ATOMIC FORCE MICROSCOPY (AFM) STUDY OF THE ADSORPTION OF SOIL HA AND SOIL FA AT THE MICA-WATER INTERFACE

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1 INTRODUCTION

1.1 The Significance of Clay-Humic Complex Morphology

Adsorption of humic molecules on clay minerals improves their geochemical stability and provides an active surface for cation exchange and sorption of organic compounds.[1-3] The importance of clay-humic complexes in contaminant binding and transport has been demonstrated.[4-10] Experimental data suggest that the interaction between humic substances and clay particles influences the conformation of the humic molecules and consequently the sorptive properties of the clay-humic complex.[11,12] Structural information about clay-humic complexes is needed to design appropriate models for clay-humic complex formation and stability under diverse environmental conditions and to understand the sorption of ions and molecules on clay-humic complexes.[13,14] Very little direct information is available concerning the mechanism of humic-fraction/surface interactions with clays and the structural characteristics of the reaction products. Relevant information about clay-humic complexes includes the topography of clay-humic surface (degree of coverage, thickness of the organic layer) and the influence of environmental parameters (humic fraction concentration, pH, ionic strength and presence of complexing cations).

1.2 Mica (Muscovite) as a Model for the Surface of Clay Minerals

Mica (muscovite) can be used as a model for clay mineral surfaces in atomic force microscopy (AFM) studies.[15,16] Muscovite plates are commercially available. They are inexpensive and easy to cleave to give a clean surface. Freshly cleaved mica provides an atomically smooth surface (flatness better than 0.3 nm over areas of tens of square microns)[16] that is similar to some of the surfaces of phyllosilicate minerals frequently found in clay fractions of soils and sediments. The muscovite surface is simple and negatively charged at intermediate pH values, with uniform characteristics on a relatively large scale and little intrinsic topographic variation (Figure 1).

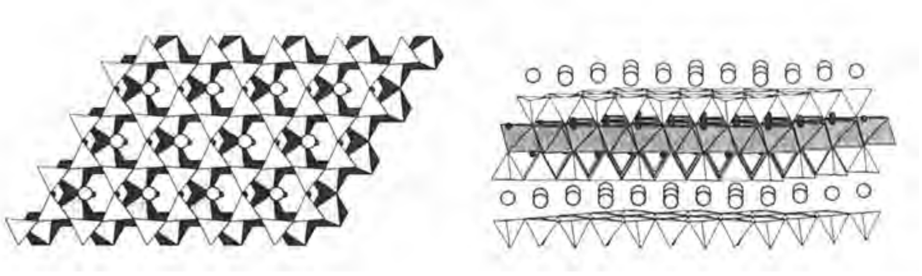

Figure 1 *Muscovite structure*

1.3 AFM in the Study of Humic and Fulvic Acid Morphology

AFM is a relatively new imaging technique used in the study of humic acid (HAs) and fulvic acid (FAs) morphology.[15-18] Compared with electron microscopy, AFM provides more flexibility in sample preparation, three-dimensional images and, in most cases, better image resolution.[15] A variety of humic materials have been studied by AFM using different materials as atomically-flat solid supports: polished graphite,[18] glass[17] and mica.[15,16] The three-dimensional images can be used to derive information about humic particle shape, dimensions, degree of aggregation and surface coverage under different adsorption conditions. Contact-mode AFM[16-18] as well as tapping-mode AFM[15] have been used to study humic acid morphology. Both methods have advantages and disadvantages when used on fragile humic samples. In an attempt to provide relevant environmental information for samples in their normal hydrated state, liquid humic-mica samples were studied.[15]

1.4 Objectives of this Work

In the present work, IHSS Standard Soil HA and FA[19] and freshly cleaved muscovite were used to model adsorption of a natural HA and FA to clay minerals and describe the morphology of the resulting surface complex.

It is well documented both experimentally and theoretically that in clay-humic mixtures both precipitation of the clay and humic colloids and adsorption of humic aggregates on the clay surface occur.[20] In order to avoid deposition of humic aggregates on the mica surface by sedimentation and study only the humic material that truly adsorbs to the mica surface, adsorption was done with the mica plate immersed vertically in the humic solution. The contact time was 24 h. Adsorption experiments were done at different humic material concentrations, pH and ionic strength. Contact-mode AFM was used for imaging the dried mica surface after adsorption.

2 MATERIALS AND METHODS

2.1 Solutions of Standard Soil HA/FA (IHSS)

IHSS Standard Soil HA and IHSS Standard Soil FA from the International Humic Substances Society collection were used.[19] Stock solutions with a concentration of 400 mg/L in double distilled water were prepared and kept under continuous stirring. The stock solutions were stirred at least 5 days before using them for the preparation of the working solutions. The concentration of the HA or FA in the working solutions was 0.4, 4 and 40 mg/L. The pH of the working solutions was adjusted to pH 1.5 with a minimum volume of HCl solution and to pH 7 and pH 10.5 with a minimum volume of NaOH solution. Some of the working solutions were adjusted to 0.01 M NaCl concentration with solid NaCl.

2.2 Mica (Muscovite) Plates

Mica (muscovite) was purchased from Asheville-Schoonmaker Mica Company, Newport News, VA. A fresh mica surface was prepared by removing the old mica surface using clear adhesive tape and the sample was immediately immersed in the working solution.

2.3 Adsorption Experiments

The mica plates were suspended vertically in 5 mL glass beakers containing the working solution. In some adsorption experiments, a second mica plate with one surface covered with adhesive tape was placed horizontally in the beaker. The plates were removed from the solution after 24 hours and the excess solution drained as well as possible by capilliarity. The samples were air dried for 2-4 h.

2.4 AFM Imaging

Images were obtained using a contact-mode, constant-force scanning microscope (SPM). A Park Scientific Instruments SPM operating at ambient room temperature and in atmospheric conditions was used throughout these investigations. The instrument was calibrated using a standard calibration grating (Ultrasharp/Silicon-MTD Ltd. TGZ02), which has a period of 3 μm (xy) and a step height of 104 nm (z). NT-MTD SCS12/W2C cantilevers were used in all experiments.

During SPM operation, the probe is brought into contact with the surface and this contact is maintained at a constant force while the probe is scanned in a raster pattern across the sample. The probe is mounted on a rectangular cantilever that bends as the force is applied. During topography measurements, a constant probe-sample contact force was maintained by detecting variations in the position of a laser beam reflected from the upper surface of the cantilever. The SPM controller[21,22] adjusts the z position of the sample to compensate for these variations. This technique and instrument are capable of achieving topographic resolution of less than 1 nm. A general description of this and similar techniques may be found in reference 23. The images obtained via the data-acquisition boards[21] and the software interface[22] were analyzed and formatted for presentation using Image SXM software.[24] On each sample between 6 and 12 different locations were imaged in order to account for spatial variability.

3 RESULTS AND DISCUSSION

3.1 Mica Blanks

A freshly cleaved mica surface was scanned; the variability in the surface relief was under 0.2 nm (Figure 2a). The mica surface (an aluminosilicate surface) is expected to be reactive under extreme pH conditions and the purity of double-distilled water and inorganic reagents may be insufficient at the sensitivity level of the analytical method used. In order to account for any changes in surface morphology not related to the interaction with humic colloids, blanks were prepared by immersing freshly cleaved mica plates for 24 h in the electrolyte solution with no humic material added. The variability of the mica surfaces that were treated in this way was found to be an order of magnitude higher than the variability of the freshly cleaved surface (Figures 2b, 2c and 2d). Similar data have been reported for mica immersed in 0.1 M NaCl at pH values from 3 to 8.[15] There seems to be no significant difference in variability between blank samples with respect to pH, but this may be due to insufficient sensitivity of the method.

3.2 Soil HA and FA Sorption at the Mica Surface as a Function of Concentration

Adsorption experiments were conducted with different humic acid concentrations (0.4, 4, 40 and 100 mg/L). At higher concentrations of the HA, a thick organic layer was formed on the mica surface and prevented proper imaging of the surface, at least by contact-mode AFM. At low concentrations (0.4 mg/L) there was little detectable sorption of humic acid on the mica surface, especially in experiments using 0.01 M NaCl as background electrolyte (Figure 3). This effect was more noticeable for FA solutions at concentrations of 40 mg/L and higher (Figure 4). In view of these results, a humic acid solution with a concentration of 4 mg/L and a fulvic acid solution with a concentration of 0.4 mg/L were used in the subsequent experiments.

3.3 Mica Plate Position in Solution

Under different pH and ionic strength conditions in solution, both sedimentation and adsorption of humic aggregates on the mineral surface may occur. Positioning the mica surface vertically in the humic solution should reduce deposition of humic aggregates by sedimentation. A number of samples obtained by placing mica plates vertically and horizontally in the same humic solution were imaged.

The differences between the vertical samples and the horizontal samples were more marked for the experiments in which 0.01 M NaCl was used as the background electrolyte (Figure 5), suggesting that precipitation and sedimentation of the humic colloids predominate under higher ionic strength conditions. The differences between the vertical and the horizontal samples were insignificant for experiments in which FA at pH 10.5 was used because under these conditions the mica surface seems to remain uncovered. The subsequent experiments were done with the mica plate immersed vertically in the humic solution in order to avoid deposition of humic aggregates on the mica surface by sedimentation and to study only the humic material that interacts with the mica surface.

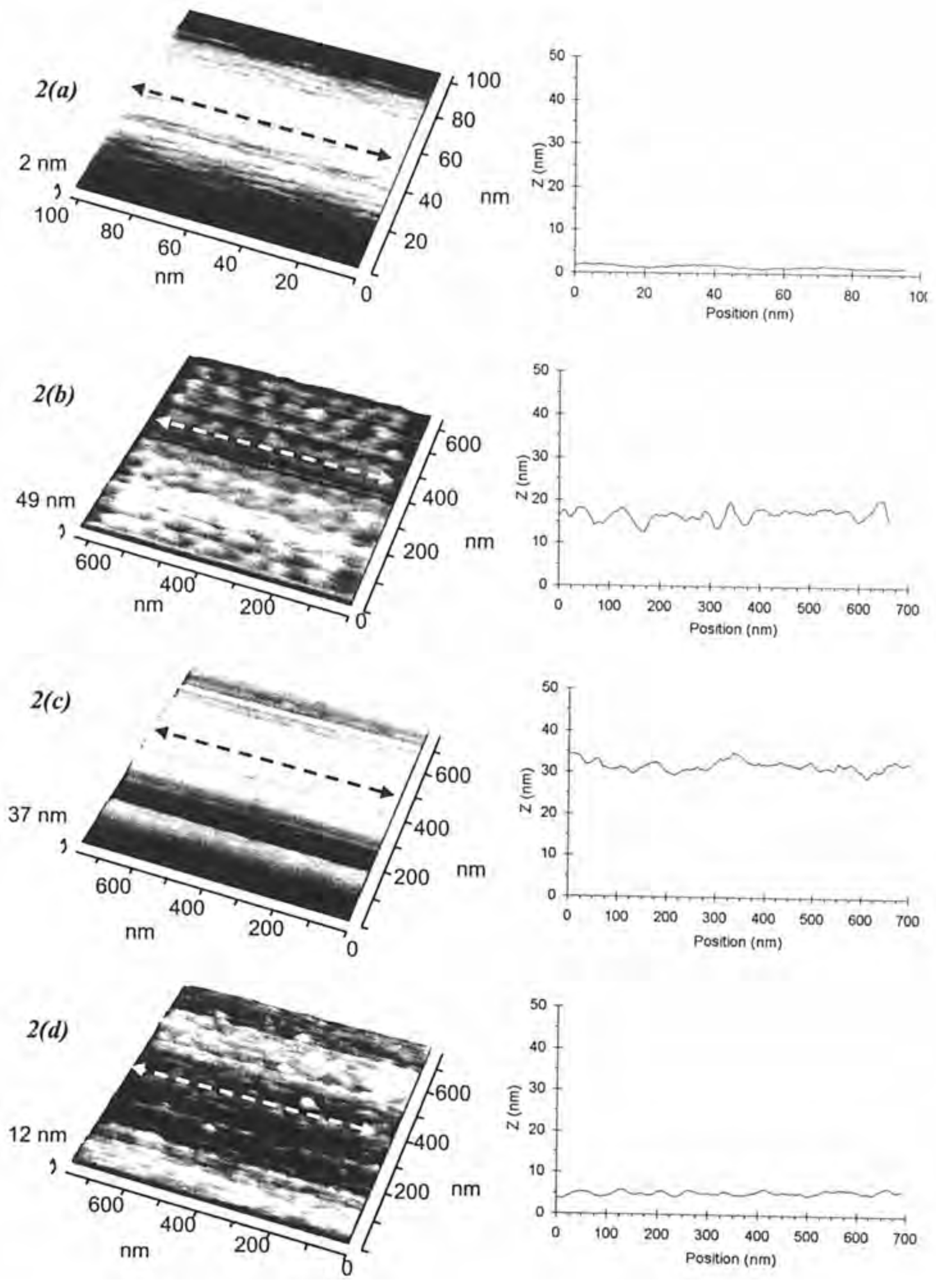

Figure 2 *3D images and line profiles of the mica surface. (a) Freshly cleaved, (b) After 24 h immersion in water at pH 1.5, (c) After 24 h immersion in water at pH 7, (d) After 24 h immersion in water at pH 10.5*

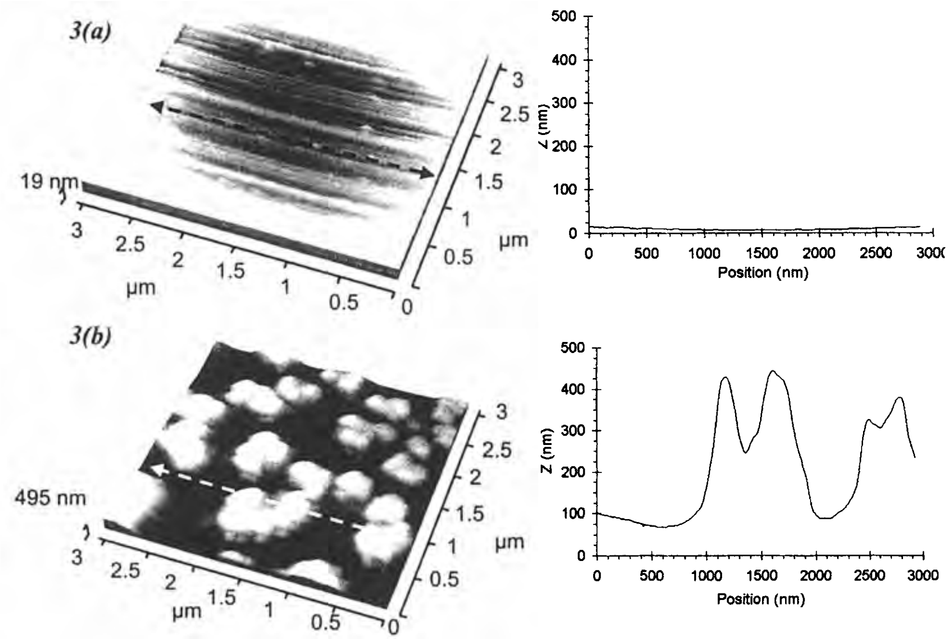

Figure 3 *3D images and line profiles of soil HA on the mica surface at pH 6.1, 0.01 M NaCl. (a) HA conc. 0.4 mg/L, (b) HA conc. 4 mg/L*

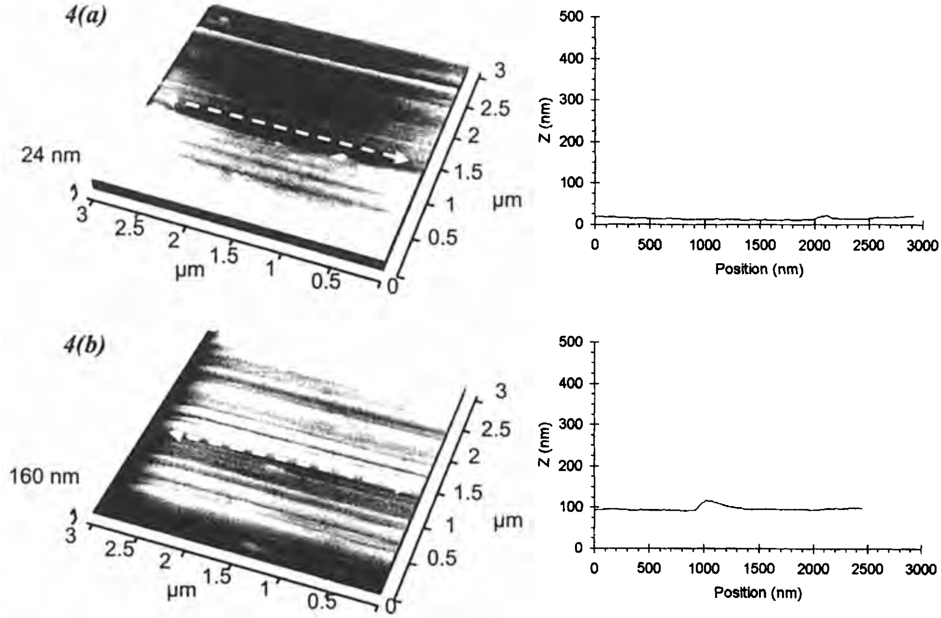

Figure 4 *3D images and line profiles of soil FA on the mica surface at pH 4.5. (a) FA conc. 4 mg/L, (b) FA conc. 40 mg/L*

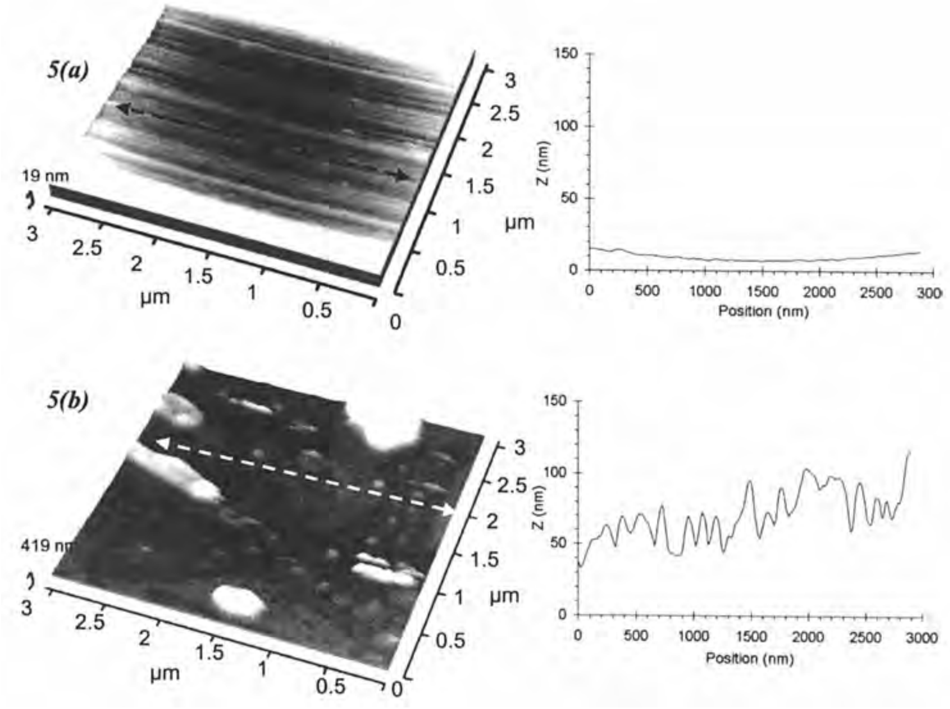

Figure 5 *3D images and line profiles of soil HA on the mica surface at pH 6, NaCl 0.01 M, HA conc. 0.4 mg/L. (a) Mica plate placed vertically in solution, (b) Mica plate placed horizontally in the solution*

3.4 Soil FA Sorption at the Mica Surface as a Function of pH

Results of the study of soil FA (0.4 mg/L) sorption on mica as a function of pH are presented in Figure 6. The dimensions of the fulvic-acid aggregates decrease with increasing pH (80-100 x 250 x 250 nm aggregates seem to be typical at pH 1.5 and 40-60 x 150 x 150 nm aggregates at pH 7). At pH 10.5 there is almost no organic layer on the mineral surface, as predicted by theory.

3.5 Soil HA Sorption at the Mica Surface as a Function of pH

Figure 7 summarizes the results of the study of soil HA (4 mg/L) adsorbed on mica. As predicted by theory, the amount of humic acid covering the mica surface decreases with increasing pH. At pH 1.5, large disc-shaped humic acid aggregates (120 x 250 x 250 nm) cover a significant part of the mineral surface; at pH 7, the humic acid aggregates have a similar disc shape but smaller dimensions (25-40 x 60 x 60 nm), whereas at pH 10.5 just a few large aggregates (150 x 250 x 300 nm) occur. The presence of 0.01M NaCl as the background electrolyte dramatically increases the amount of humic material on the mica surface: very large composite aggregates (200-500 x 500 x 500 nm) cover most of the mineral surface. The humic acid aggregates appear to be larger than the fulvic acid aggregates.

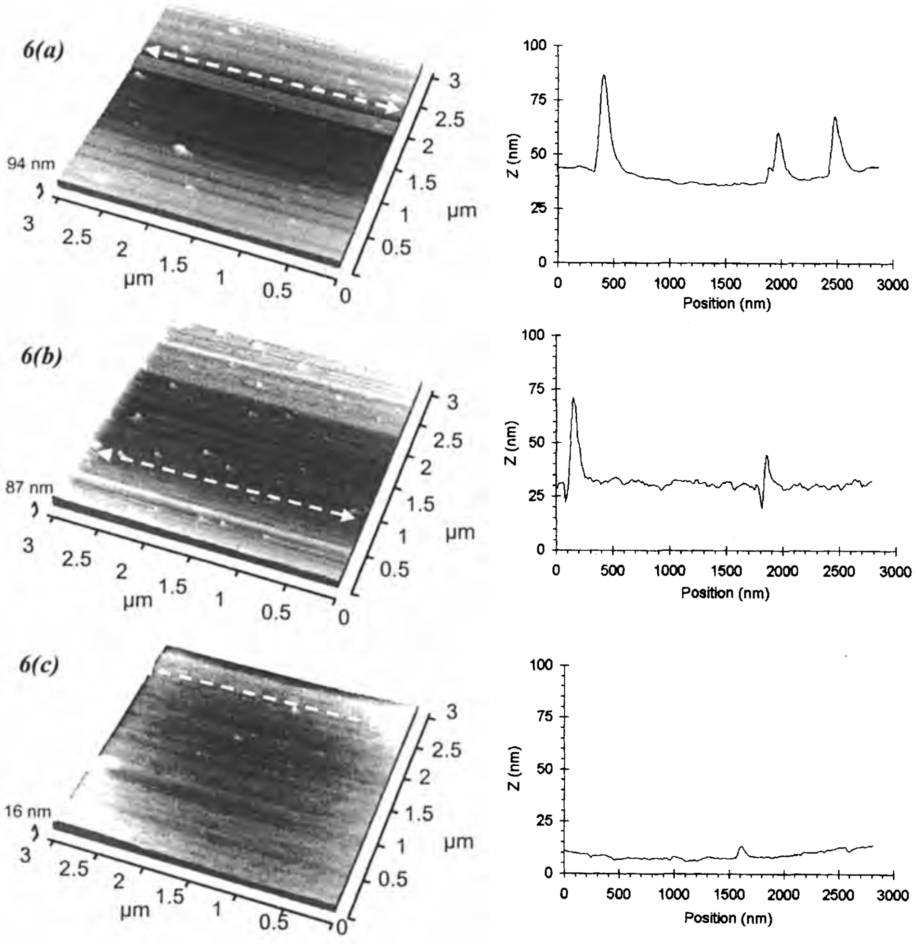

Figure 6 *3D images and line profiles of soil FA on the mica surface, FA conc. 0.4 mg/L/. (a) at pH 1.5, (b) at pH 7, (c) at pH 10.5*

4 CONCLUSIONS

The variability of mica surfaces immersed in electrolyte solutions for 24 h is an order of magnitude larger than the variability of the freshly cleaved mica surface, which makes it difficult to distinguish small aggregates (height smaller than 4 nm) and to estimate the degree of coverage of the surface. In order to distinguish between adsorbed humic colloids and background, each sample has to be compared to the appropriate blank.

At higher concentrations of the HA in solution, a thick organic layer formed on the mica surface, making proper imaging of the surface difficult and limiting the amount of information that can be obtained from the images (there was very little topographic variation). This effect was more noticeable for FA solutions at concentrations of 40 mg/L and higher.

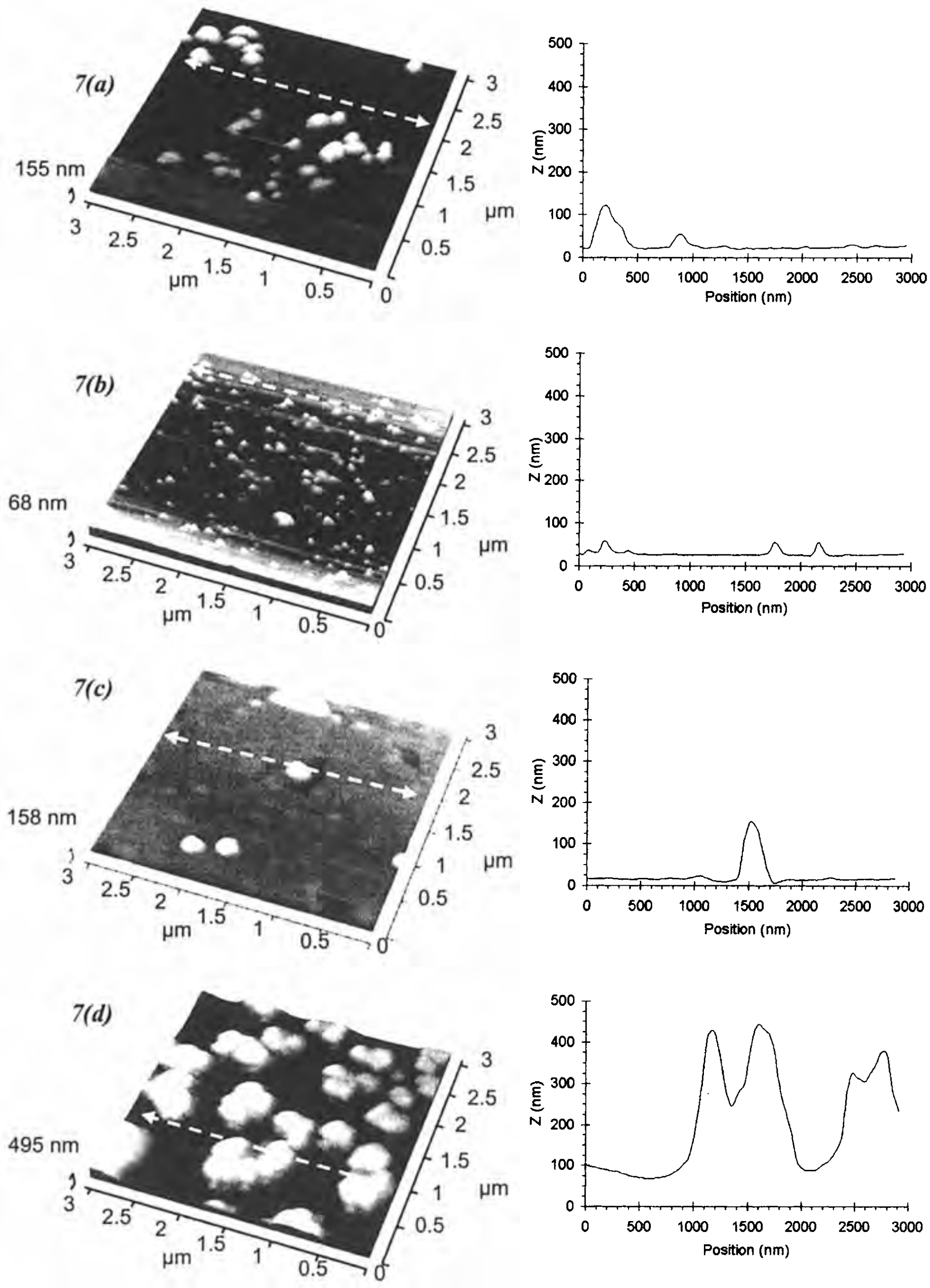

Figure 7 *3D images and line profiles of soil HA on the mica surface, HA conc. 4 mg/L. (a) at pH 1.5, (b) at pH 7, (c) at pH 10.5, (d) at pH 6.1, NaCl 0.01 M*

Positioning the mica plates vertically in the humic solution reduces the deposition of humic aggregates by sedimentation. The comparative study of samples obtained with vertically and horizontally positioned mica plates can provide information on the relative importance of precipitation-sedimentation processes versus adsorption processes in the humic substance-mica surface interaction under various environmental conditions, a differentiation that is not otherwise easy to achieve. The differences between the vertical and horizontal samples was especially important for experiments in which 0.01 M NaCl was used as the background electrolyte, suggesting that under higher ionic-strength conditions precipitation and sedimentation of the humic colloids predominate over adsorption.

Adsorption of soil HA (4 mg/L) on mica occurs as predicted by theory: the amount of humic acid covering the mica surface decreases with increasing pH. The disc-shaped humic acid aggregates also decrease in size with increasing pH. At pH 10.5, just a few large aggregates are formed. The presence of 0.01M NaCl as the background electrolyte dramatically increases the amount of humic material accumulated on the mica surface as well as the size of the aggregates. This suggests that ionic strength may play a more significant role than pH in determining both the amount of humic material associated with the clay fraction of soils and sediments and the conformation of the organic interface, with important consequences for the hydrophobicity of this surface. Fulvic acid aggregates appear smaller than humic acid aggregates. The dimensions of the fulvic acid aggregates decrease with increasing pH but the variation seems less important than for humic acid.

Even semi-quantitative estimation of the amount of material deposited on the mineral surface is a challenge, mainly due to difficulties in distinguishing between the intrinsic variability of the mica surface after treatment with electrolyte and flat layers of organic macromolecules (less than 4 nm high), which seem to be present and could reasonably be expected to be present on the mica surface. This is an important aspect of the morphology of clay-humic complexes and requires further work.

ACKNOWLEDGEMENTS

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24. *Image SXM is a version of NIH Image* (http://rsb.info.nih.gov/nih-image/) specifically adapted for scanning microscope images and can be obtained from http://reg.ssci.liv.ac.uk/.