

ATOMIC FORCE MICROSCOPY OF ADSORBATES FROM I_E SOLUTIONS

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Atomic force microscopy (AFM) is an advanced microscopic method which provides comprehensive information about morphology, nanostructure, molecular and atomic organization for a broad range of materials. In recent attempts to apply AFM to study I_E aqueous solutions, well-defined granular structures were observed. A tentative analysis of the data is discussed.

1. Introduction

Atomic Force Microscopy (AFM) is a revolutionary technology that provides three-dimensional information about structures on micron to atomic scale. AFM is widely used for evaluation of sample composition, local mechanical and adhesive properties of heterogeneous materials. The method is based on the measurement of the attractive or repulsive forces between an AFM probe tip and a sample. In its most basic, contact mode, AFM measures topography of a surface by dragging the probe, consisting of a cantilever with a sharp tip at the end, across the sample (Figure 1). The cantilever deflection during scanning is monitored with a laser beam focused on the back of the cantilever. The beam is reflected off the back of the cantilever onto a photodiode detector. In the constant force operation, the cantilever deflection is kept constant by adjusting the vertical position of the sample with a piezo-scanner. These vertical adjustments are reproduced in height images, which describe the sample topography. This method, while quite successful in many applications, has a drawback of creating very strong friction forces which can cause serious damage to more delicate and softer samples. A recently introduced TappingModeTM technique overcomes this problem by oscillating the tip holding cantilever while scanning the surface of a sample. The method creates very short contact between tip and sample, and almost completely eliminates lateral forces. A reduction in amplitude of oscillation, as the cantilever contacts the sample surface, is used to identify and measure surface features (Figures 2 and 3). TappingMode AFM allows high resolution measurements of soft or fragile samples that are easily damaged and/or loosely held to their substrate in

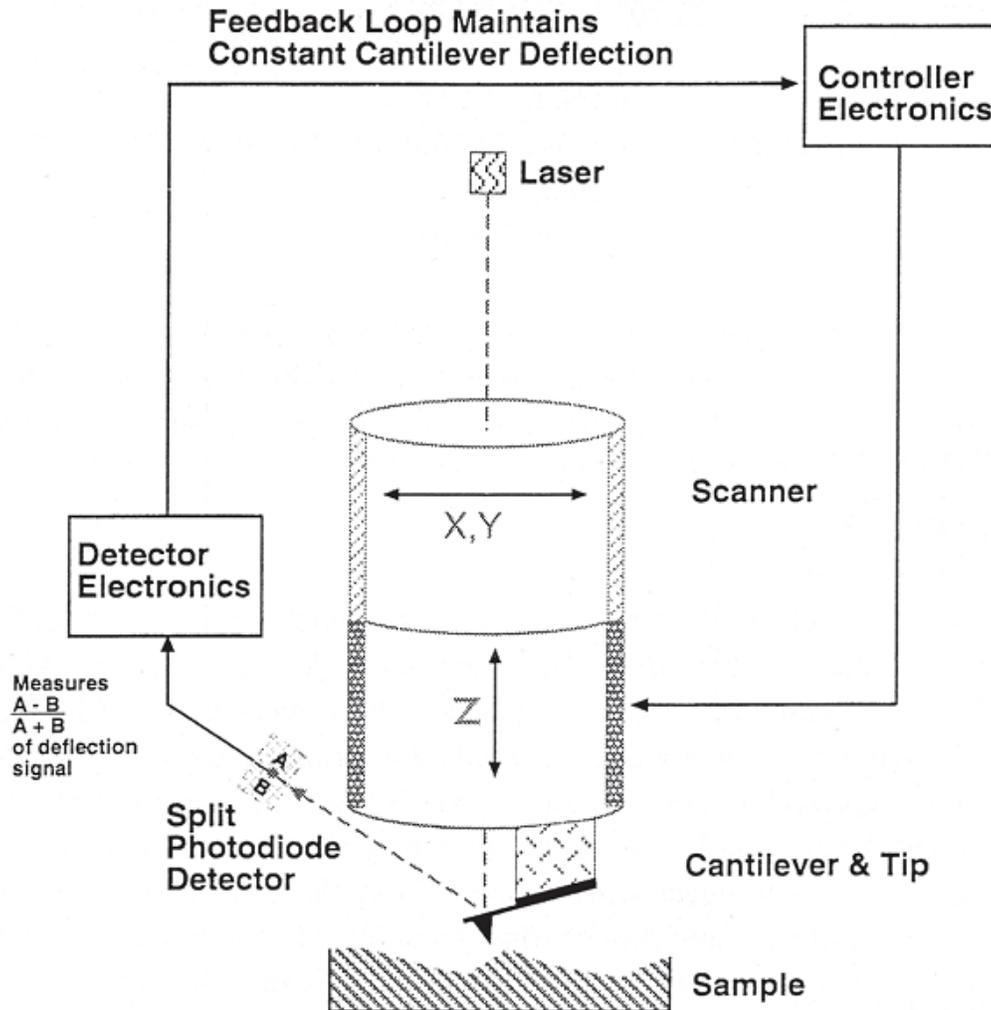


FIGURE 1 Contact Mode AFM.

In contact mode AFM, a probe tip attached to the end of the cantilever is dragged across the surface of the sample. The image is created based on a change in cantilever deflection which is continuously monitored with a photodiode detector. [From *Digital Instruments Scanning Probe Microscopy Training Notebook*].

both air and liquid environments. Etched silicon probes used in TappingMode AFM have a sharp tip with a diameter of 10-20 nm. In the low-force operation (carried out with the appropriate choice of instrumental parameters) the tip-sample contact area is even smaller than the tip diameter, allowing lateral resolution of 2-3 nm. This technique has found a wide range of applications, including studies of silicon wafer surfaces, metals and insulators, polymers, and biological samples

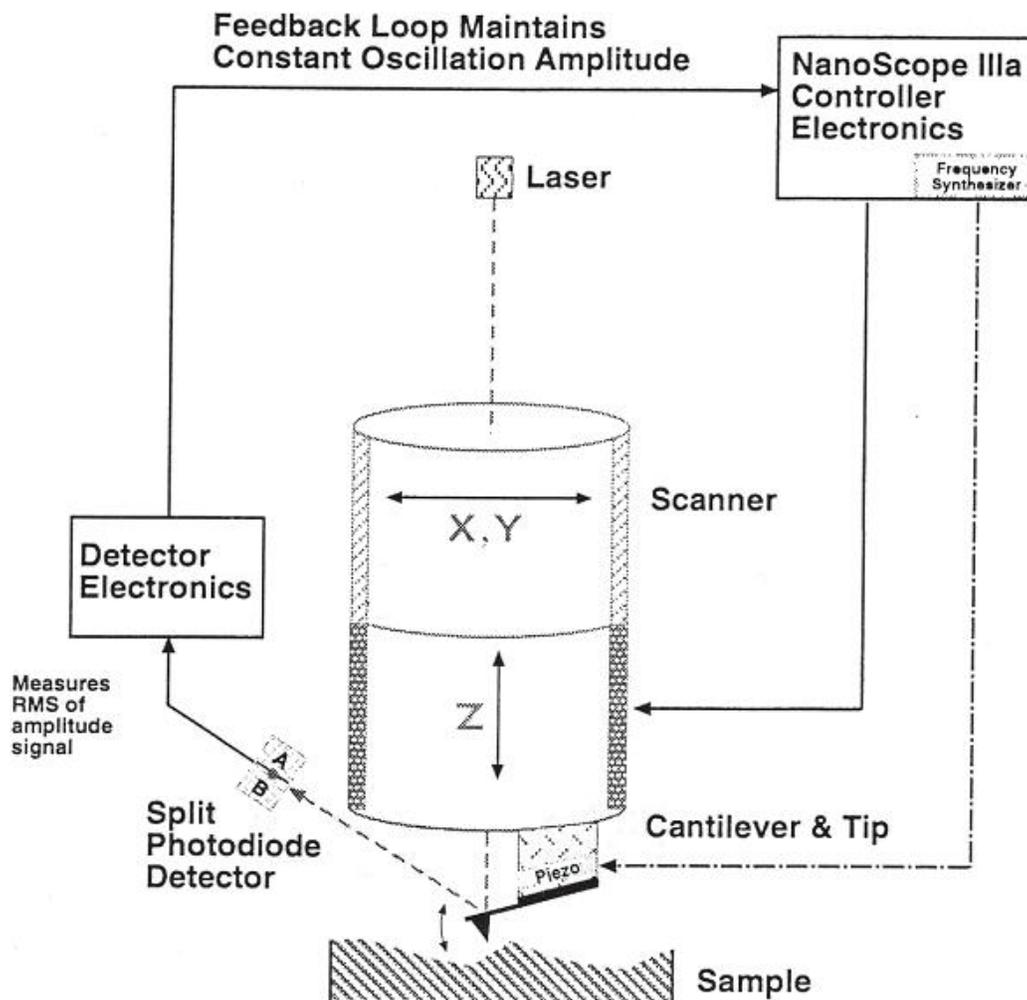


FIGURE 2 Tapping ModeTM AFM.

In TappingMode AFM, a probe tip attached to the end of cantilever is oscillated and “taps” on the sample surface during scanning. The image is created based on a change in amplitude of oscillation. [From *Digital Instruments Scanning Probe Microscopy Training Notebook*].

Self-organization of organic amphiphatic compounds, substances that contain both hydrophilic and hydrophobic functional groups, is a common phenomenon in aqueous solutions. The structure of such supramolecular assemblies was recently successfully studied by AFM¹⁻³. The high resolution AFM images obtained, of amphiphathic adsorbates on graphite and mica, revealed their morphology and led to a structural model in which the supramolecular structures are formed by the fusing of spherical miscelles.

Stable associations of water molecules, called I_E TM Crystals, were developed by Lo^{4,5} several years ago. It has been established that I_E Crystal aqueous

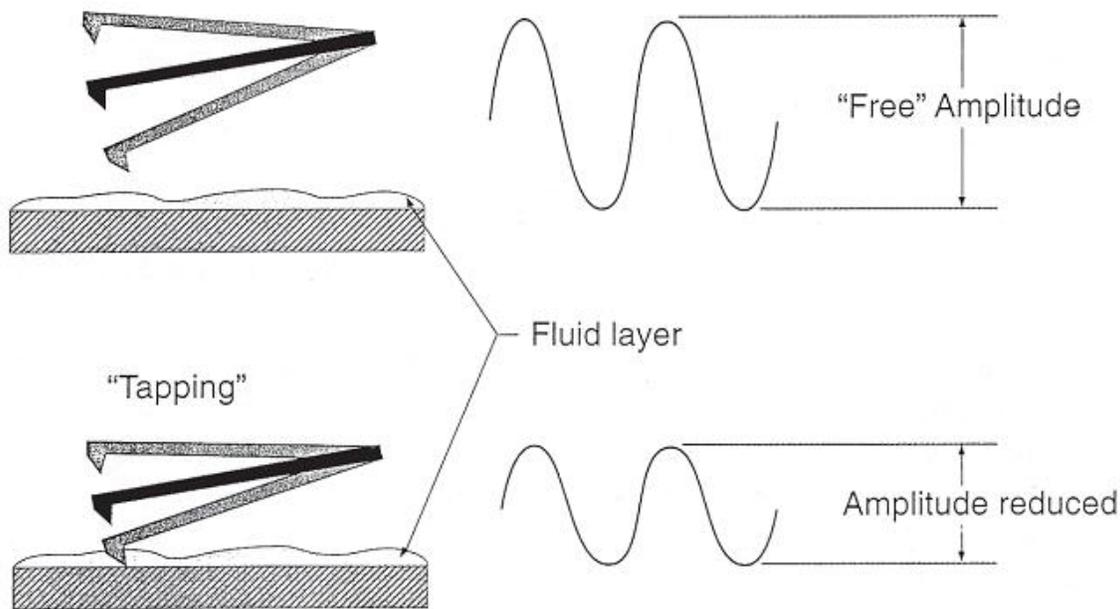


FIGURE 3 Tapping Mode cantilever oscillation amplitude.

A reduction in amplitude of oscillation is reduced when the tip contacts a sample surface. [From *Digital Instruments TappingMod™ Imaging; Applications and Technology*].

solutions have distinctive physical and chemical properties^{4,5}, as well as exert strong stimulating activity on various biological systems⁶⁻⁸. In order to explain the unusual properties of these solutions, it is necessary to characterize the structure of I_E crystals. The objective of this work was to examine the morphology of I_E crystal adsorbates on mica surface.

2. Materials and Methods

Drops of aqueous I_E crystal solutions V_E -34, D_S -240, and Y_S -55 provided by American Technologies Group (ATG) were placed on freshly cleaved atomic smooth mica substrate surface and left to air dry. Height and lateral force images of I_E adsorbates were recorded in TappingMode with Scanning probe microscopy "Nanoscope III" (Digital Instruments, Inc., Santa Barbara).

3. Results

The structures observed with AFM in all samples were well-defined and consisted of numerous grains (Figures 4-6). The smallest grains had a diameter of about 10-50 nm and height of 1-5 nm. Larger linear structures made up of fused grains with lengths of 100-500 nm (Figure 6) and 1-5 μ m (Figure 5) were also identified in all samples.

I_E structures are soft and springy: when higher force is applied during AFM scanning they become more flat but compact (Figure 7a). When the force is decreased, they bounce back to the original height and shape (Figure 7b). However, very high force leads to scraping of the adsorbate from the mica substrate (8). The thickness of the adsorbate layer scratched away with

high-force scanning was determined to be 25 nm.

Although additional research is required before definite conclusions about the dynamics of I_E self-assembling can be made, the above data indicates that I_E crystals are, in fact, ordered structures with granular substructure.

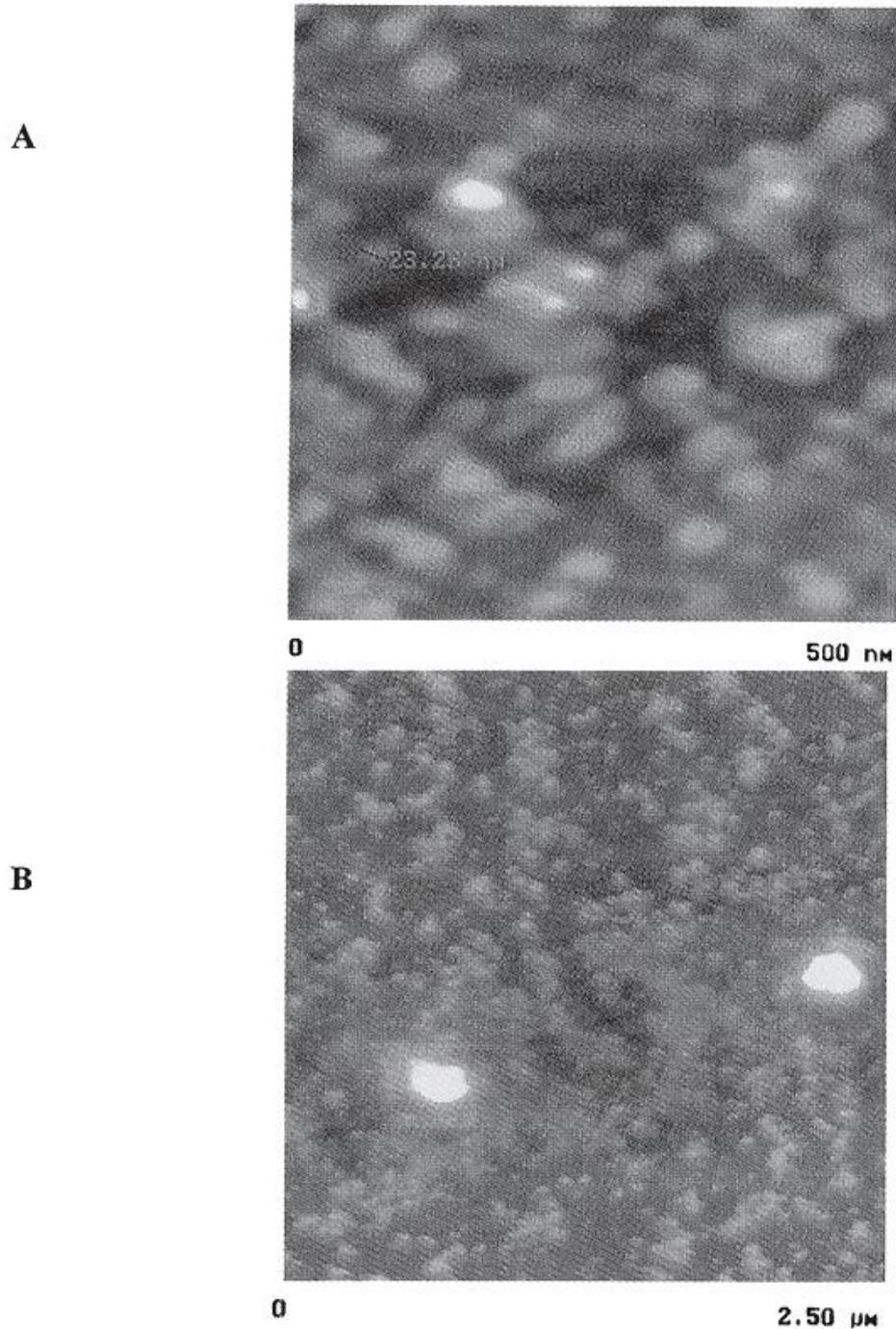


FIGURE 4 AFM height images of V_{E-34} type I_E adsorbate on mica. The contrast of the pictures covers height variations from 0.1 to 5 nm (A) and from 0.1 to 10 nm (B). The scanned area was 500 x 500 nm (A) and 2.5 x 2.5 μm (B).

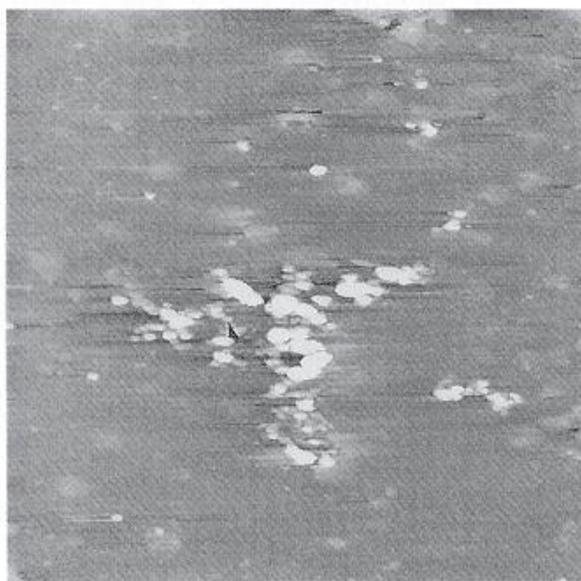
A



0

25.0 μm

B



0

30.0 μm

FIGURE 5 AFM height images of D_S -240 type I_E adsorbate on mica. The contrast of the pictures covers height variations from 0.1 to 25 nm (A) and from 0.1 to 100 nm (B). The scanned area was 25 x 25 μm (A) and 30 x 30 μm (B).

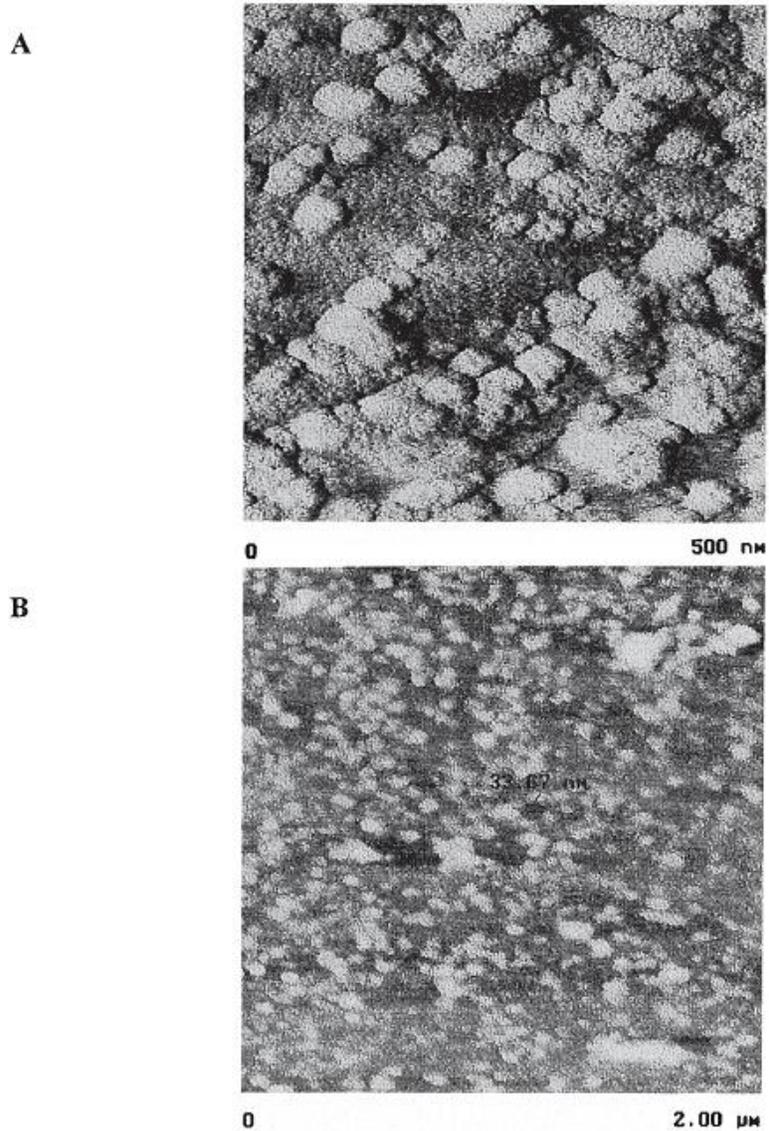


FIGURE 6 AFM lateral force image of V_E -34 type I_E (A) and height image of Y_5 -55 type I_E (B) adsorbates on mica.

The contrast of the pictures is proportional to the lateral force variations in relative units (A) and it covers height variations in the 0.1-5 nm range (B). The scanned area was 500x500 nm (A) and 2x2 μm (B).

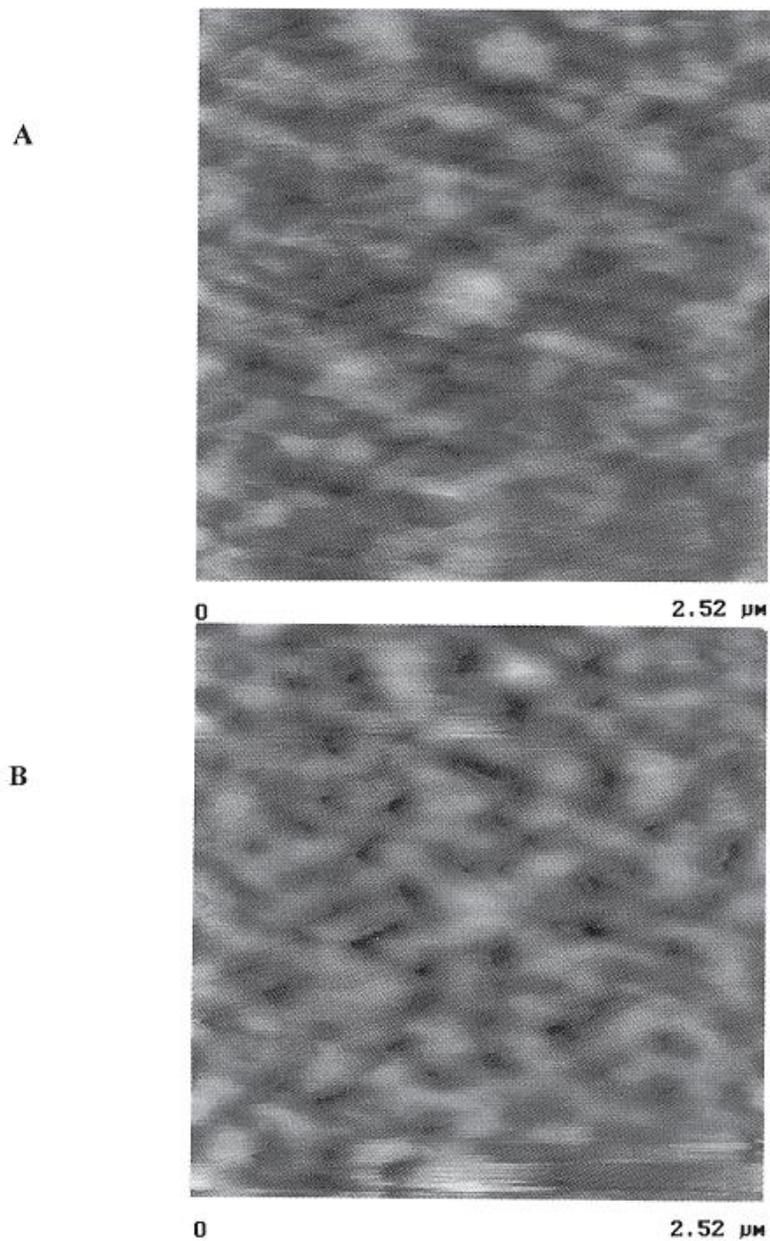


FIGURE 7 AFM height images of D_S -240 type I_E adsorbate on mica. The contrast of the pictures covers height variations from 0.1 to 4 nm (A) and from 0.1 to 10 nm (B). The scanned area in both cases was $2.5 \times 2.5 \mu\text{m}$. The images were obtained in TappingMode by scanning with high (A) and low (B) force applied to the tip.

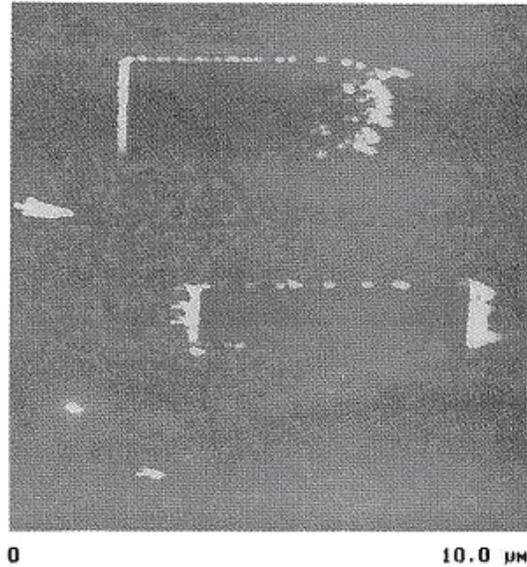


FIGURE 8 AFM height image of V_E -34 type I_E adsorbate on mica. The contrast of the picture covers height variation from 0.1 to 25 nm, the scanned area was 10 x 10 μm . Two areas with the scratched away adsorbate are shown (two “windows” in the central part of the image).

4. References

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