silanes on substrates such as gold, silicon oxide, mica, glass, and others.[1–8] Molecules with other head groups, notably amines have also been studied.[9,10] Alkylamine self-assembly has been shown to be strongly influenced by humidity probably through formation of NH_3^+ by reaction of the NH_2 head groups with water.[11,12] Bonding of the molecules to the negative mica substrate is expected to be largely electrostatic in nature.

On flat substrates most linear alkyl chain molecules self-assemble vertically or in a tilted configuration with a separation d of about 4.3 Å, the van der Waals diameter of the alkyl chain. A simple geometrical model describes with surprising accuracy the tilt angle that the molecules may adopt, either spontaneously or as a result of applied loads.[13] The model assumes that maximum cohesive energy is obtained when the zigzag skeletons of the chains are interlocked in neighboring molecules. If the molecules were axiosymmetric or able to freely rotate around their axis, the geometrical constrains imposed by interlocking results in discrete tilt angles (θ) from the surface normal satisfying the condition

$$\tan(\theta) = na/d, \tag{1}$$

where a is the distance (2.5 Å) between alternating C atoms projected on the molecular axis of the alkyl chain and n an integer defining the tilting state ($n=0$ fully vertical). In terms of the island height h and the molecular length L the above formula is equivalent to $\cos(\theta)=h/L=[1+(na/d)^2]^{-1/2}$. If the axial symmetry is broken by crystalline packing one needs to consider tilts in two directions, along nearest (molecular separation d_x) and next-nearest neighbor directions (molecular separation d_y). Two indices, n and m, are then needed satisfying the conditions

$$\tan(\theta_x) = na/d_x \quad (n = 0, 0.5, 1, 1.5, \ldots),$$

$$\tan(\theta_y) = ma/d_y \quad (m/2 = 0, 0.5, 1, 1.5, \ldots). \tag{2}$$

This was shown to satisfactorily explain the tilts observed for hexagonal arrangements of alkylthiols on Au(111).[14]

In this article we present a study of the structure of self-assembled films formed by three alkylamines, tetradecyl, hexadecyl, and octadecyl (referred to as C_{14}, C_{16}, and C_{18}, respectively, in the following) on mica and of the effect of ripening time. As we will show, the findings can be explained on the basis of the packing models described above and of the effect of water, which plays a crucial role in the case of amines.

II. EXPERIMENT

Tetradecylamine (C_{14}) (Fluka, ⩾98.5%), hexadecylamine (C_{16}) (Fluka, ⩾99%), and octadecylamine (C_{18}) (Fluka, >99%) were used as received and dissolved in chloroform (Aldrich 99.8%) to prepare 15 mM solutions. Samples of muscovite mica [$KAl_2(Si_3AlO_{10})(OH)_2$, Mica New York Corp.] were cleaved under ambient conditions (20–25 °C, 40%–55% RH) and immersed in the solution for 30 s. After removal they were dried without rinsing under

a)Electronic mail: benitez@icmse.csic.es
b)Author to whom correspondence should be addressed. Electronic mail: mbsalmeron@lbl.gov

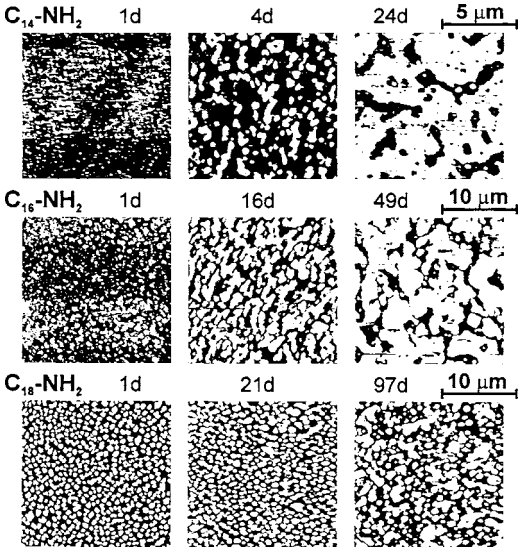

FIG. 1. Constant force (0 nN) topographic AFM images showing the evolution of tetradecyl (C_{14}–NH_2), hexadecyl (C_{16}–NH_2), and octadecyalmine (C_{18}–NH_2) islands on mica during exposure to ambient laboratory air (ripening). The numbers at the top of each image indicate days elapsed after preparation.

dry N_2 stream and kept in a hermetic test tube for 24 h. They were later transferred to a Petri dish where ripening continued in the laboratory atmosphere.

The atomic force microscope (AFM) is a Topometrix Explorer (TMX2000) operating in air at room temperature (20–24 °C) and a humidity of 40%–55%. A 130 $\times$130 μm^2 *X*, *Y*, 13 μm *Z* range scanner was used to image the surface down to 5×5 μm^2. A higher resolution scanner (2.3 μm *X*, 2.3 μm *X*, *Y*, and 0.8 μm *Z*) was used for height and friction measurements. Additional image analysis has been carried out using the VSxM program from Nanotec Electronica.[15] Si_3N_4 cantilever (NanoProbes™, Digital Instruments, Santa Barbara, CA) with 0.12 N/m nominal force constant was employed in all experiments. The *z* distance scale (normal to the surface) was calibrated using a commercial test silicon grating (TGZ01, Silicon-MDT, Moscow) with nominal step heights of 22.0 nm.

To obtain representative results several images of the same sample were analyzed with the large range scanner, using at least two different preparations.

III. RESULTS

A. Island growth and morphology

During ripening slow diffusion processes take place that cause structural changes in the amine films as shown in the AFM images of Fig. 1. After 1 day ripening the C_{18}-dipped mica displays a uniform coverage of islands with an average diameter of 0.5 μm. On the C_{16}-dipped mica islands are also formed but with smaller dimensions, and in the case of C_{14} no well-defined features except for small dots could be detected. The shorter molecules formed islands only after ripening for 2–4 days. After 4 days, ripening produces a differentiation of the island structures that depends on chain length. While in the case of C_{18} several weeks (>3) are

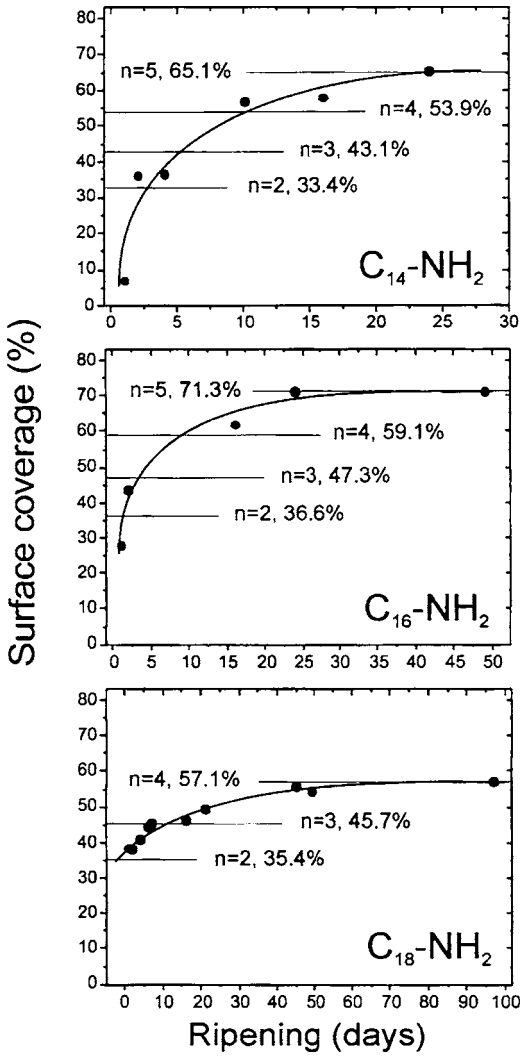

FIG. 2. Fractional surface area covered by islands of C_{14}, C_{16}, and C_{18} alkylamines vs ripening time. The horizontal lines have been drawn to mark the coverage expected from a tilted configuration (n,m=0). The value of n indicates the number of methylene groups unmatched in neighboring molecules (see text for details).

needed for large aggregates to form, C_{14} amines form large aggregates within the first week. For C_{16} large islands form after about 2 weeks.

The aggregation of molecules to form islands and their subsequent growth were analyzed by measuring the fraction of surface covered by islands. The results are shown in Fig. 2. In 24 days the surface coverage increases from 5% to 65% for C_{14} and from 25% to 70% for C_{16}. For C_{18} the increase is from 35% to 55% after four times the same period. It is also interesting to notice the formation of small rounded dots after long ripening on the sample with C_{14} molecules. Such features are not observed for the longer C_{16} and C_{18} alkylamines, even after more extensive ripening. This excludes contamination from laboratory atmosphere as the reason for its formation. We interpret them as globular micelarlike structures coexisting with the flat, monolayer thick islands driven by water adsorption.

There are two processes that contribute to the observed growth in island size and coverage. One is simple diffusion and accretion of dispersed molecules into existing islands.

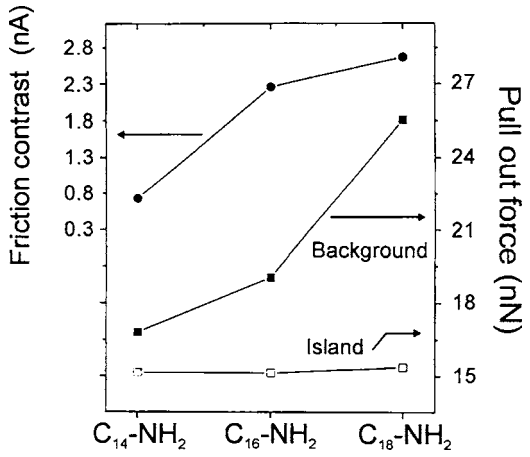

FIG. 3. Left axis: Friction contrast between alkylamine islands and the surrounding mica substrate. Right axis: pull-off force measured on top of the islands and on the mica substrate for C_{14}, C_{16}, and C_{18} alkylamines during the accretion stage, where scattered molecules diffuse on the mica before attaching to the islands. Friction values are obtained from the difference between left to right and the right to left traces in friction force images, using the same tip and experimental conditions for C_{14}, C_{16}, and C_{18}.

The dispersed molecules are presumably lying flat initially on the surface and are easily displaced by the tip, so that they are not visible in the images. Their presence, however, can be ascertained by measuring the adhesion and friction properties in the area between islands. Figure 3 shows the frictional contrast (left y axis, calculated from the difference of left to right and right to left traces in lateral force images) and pull-off forces between islands and background (right y axis) observed during the initial assembly stage of C_{14}, C_{16}, and C_{18}. While the pull-off force on top of already formed self-assembled monolayer (SAM) islands is quite similar it becomes significantly higher on the mica outside the island region in going from C_{14} to C_{18}. Since capillarity forces are strongly affected by condensation, the lower values observed for C_{16} and C_{14} are indicative of a more hydrophobic background as a consequence of the presence of scattered alkylamine molecules. The graph indicates that the self-assembly is more completed, i.e., there are less scattered molecules between islands for the longer chains. Frictional contrast between low friction islands (methyl terminated) and high friction mica is reduced in going from C_{18} to C_{14} as a result of the contribution of scattered alkylamine molecules on mica.

B. Island height evolution

In addition to the changes in aggregation state due to scattered molecules joining and enlarging the existing islands, we found that ripening gives also rise to changes in the height of the islands and in the coverage, even when the accretion stage is finished (i.e., when most molecules are already attached to islands). At the start of the ripening period (between 1 and 5 days) the C_{18} islands are about 16.5 Å high, which according to formula (1) corresponds to the state with $n=2$, with a tilt angle of 47° from the surface normal.[9] For C_{16} and C_{14} the island heights are 15.3 and 13.2 Å, respectively, consistent with the same $n=2$ state and tilt angle.

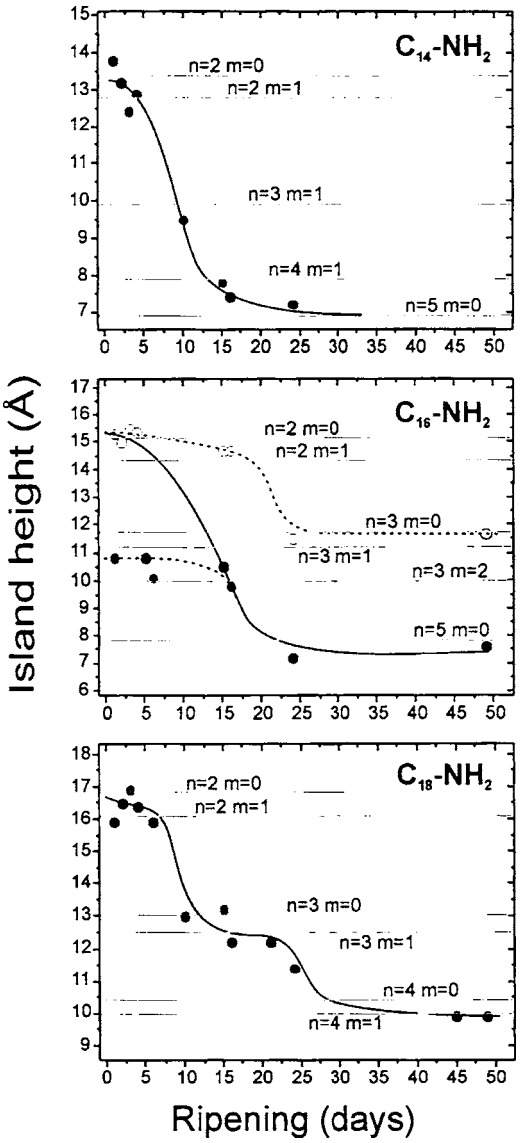

FIG. 4. Island height vs ripening time for C_{14}, C_{16}, and C_{18} alkylamines on mica. The horizontal gray lines indicate theoretical heights for states characterized by discrete tilt angles in the nearest neighbor (n) and next-nearest neighbor directions (m), as explained in the text.

We have shown in a previous paper that the tilt state of assembled C_{14} molecules depends on the amount of water present on the surface, which in turns depends on humidity and exposure time. As ripening continues the island height decreases with time, as shown in Fig. 4. For C_{14} and C_{18}, the height decreased to values of 7.0 and 10.0 Å, respectively, after long ripening time. For C_{16} islands with two different heights coexist, with high islands predominating initially. These two heights decreased to 11.6 and 7.6 Å. After 2 weeks of ripening the situation is reversed and low islands became the most abundant. The initial $n=2$ phase became negligible except for residual patches at the periphery of the islands, as shown in Fig. 5. Although the origin of this coexistence is not known, it is likely that the higher phase is metastable and its formation might be the result of nucleation in some defect. A similar coexistence of different height phases was observed for alkylthiols on Au(111).[16]

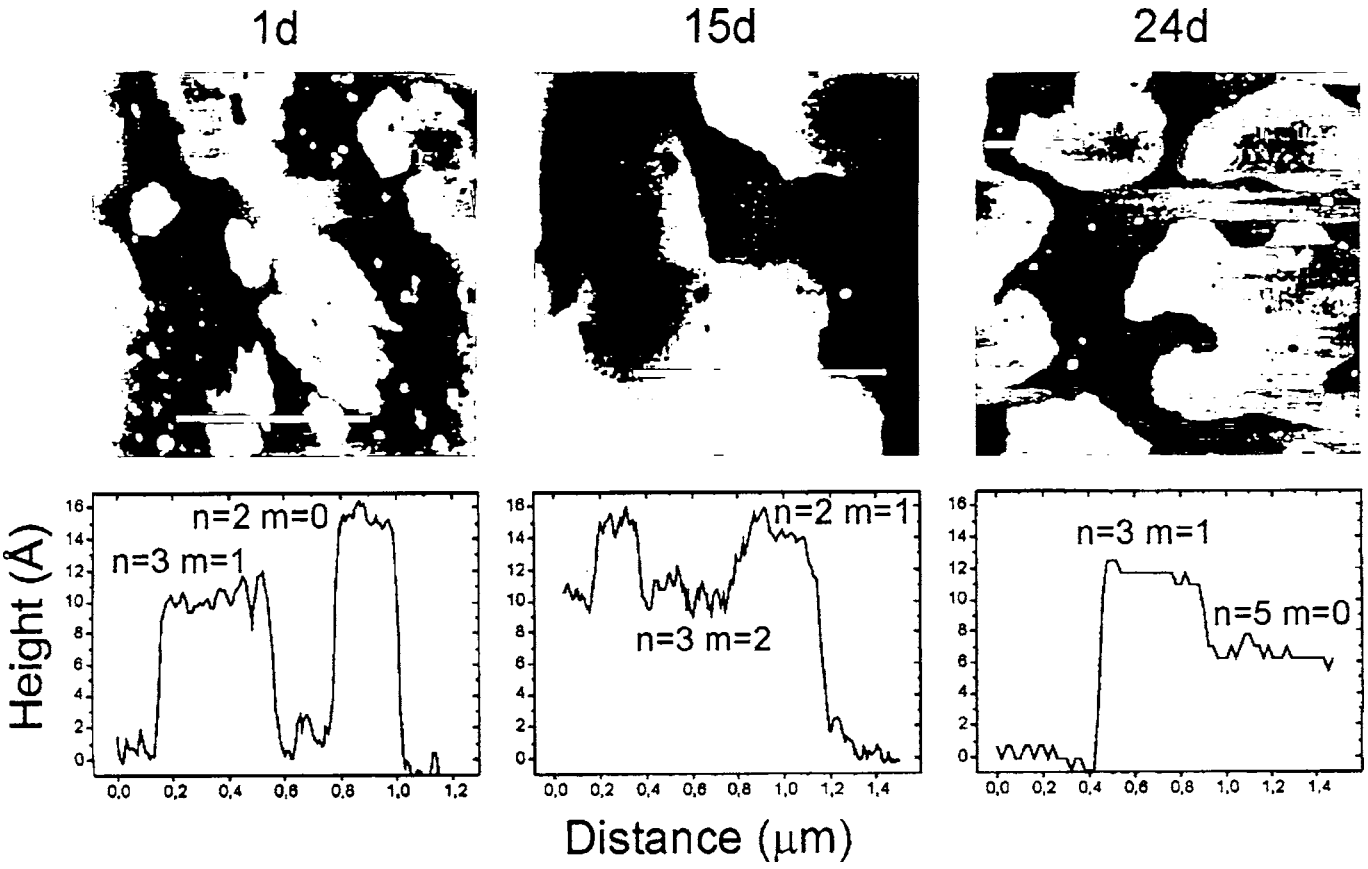

FIG. 5. Topographic AFM images of hexadecylamine SAM islands showing coexistence of two heights (images at 1, 15, and 24 day ripening). Tilting state is indicated in line profiles.

IV. DISCUSSION

The procedure used to prepare the samples ensures that the total amount of alkylamine molecules on the surface remains constant throughout the ripening period. This amount is less than a full monolayer as shown by the images obtained after long ripening times. We have reported in previous work that the binding of the amines to mica is mediated by water that reacts to form most likely NH_3^+ and OH^-. The coverage is therefore strongly dependent on the amount of water present on the mica surface at the time of dipping into the solution. The chloroform used to dissolve the amines does not completely displace this preadsorbed water, in spite of its hydrophobic character. The crucial role of water was shown by using alcohol solvents instead of chloroform. In that case not only monolayers but multilayers of alkylamines were readily formed.[10]

The images and the graphs in Fig. 2 indicate that initially only a fraction of the adsorbed alkylamines are self-assembled in the form of islands, while the rest must be scattered in the remaining areas, probably lying down and easily displaced by the tip during scanning. Slowly, however, the scattered molecules diffuse and attach to the existing islands. This accretion process ends up after most of the molecules have been collected into islands. As we have seen, early in the ripening process the molecules in the islands are tilted by 47° relative to the surface normal, corresponding to state $n=2$, $m=0$. As ripening continues a progressive tilting occurs down to state $n=5$, $m=0$ for C_{14} and C_{16}, which corresponds to $\theta=69°$, and to $n=4$, $m=0$ ($\theta=65°$) for the longer C_{18}.

The ripening-induced tilting is in line with the previous finding that water is involved in the bonding between mica and the NH_2 head group. We thus propose that after assembly slow water uptake from the atmosphere induces molecular tilts that modify the separation between head groups as a result of repulsive electrostatic forces from the increasingly protonated fraction of head groups to form NH_3^+. Tilting reduces the cohesive energy of alkylamines within the islands by decreasing the contact length. Therefore the final state should be the result of the balance between relaxation of electrostatic repulsive interactions and loss of internal cohesive energy. For this reason tilting is more severe in shorter C_{14} and C_{16} alkylamines ($n=5$) where the van der Waals chain-chain cohesive energy is smaller compared to that in C_{18}.

There are two contributions to the increase in fractional surface coverage by islands upon ripening. The initial increase is mostly due to accretion of scattered molecules into islands. In our conditions this process takes place in the first few days. After this accretion stage is completed the subsequent increase is due to tilting of the molecules, which increases the area by reason of volume conservation. From the measured island heights the tilt state of the most ripened islands corresponds to $n=5$ for C_{14} and C_{16} and to $n=4$ for C_{18}. In Fig. 2 the horizontal lines mark the expected area

increases corresponding to various tilt angles. As we can see, molecular tilt is enough to account for the dependence of surface coverage with ripening time after the initial accretion stage. The effect of the initial accretion can be seen in the case of C_{14} and C_{16} where the theoretical coverage corresponding to the initial $n=2$ state is larger than that measured from AFM images. For C_{18} the accretion stage takes place in less than 1 day, while it takes 2 days for C_{16} and 3–4 days for C_{14} under our laboratory experimental conditions.

It can also be seen that the predicted coverage value for the initial $n=2$ state of 0.35 is the same for all three chain lengths. This observation reveals that the total number of adsorbed molecules is the same, independent of chain length. This is not surprising since adsorption on mica is controlled by the precoverage of water, which helps bind the terminal NH_2 groups.

V. SUMMARY AND CONCLUSIONS

We have presented a series of new results on the evolution of the structure of islands of alkylamines with three different chain lengths. They provide new insights into the nature of the intermolecular and molecular-substrate interactions and the influence of environmental agents such as water. Notable changes in structure were observed starting from the preparation from a chloroform solution to their ripening in the presence of ambient laboratory air. The analysis of the results provides the following picture of the self-assembly process.

First the alkylamine molecules, which are basic, adsorb on mica in a typical acid-base reaction mediated by water. The reaction involves protonation of the amino head groups by residual water acting as a Brönsted acid. The adsorption energy is mostly due to this water-amino-mica site interaction, with negligible effect from the alkyl chains, although small changes in basicity of the amino group can be expected from the contribution of the alkyl groups in going from C_{14} to C_{18} (inductive effect). The initial amount of water determines the number of molecules initially anchored to the surface. In our experiments this is confirmed by the finding of the same initial coverage regardless of chain length.

After this relatively fast initial stage, a second stage takes place that is dominated by slow diffusion and aggregation of molecules to form self-assembled islands (the accretion stage). In this stage attractive van der Waals interactions between alkyl chains control the process.

A third and slow stage follows the accretion stage, which is manifested by an increase in the molecular tilt of the islands. We believe that this process is controlled by water penetration inside the island region, probably starting at the edges of the islands. Water affects the interaction between head groups by increasing the extent of protonation and hydration of the amino head groups. This favors a larger tilt angle because it increases the separation of the head groups, shielding and relaxing their electrostatic repulsion.

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