Ultrathin Hybrid Films of Clay Minerals

E. B. Prinsen

Bachelor Thesis in Physics

June 17, 2008

Surfaces and Thin Films, University of Groningen

Supervisor: Prof. Dr. P. Rudolf
Daily supervisors: Dr. L. Toma and Drs. R. Gengler

Contents

1   Introduction

In the last few decades, thin films of organic and inorganic materials have been extensively studied for applicability.[*]
An elegant approach to arrange molecules into well-organized multilayered films is the Langmuir Blodgett (LB) technique.[†] The layer of molecules on a liquid surface is termed a *Langmuir monolayer*, and after transfer, it is called a *Langmuir-Blodgett film*. The technique is named after Irving Langmuir and Katharine Blodgett, researchers at the General Electric Company in the first half of the 20th century. Langmuir, awarded the Nobel Prize for Chemistry in 1932 for his studies of surface chemistry, used floating monolayers to learn about the nature of intermolecular forces. Working principally with fatty acids, Katharine Blodgett, together with Langmuir, refined the method of transferring the floating monolayer onto solid supports. A multilayered film is obtained by repeatedly transferring a floating monolayer formed at the air-water interface onto a solid substrate.[‡]

Compared with other processing techniques, LB approach offers several advantages. First of all, the LB method allows the processing of molecules in the form of thin films, which are preferred for many applications. Second, it permits to control the two-dimensional structure of these films at the molecular level. In fact, it provides a level of control over the orientation and placement of the molecules that is not available with other techniques. For this reason, the LB technique has been widely applied to create ultrathin films with a specific architecture which can be used as chemical sensors, modified electrodes or molecular electronic devices. [†,§]

In this research project the Langmuir Blodgett technique was used to produce hybrid monolayers consisting of one layer of elementary clay mineral platelets covered on one side by amphiphilic cations.

Smectite-type clay particles are known to be dispersed in water as negatively charged platelets with thickness around 1 nm.[**] When a solution of an amphiphilic cation in a volatile organic solvent is spread at the air-clay suspension interface in the LB trough, a rapid ion exchange reaction takes place between the smectite particles and the amphiphilic cations, leading to a hybrid monolayer of amphiphilic cations and one layer of elementary smectite smectite sheets.

The organization of the elementary clay mineral platelets and that of the absorbed amphiphilic cations in the nanofilm has been studied in this work by surface pressure *versus* molecular area (π-*A*) isotherm measurements and atomic force microscopy (AFM). Varying the clay dispersion concentration in the subphase, the density of the

---

[*] H. Fuchs, H. Ohst, W. Prass, Adv. Mater. 3, 1991, 10-18.
[†] A. Ulman, An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly. Boston: Academic Press; 1991.
[‡] K. B. Blodgett, *J. Am. Chem. Soc.* **1935**, *57*, 1007
[§] D. R. Talham, *Chem Rev* 2004;104:5479.
[**] B. K. G. Theng, The chemistry of clay-organic reactions, Adam Hilger, London, 1974.

amphiphilic molecules adsorbed onto the clay mineral lamella is changing and so the surface charge density of the clay mineral and the lift-off area in the surface pressure *versus* molecular area isotherms.

Furthermore, the hybrid monolayer of surfactant-clay mineral platelets was transferred onto a glass substrate at different surface pressures and clay concentrations and its morphology analyzed.

2 Theory

2.1 The Langmuir Blodgett Technique

The Langmuir Blodgett (LB) technique is one of the most useful techniques to prepare thin films.[1,3] The Langmuir-Blodgett (LB) method consists in organizing a single layer of molecules at a liquid/gas interface, usually water/air, and then transferring it onto a solid support to form a thin film with the thickness of one constituent molecule.

A typical LB setup is composed by a water trough, a pressure sensor and one or two moving barriers.

Langmuir films are composed of surfactants trapped at the interface between the water in the LB trough and the air. These surfactants are amphiphillic molecules, *i.e.* molecules which contain both a hydrophilic and a hydrophobic part. The hydrophilic group can be an anionic charged group (such as a carboxylate RCO_2^-, a sulfate RSO_4^-, a sulfanate RSO_3^- etc.), a cationic charged groups (for example an amine RNH_3^+), or a polar, uncharged group (for instance an alcohol). The hydrophobic group is normally a large hydrocarbon moiety, such as a long chain of the form $CH_3(CH_2)_n$. A solution of an amphiphillic cation in a volatile organic solvent is spread at the air-water interface of the LB trough. The volatile solvent will evaporate leaving the molecules behind. To form an insoluble monolayer on an aqueous subphase, the amphiphile should posses an alkyl chain longer than twelve ($>C_{12}$) carbon atoms.[4]

The amphiphillic molecule we used in this work is dimethyldioctadecylammonium bromide (DODA). Figure 2.1-1 shows the DODA molecule with its cationic charged head and hydrophobic tails.[5] When put in water the bromide will dissolve leaving the DODA positively charged.
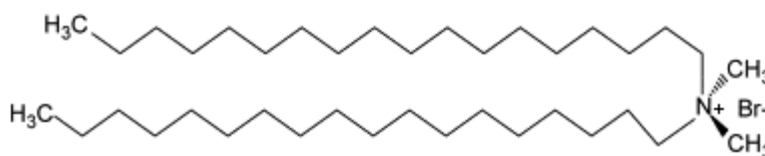

Figure 2.1-1 *Dimethyldioctadecylammonium bromide (DODA) cation.*

The barriers can sweep over the water surface and compress the layer of molecules until they form an ordered monolayer much like when one forces marbles together. This is illustrated in figure 2.1-2.
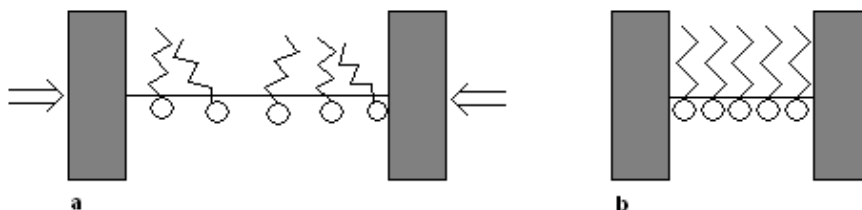

Figure 2.1-2 *Compressing of the amphiphilic molecules: (a) after spreading, the molecules float randomly at the air-water interface (b): the molecules are packed together in an ordered monolayer.*

During the compression a surface pressure *versus* molecular area (π −*A*) isotherm will be constructed, of which a more detailed description will be given later on. After the monolayer has been spread and compressed to the desired transfer pressure, the monolayer can be transferred onto a substrate either by vertical or horizontal deposition. For the vertical deposition the substrate can be either hydrophilic, as shown in Figure 2.1-3, or hydrophobic as illustrated in Figure 2.1-4.

Langmuir-Blodgett Films

A hydrophilic substrate is submerged in the aqueous subphase prior to the spreading and compressing of the monolayer film. After the monolayer has been stabilized, the substrate is withdrawn from the subphase, and the transfer of molecules onto the substrate is driven by hydrophilic interactions [see Figure 2.1-3].
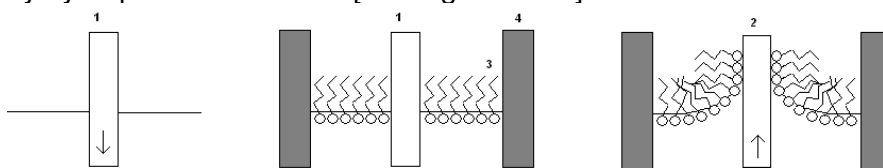

Figure 2.1-3 *Vertical deposition using a hydrophilic substrate: the substrate is immersed prior to the spreading of the surfactant; when removed, the hydrophilic part of the surfactant will attach. (1) the substrate (2) the substrate with the surfactant attached (3) the surfactant and (4) the barriers.*

When the substrate is dipped vertically through the monolayer after the latter has been spread and compressed to the desired transfer pressure, the transfer occurs via hydrophobic interactions between the alkyl chains and the surface; a second layer will attach head to head when the substrate is removed from the subphase as illustrated in Figure 2.1-4
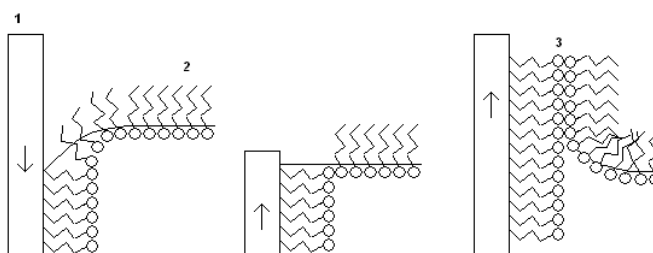

Figure 2.1-4 *Vertical deposition onto a hydrophobic substrate: during the down-stroke the alkyl chains attach to the substrate; the hydrophilic interaction during the up-stroke afford a second monolayer. (1) indicates the substrate, (2) the surfactant and (3) two layers of surfactant interacting via hydrophilic interactions.*

In the case of horizontal deposition, also called Langmuir Schäfer methos after Vincent Joseph Schaefer, the substrate needs to be hydrophobic. In this case the hydrophobic part of the surfactant will adsorb when the substrate comes in contact with molecular layer on top of the water as sketched in Figure 2.1-5.
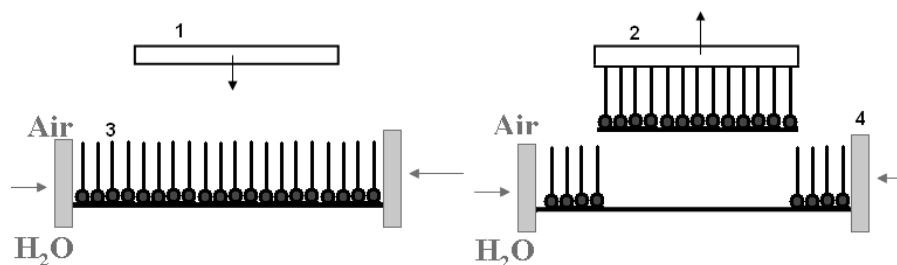
Figure 2.1-5 Horizontal deposition, also called Langmuir Schäfer deposition, with a hydrophobic substrate; as the substrate touches the surface of the subphase, the hydrophobic part of the surfactant attaches to it. (1) the substrate (2) the substrate with the surfactant attached (3) the surfactant and (4) the barriers.

Different film architectures can result upon deposition (Figure 2.1-6). The figure shows the three deposition modes possible, the X, Y and Z-type. [6]

Y-type multilayers are most common and can be prepared on either hydrophilic or hydrophobic substrates. They are typically the most stable because of the strength of the head-head and tail-tail interactions. X-type and Z-type films are rare.

The X-type deposition results using a hydrophobic substrate with a head to tail fashion, whilst Z-type deposition can be obtained using a hydrophilic substrate.
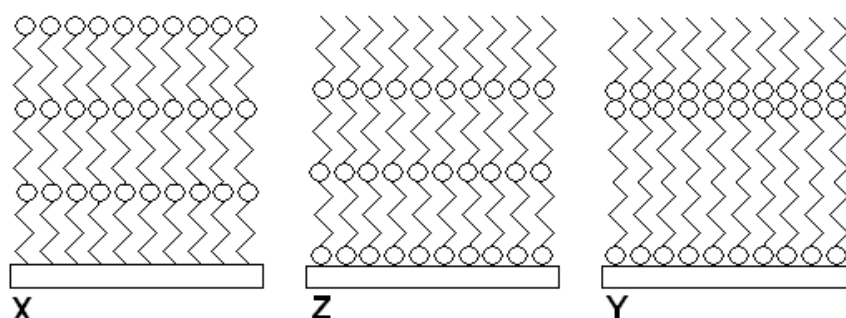

Figure 2.1-6 Possible film architectures in idealized Langmuir Blodgett films

2.2 Surface pressure versus molecular area (π – A) isotherms

A way of characterizing the molecular interaction at the water surface is by monitoring the surface pressure *versus* molecular area isotherms. during the compression of the molecular layer. The increase of the surface pressure will be measured and plotted against the area per molecule. Such a plot is called an isotherm curve because it refers to compression at constant temperature, in our case 20 degrees Celsius.

The forces between the hydrophilic heads in the aqueous subphase are ionic and therefore proportional to $1/r^2$ (r being the intermolecular separation). The forces between the hydrocarbon chains are due to van der Waals interaction and therefore proportional to $1/r^6$ and $1/r^{12}$. This will affect the curves as will be shown later. [7]

Figure 2.2-1 shows a typical isotherm curve. This plot should be read from right to left since it follows the compression of the molecular layer and thus the area per molecule will decrease in time. As shown in the graph, the molecules initially behave as a two-dimensional gas where no repulsive interactions are present between the molecules and the surface pressure is zero. Hereafter the lift-off area is defined as the molecular area where the surface pressure rises from zero. At the lift-off area the pressure starts to rise due to repulsion of the particles that start to order and therefore to interact as a two-dimensional liquid. The molecules will order further on until a quasi-solid phase is reached where the molecules are packed together. This phase is characterized by a steep and usually linear part of the isotherm curve. If the pressure is increased further, the molecules can no longer form a uniform monolayer but will stack on top of each other reaching the so-called collapse.
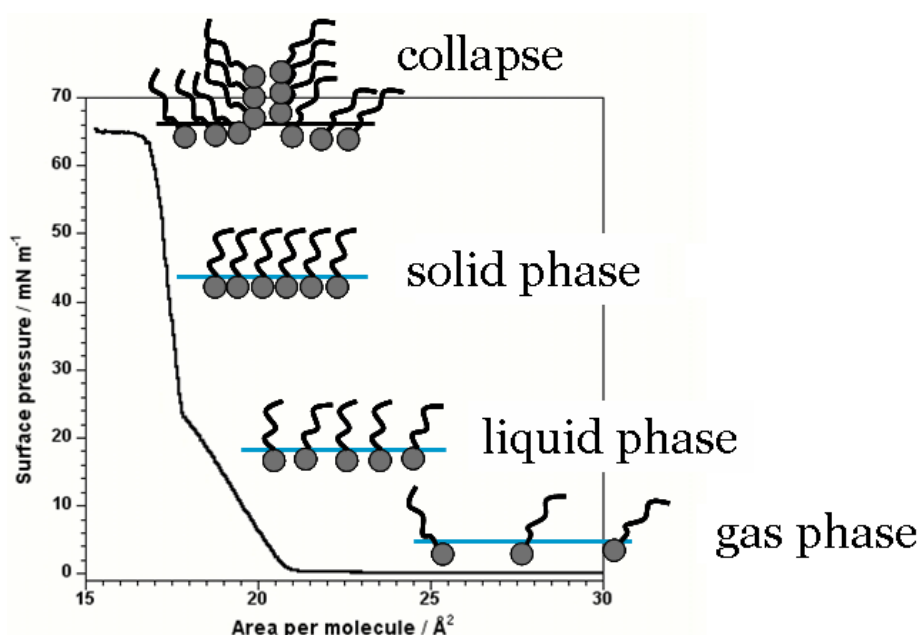

Figure 2.2-1 *Idealized pressure vs area isotherm indicating phase transitions of the monolayer: after spreading the molecules behave as a two-dimensional gas (no interaction between the molecules). Compressing the monolayer the increase in pressure causes ordering of the film; the monolayer will behave first as a two-dimensional liquid then as a quasi-solid phase ending with the collapse.*

2.3 Smectite clay minerals

During the experiments carried out in this bachelor project we used as a subphase in the LB trough a diluted aqueous dispersion of smectite clay minerals.
Natural clays are the products of weathering of rocks and make up 40% of the earth crust. Also called phyllosilicates (phyllo=leaf-like), they were one of the first materials used by mankind in a manufacturing process (pottery making) and yet they are here to stay

to develop in the 21st century into inexpensive building blocks for ever new technological applications which go beyond todays use as adsorbents, ion exchangers, pharmaceutical additives, fertilizers, etc. Besides natural clays there are also synthetic clays (laponite, smecton, fluorohectorite etc), which contrary to their natural counterparts can also be made conducting.

Smectite clays are minerals exhibiting a unique combination of swelling, intercalation and ion exchange properties that makes them valuable nanostructures in diverse fields[17]. An elementary clay sheet is composed of one octahedral alumina layer sandwiched between two tetrahedral silica layers (Figure 2.3-1). [7] The thickness of such an elementary sheet is 0.96 nm. [8,9] These sheets are hereafter referred to as elementary clay platelets. The type of smectite clay used in the work included in this thesis was Montmorillonite with structural formula per unit cell (Si_8O_{20} unit) $Na_{0.89}Ca_{0.11}(Al_{3.053}Fe_{0.25}Mg_{0.65}Ti_{0.015})(Si_{7.63}Al_{0.37})O_{20}(OH)_4$.

In both the tetrahedral and the octahedral layers isomorphous substitution occurs. The partial replacement of Si(IV) by Al(III) in the tetrahedral layers and of Al(III) by Mg(II) in the octahedral ones gives a negative lattice charge. This is compensated by exchangeable cations (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) that separates adjacent layers of platelets. [10,11]
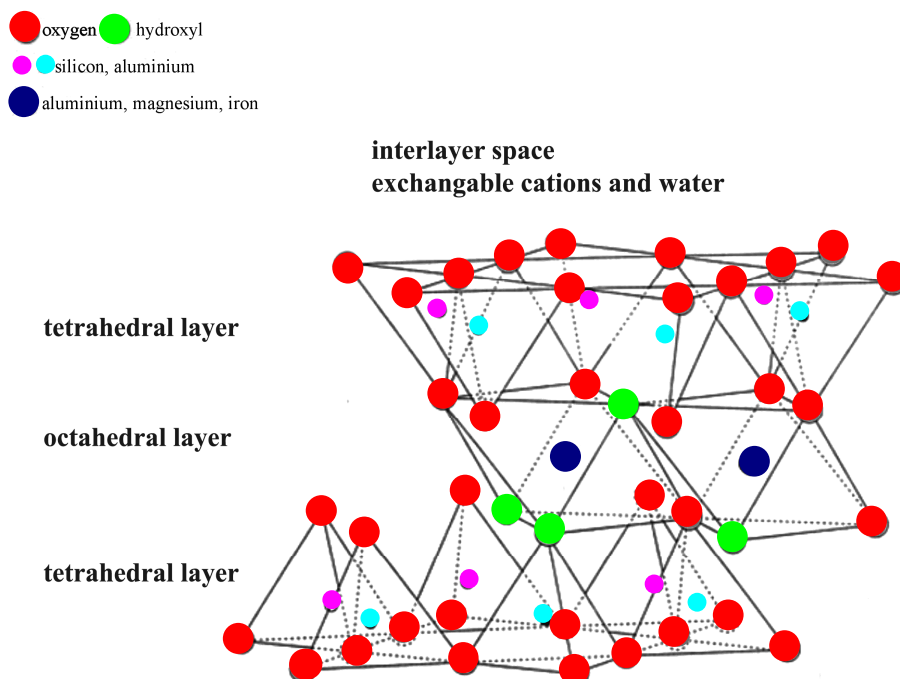

Figure 2.3-1 *Schematic representation of clay structure: one layer of edge-shared octahedra of Al^{3+} or Mg^{2+}, sandwiched between two layers of corner-shared tetrahedra of Si^{4+}.*

In aqueous dispersions these cations can absorb large amounts of water, which can push the platelets apart and lead to the complete exfoliation of the smectite into elementary clay platelets randomly diffusing in the water. This property is called the swelling of the smectites and sketched in Figure 2.3-2.[7] It is a reversible process, but can only be observed if the clays have the appropriate charge density and cations. At low concentrations the aqueous suspension of

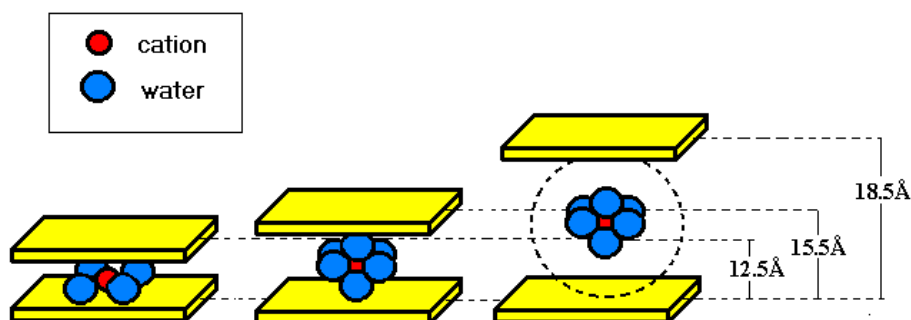smectite clays will be completed exfoliated into elementary negatively charged clay platelets. [8]

Figure 2.3-2 *Schematic representation of the swelling of the smectites. The cations in the interlamellar space absorb large amounts of water leading to the exfoliation of the smectite into elementary clay platelets.*

In any case, the presence of water in the interlamellar space is sufficient for ion exchange. Almost every cation can be exchanged no matter what is its charge or size, including heavy metals, organic cations, dyes and cationic polymers. [8, 12, 13] (see Figure 2.3-3)
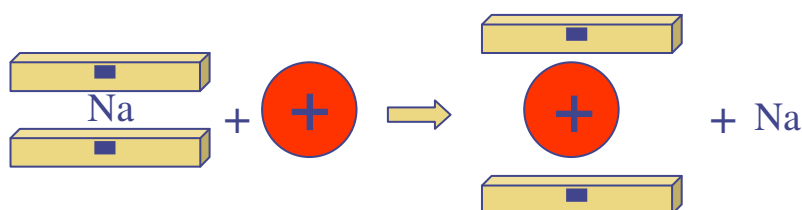

Figure 2.3-3 *Schematic representation of the ion exchange in the interlamellar space. The cations can be exchanged no matter what its charge or size.*

For example, when amphiphillic positively charged molecules are spread onto the clay suspension the clay particles are absorbed onto the bottom side of the surfactant leading to a hybrid monolayer at the air-water interface. This monolayer consists of one layer of amphiphilic cations and one layer of smectite sheets. The hybrid monolayer can be compressed and surface pressure *versus* molecular area isotherms constructed. At a desired surface pressure the floating hybrid monolayer can be transferred onto a substrate by horizontal dipping to build up multilayered films in a layer-by-layer fashion. Moreover, by ion-exchange one can introduce a third component into the hybrid film, for example another cationic species. [14,15] This property makes hybrid films suitable for practical use. Figure 2.3-4 schematically shows the clay layers with other compounds attached to them; obviously such compounds can have interesting magnetic or optical properties.
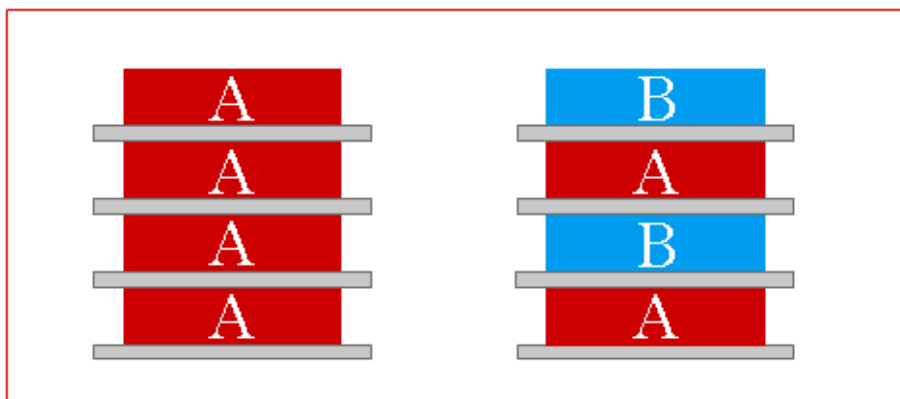
Figure 2.3-4 *Schematic drawing of clay platelets (in grey) as template: the clay layers can be used to assemble other materials with interesting properties.*

2.4 The Hydrophobic Substrate

Once the hybrid film of amphiphilic cations and clay platelets is formed, it can be horizontally transferred from the clay suspension subphase onto a solid support such as glass, mica, quartz, etc. In this work, hydrophobic glass substrates have been employed.
The orientation of the molecules in the film depends on the type of deposition used. In the case of horizontal transfer, which is our case, the surfactant is sandwiched between the hydrophobic substrate and the clay mineral platelets. In this way the clay platelets are available as host medium to assemble and organize guest molecules.

To make the glass hydrophobic a procedure called glass silanization was used. The glass is first cleaned in a piranha solution [H_2O_2 +H_2SO_4, 3:1 (v:v)], which will also hydroxylate the glass surface. Then the freshly prepared hydroxylated surface is dipped into a reaction bath containing a silane solution [in our case octadecyltrichlorosilane, CH_3-$(CH_2)_{17}$-$SiCl_3$)] to achieve chemisorption of silane molecules on the hydroxylated surface (Figure 2.4-1). The reaction is usually carried out in a 10^{-3} M solution of silane in an alkane solvent (toluene in our case). During the silanazition process a self-assembled monolayer is formed on the glass surface rendering it hydrophobic.
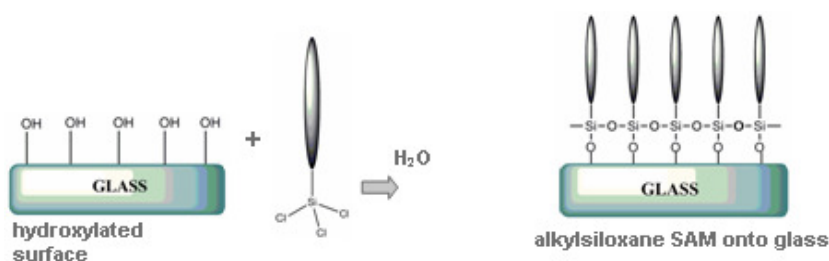

Figure 2.4-1 *Schematic illustration of the formation of the self-assembled monolayer on the hydroxylated glass surface.*

To check the hydrophobicity of the glass surface, we performed contact angle measurements. The contact angle is the angle at which a liquid interface meets the solid surface and determined by the

interactions across the three interfaces, namely at the solid-liquid, at the solid-gas one and at the liquid-gas interface. Figure 2.4-2 shows the contact angle formed by a water droplet on two different substrates. In the case of a hydrophilic substrate the droplet will spread out on the solid surface and the contact angle will be very small. On a hydrophobic substrate the water will instead try to avoid wetting the surface as much as possible and the angle measured will be large.
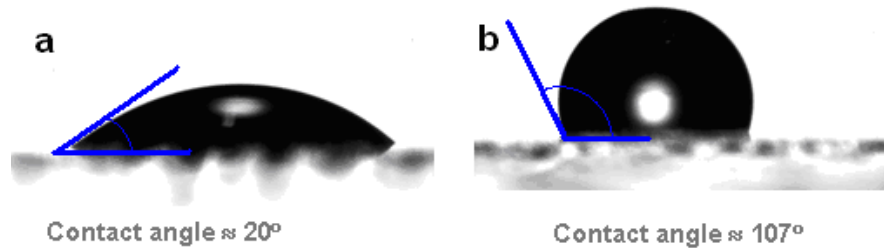

Figure 2.4-2 *Image from a video contact angle device: water drop on a hydrophilic (a) and hydrophobic (b) glass. The contact angle is shown by the blue lines.*

2.5   Atomic Force Microscopy

To characterize the morphology of the samples, we employed atomic force microscopy (AFM). AFM is one of the many scanning probe microscopies which can measure height (topography), phase contrast ('chemical map of the sample') and various other properties like optical absorption or magnetism.[16]

As shown in figure 2.5-1 AFM can be used in different interaction regimes, which in turn correspond to different operational modes, the most important ones being the contact and the non-contact (tapping) mode. For collecting our height images we used the tapping mode, where the tip is vibrating at the resonance frequency of the cantilever; while scanning the tip over the surface the tip attached to the cantilever will feel a weaker or greater interaction with the analysed specimen as the height changes.
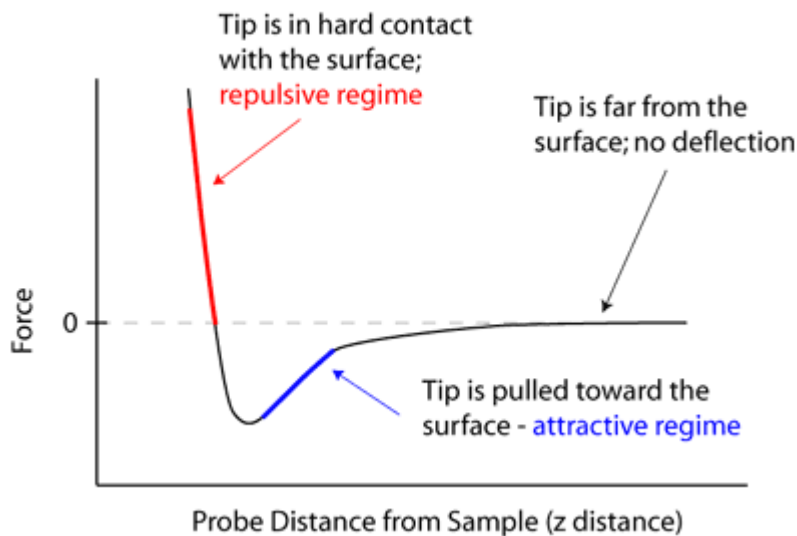
Figure 2.5-1 *Curve showing the different interaction regimes of the AFM. While scanning over the sample the tip will feel a weaker or greater interaction with the sample as the height changes.*

As Figure 2.5-2 illustrates a laser is aimed at the cantilever and a position sensitive detector can measure the vertical deflection of the cantilever, which like explained above indicates the local sample height. The vertical deflection measured by the cantilever will be translated into height variation by the computer producing a topographic map of the sample height by colour contrast.
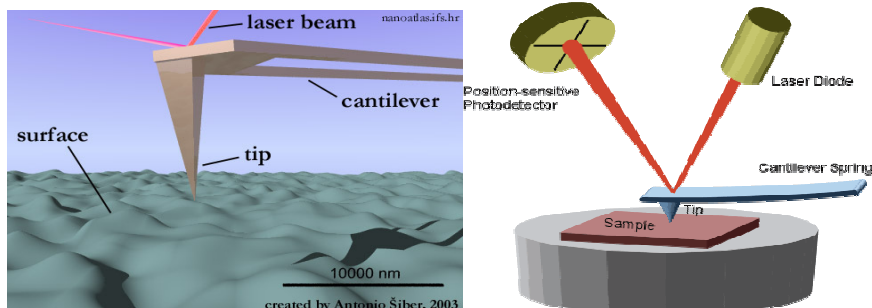

Figure 2.5-2 *Two pictures showing the AFM technique: a tip attached to a cantilever scans over the surface of a sample; the deflection of the cantilever is measured by a laser and a detector.*

2.6   Phase Contrast

Another operational mode of the atomic force microscopy is the phase contrast mode. The phase contrast measures the different elasticity of the material, giving important information on the scanned material. When the tip is driven to tap on the surface with a known frequency, its response depends on whether it scans over a soft or a hard spot on the sample as shown in Figure 2.6-1. This response is measured as a phase difference between the input signal applied to the tip and the response of the tip to the excitation. A phase contrast image is generated on the computer screen which permits to

distinguish different materials. This can be used for example to determine whether different heights measured by AFM correspond to different materials or to the same material with different height.
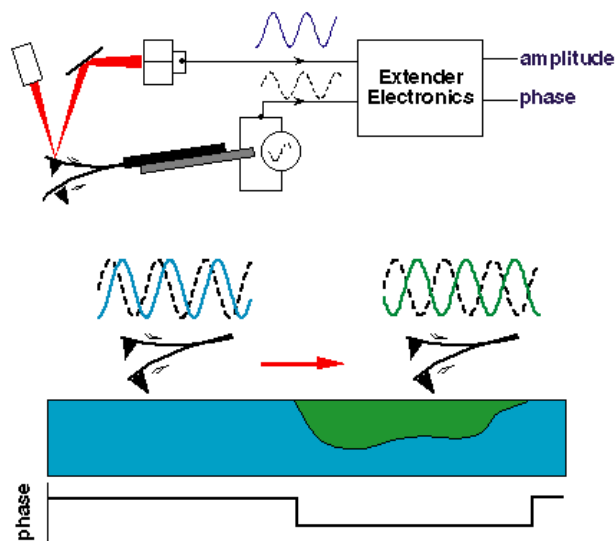

Figure 2.6-1 *The phase contrast of the AFM technique is determined by the difference of the input frequency applied to the tip and the response measured by the detector.*

3   *Experimental setup*

Dimethyldioctadecylammonium bromide (DODA) from Across Organics was used as received. It was dissolved in a mixed solvent of HPLC-grade chloroform and methanol 9:1(v:v) to prepare a spreading solution of 0.1 mg/ml.

As clay mineral a highly purified [††] natural montmorillonite 'Kunipia P' from Kunimine Industries Co., Japan was used. A stock suspension of the clay was prepared by dispersing 1 g of clay in 1 dm^3 of Mili-Q water and stirred overnight. Just prior to use as a subphase this suspension was diluted to give the concentrations needed.

The Langmuir trough from Nima Technology was thoroughly cleaned with chloroform before use. It was then filled with the clay suspension and the pressure sensor was put to zero. After filling the trough the water has to stabilize; this can be monitored by the pressure which decreases until stabilized over a period of at least 20 minutes. The surface of the subphase is cleaned by a small vacuum cleaner. To ensure the surface is clean, an isotherm measurement can be done

---

[††] *The purification of natural clays comprises various steps, namely: dispersion in water, fractionization to <2 μm by gravity sedimentation; removal of carbonates according to the acetate method; removal of iron oxides according to Mehra & Jackson method; formation of homoionic clays with saturation of cation exchange sites with the corresponding metal chlorides (e.g. Na+, Li+, etc); removal of chloride anions by transfer into dialysis tubes; drying at room temperature; collection and grinding.(see Mehra O.P., M. L. Jackson. 1960. Clays and Clay Miner)*

starting when the barriers are closed and pressure is set on zero and then expanding, if the pressure stays at zero the surface is clean, if not, than it is not clean.

When the water was stabilized and the surface was clean the surfactant was spread onto the subphase. For the clay concentrations of 9 ppm and higher, 150 µl of surfactant was spread, for the concentrations of 0, 2, 5, and 7 ppm clay concentration, 200, 500, 400 and 300 µl, respectively, were used.
After spreading the surfactant, the volatile solvent evaporates leaving the molecules behind, an operation for which we allowed approximately 10 minutes. After this the floating monolayer was compressed with a barrier speed of 30 cm^2/min and a π-A isotherm at ambient temperature was measured.

For the depositions, a MELFA RV2A Mitsubishi robot was used which approaches the glass substrate to the surface of the subphase at a speed of 12 mm/min and withdraws the glass from the surface of the subphase at a speed of 2,25 mm/min. After each deposition of a hybrid monolayer, the surface of the transferred film was rinsed with pure water and then dried in a flow of N_2 gas.

Atomic Force Microscopy images were obtained with a PicoLE System by Molecular Imaging, Arizona, USA scanning with a Si_3N_4 cantilever with a force constant of 0.04 N/m.

4 Results

In this work the formation of a hybrid monolayer of DODA cations and clay minerals at the air-water interface has been confirmed by surface pressure *versus* molecular area (π-A) isotherm measurements and atomic force microscopy (AFM).

4.1 Surface pressure versus molecular area isotherms

The surface pressure *versus* molecular area (π-A) isotherms of dimethyldioctadecylammonium bromide monolayers on montmorillonite dispersions are shown in Figure 4.1-1 for different clay concentrations in the subphase ranging from 0 to 200 ppm.

On pure water, the π-A isotherm is a smoothly increasing curve with a lift-off area of around 200 Å^2/mol and does not show a clear collapse. Upon adding small amounts of clay minerals (2, 5 and 7 ppm) to the aqueous subphase the lift-off area is shifted to smaller values while retaining a similar shape as the water-only π-A isotherm. Increasing the clay concentration further results in the lift-off area shifting to higher values and the overall shape of the π-A isotherms altering.
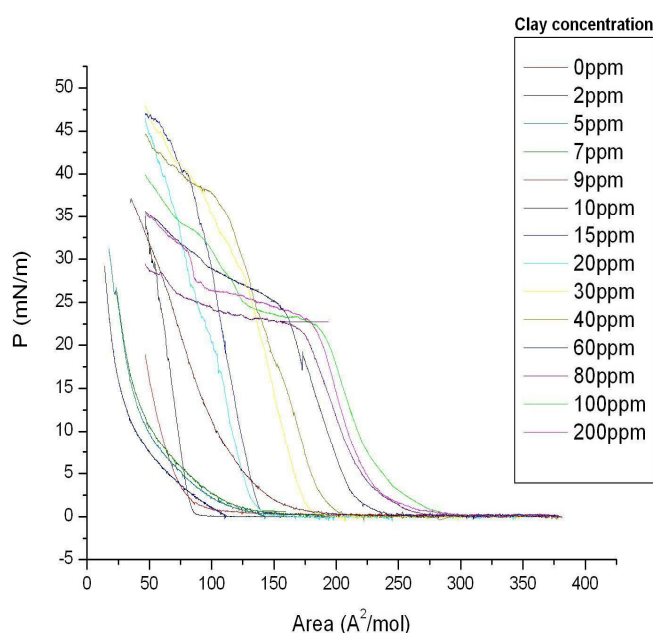

Figure 4.1-1 *Surface pressure versus molecular area (π-A) isotherms of monolayers of DODA prepared on montmorillonite clay mineral dispersions at different clay concentrations (0 – 200 mg dm^{-3})*

A minimum lift-off area is found with a clay concentration of 10 ppm (95 Å^2/mol) which is lower than the lift-off area from

dimethyldioctadecylammonium in the absence of clay (200 Å^2/mol). This indicates that the electrostatic repulsions between the ammonium lipid groups are counterbalanced, at least partially, by the absorption of the clay platelets along the interface. The molecules will then be able to get much closer before mutual interaction sets in. This observation corresponds to a general behaviour of all LB films involving clay minerals, independent of the nature of the amphiphillic cations.[2]

Increasing the amount of clay in the subphase, the lift-off area per molecule shifts to larger values as it can be seen in Figure 4.1-1. This can be explained in the following way: studies of monolayers on water have shown that after initial spreading of the surfactant the molecules have little interaction and the surfactant density is low. In time, surfactant molecules will interact and form domains of high surfactant density.[2] When clay platelets are present in the subphase, hybridization will occur (Figure 4.1-2). In case of slow hybridization, which will occur when the clay concentration is low (for instance 10 ppm), clay minerals are adsorbed onto surfactant domains. For fast hybridization, which will occur when clay concentration is high (for example 200 ppm), clay minerals are adsorbed before these domains have formed. The compression is then limited by the clay interaction. Therefore, the lift-off area for high clay concentration will be larger than in the case of low clay concentration in the subphase.
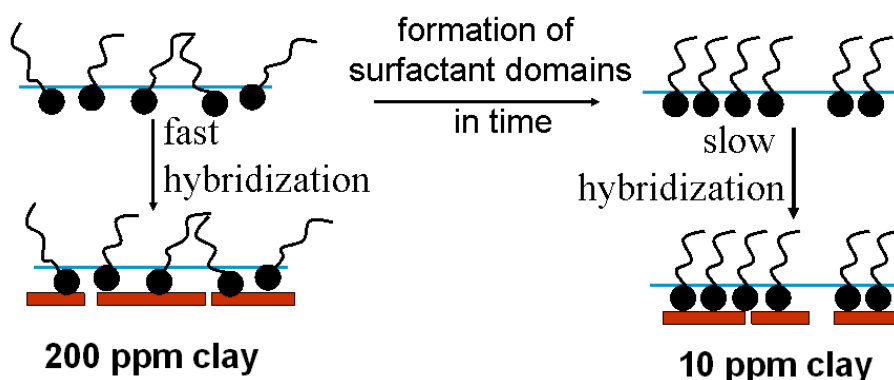

Figure 4.1-2 Schematic representation of the hybrid film formation showing the organization of surfactant molecules and the clay mineral lamellae at the air-water interface when cationic surfactants are spread on different clay mineral dispersion concentrations.

4.2   Film Depositions

Film depositions following the procedure explained in chapter 2.1 were made at two different concentrations (10 and 40 ppm) of clay suspension in the subphase. At each concentration, four depositions were made at approximately 0, 10, 15 and 23 mN/m surface pressure. Figure 4.2-1 shows on the isotherm curve where these depositions were made during the compressing,.
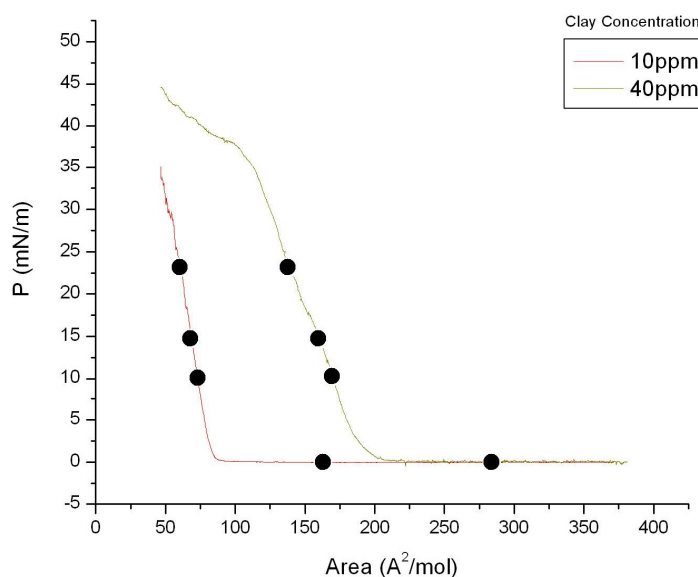
Figure 4.2-1 *Surface pressure versus molecular area (π-A) isotherms of monolayers of DODA prepared on montmorillonite clay dispersions at different concentration (10 and 40 ppm). The dots indicate the surface pressures where the depositions of the hybrid films on a glass substrate were made.*

4.3 Atomic force microscopy analysis of clay particles in the hybrid films

AFM of LB monolayers prepared from a montmorillonite dispersion with a clay concentration of 10 ppm.

To characterize the monolayers deposited on glass substrates AFM measurements were carried out. Figure 4.3-1(a)-(d) shows the AFM images of different DODA-clay particles hybrid monolayers on glass obtained using a concentration of 10 ppm clay platelets in the subphase. The bar in the corner of each of these images gives the colour contrast.

First of all we note that clay particles can be seen in all these images, which confirms the hybridization of DODA with the clay platelets at the air-water interface.

Image (a) shows a couple of lighter spots which are the clay platelets against the rough background of the glass substrate. Image (b) shows large domains which are lighter against a dark background; in (c) a light surface can be seen with dark gaps; image (d) shows a nearly uniform layer, with only some dark gaps. In all these images we interpret the lighter parts as the clay platelets and the darker areas as the glass substrate.
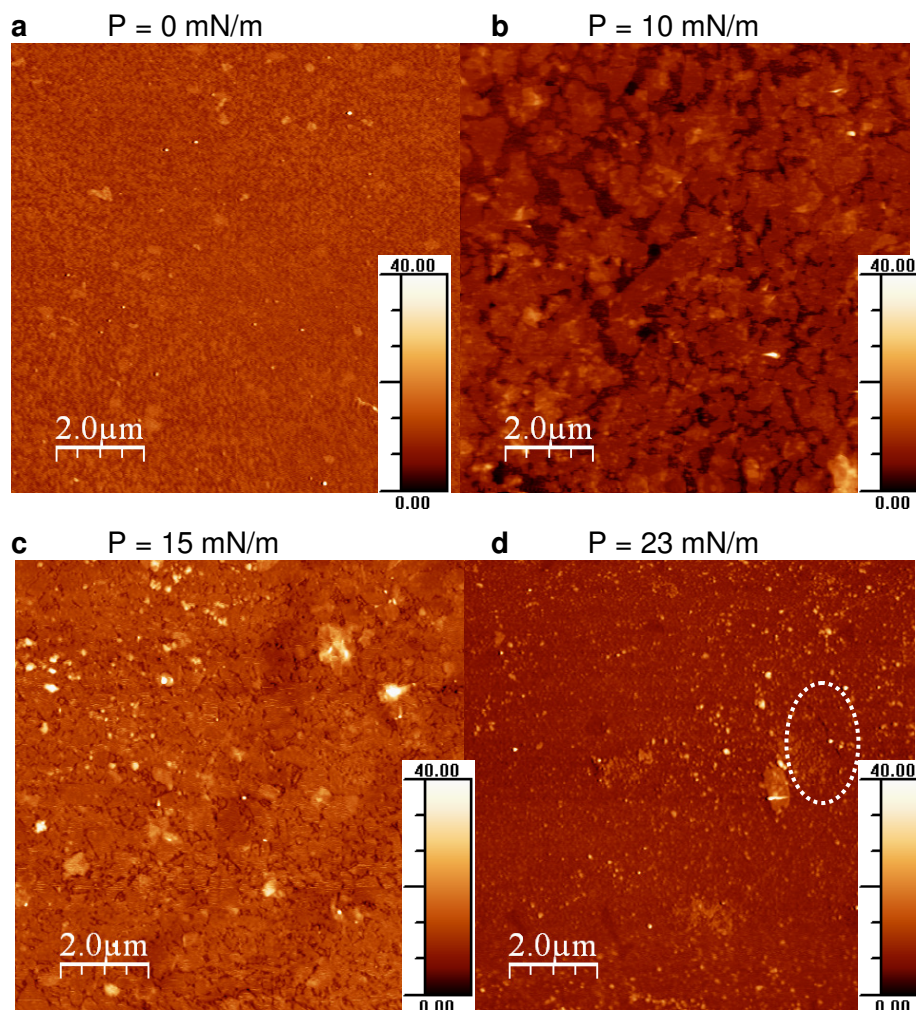
Figure 4.3-1 *AFM height images of hybrid films of DODA and clay minerals (clay concentration 10 ppm) transferred onto a glass substrate. Film transfer was performed at a surface pressure of 0 mN/m (a), 10 mN/m (b), 15 mN/m (c) and 23 mN/m (d). The colour scale is given by the bar at the side of each image, with a range from 0 to 40 nm.*

Image (a) of the hybrid monolayer of DODA-clay minerals before compression shows large empty spaces between the clay particles. For the film transferred at 10 mN/m, the clay particles are in contact with each other although some empty spaces still remain between the clay platelets. At 15 mN/m the clay platelets are closely packed and only small gaps can be seen. The image from 23 mN/m shows a very closely packed surface and only some very small gaps can be detected, one of these been encircled for clarity.

Multiple images have been collected for each sample but are not included in this thesis because they are very similar to the ones included here and prove the homogeneity of each sample.

Furthermore, for a better characterization of the hybrid monolayers transferred on the glass substrate, a statistical analysis of the images

was performed. First of all, a roughness analysis was carried out which gave the height distribution for each image. Secondly, the coverage of the DODA-clay minerals monolayer on the glass substrate was determined using a 'flooding' technique.

Since there is a really low concentration of clays transferred at pressure zero, real statistics are difficult in this case. Discrete measurements of profiles may lead to a huge error.

In the case of the hybrid monolayer transferred at pressure 10 mN/m the roughness analysis yielded at least to different values as shown in figure 4.3-2: two distinct peaks can be observed, the first at approximately 4 nm and the second one at approximately 7.5 nm. The spacing between these peaks is attributed to one hybrid monolayer of DODA-clay platelets. Since the thickness of the clay elementary sheet is around 1 nm and DODA length is around 2.3 nm, the spacing between the peaks is in good agreement with the data of the thickness of a DODA-clay monolayer.
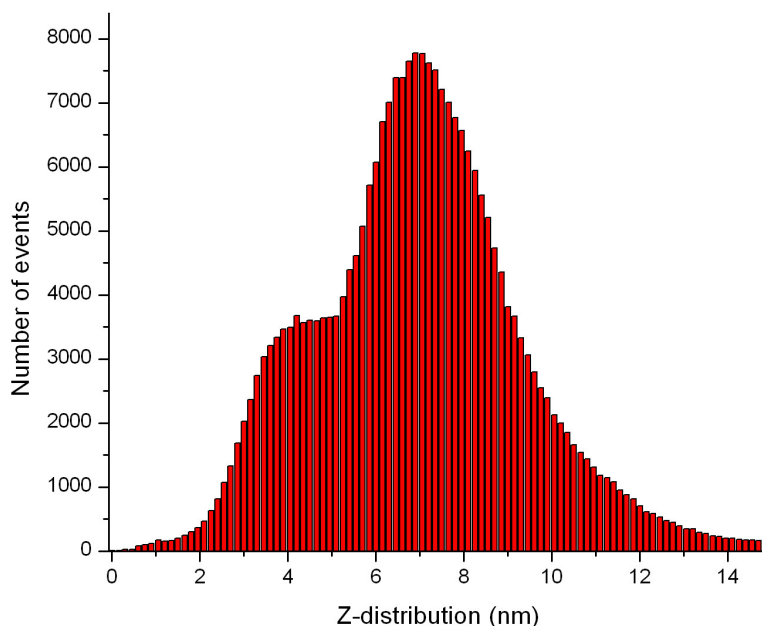

Figure 4.3-2 *Roughness analysis made for the hybrid DODA-clay platelets ((clay concentration 10 ppm) monolayer transferred onto a glass substrate at a pressure of 10 mN/m.*

Like in the previous case, a roughness analysis for the film transferred at pressure 15 mN/m was done but it does not give useful information because only one sharp peak can be observed. This can therefore not give information about the distance between the background and the hybrid monolayer which was measured by the distance between two peaks.. The same problem occurs for pressure 0 and 23 mN/m and these figures have been excluded from this work.

Another useful output of the analysis of the AFM images is the coverage measurement. The surface coverage by clay platelets can

be determined by 'flooding' the images. With this image treatment procedure the computer brightly colours every point which has a height above a certain level. This level indicates where the substrate has been covered with the DODA-clay mineral platelets. It then gives the percentage of the image that has been 'flooded' and thus is covered with the DODA-clay mineral platelets. An example is given in Figure 4.3-3 which refers to one of the images obtained for the hybrid DODA-clay mineral platelets (10 ppm) transferred onto a glass substrate at pressure 10 mN/m.

For the different pressures the average coverage deduced from all the images (even the ones not included in the thesis) are given in table 4-1. It can clearly be seen that the coverage increases with the pressure. The coverage is calculated as percentage of the total surface area and amounts to 99,31 for the film lifted of at a pressure of 23 mN/m which means that in this case a nearly perfect monolayer has been transferred onto the glass substrate.
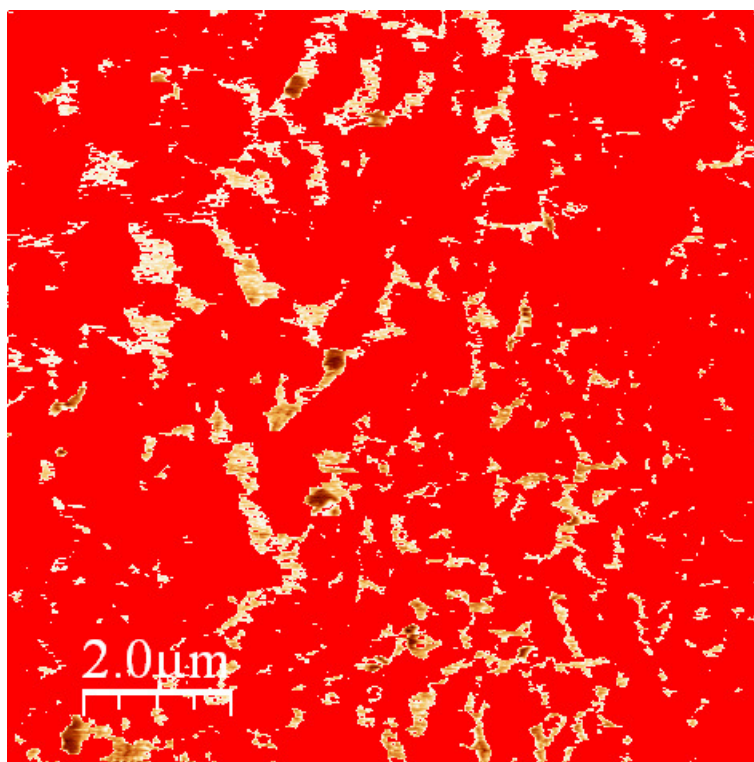

Figure 4.3-3 *Flooding of AFM image of the hybrid DODA-clay particles (10 ppm) monolayer deposited at a surface pressure of 10 mN/m: the flooded parts (clay particles coverage) have turned red.*

Pressure (mN/m)	Coverage (%)
0	2,21
10	89,64
15	95,08
23	99,31

Table 4-1 *Coverage of the hybrid DODA-clay particles monolayer deposited on glass substrate at different surface pressures (initial clay concentration 10 ppm).*

***AFM of LB monolayers prepared from a montmorillonite
dispersion with a clay concentration of 40 ppm***

Figure 4.3-4 (a)-(d) show AFM images of DODA-clay platelets hybrid
monolayers deposited onto a glass substrate at different surface
pressures (0, 10, 15 and 23 mN/m). The bar in the corner of each of
these images gives the colour contrast.

Image (a) shows lighter regions which are the clay platelets against a
darker background which is the substrate. Image (b) shows large
domains which are lighter (clay platelet) and also large domains
which are darker (the substrate). In (c) a light surface can be seen
with dark gaps, the surface being the clays and the gaps resemble
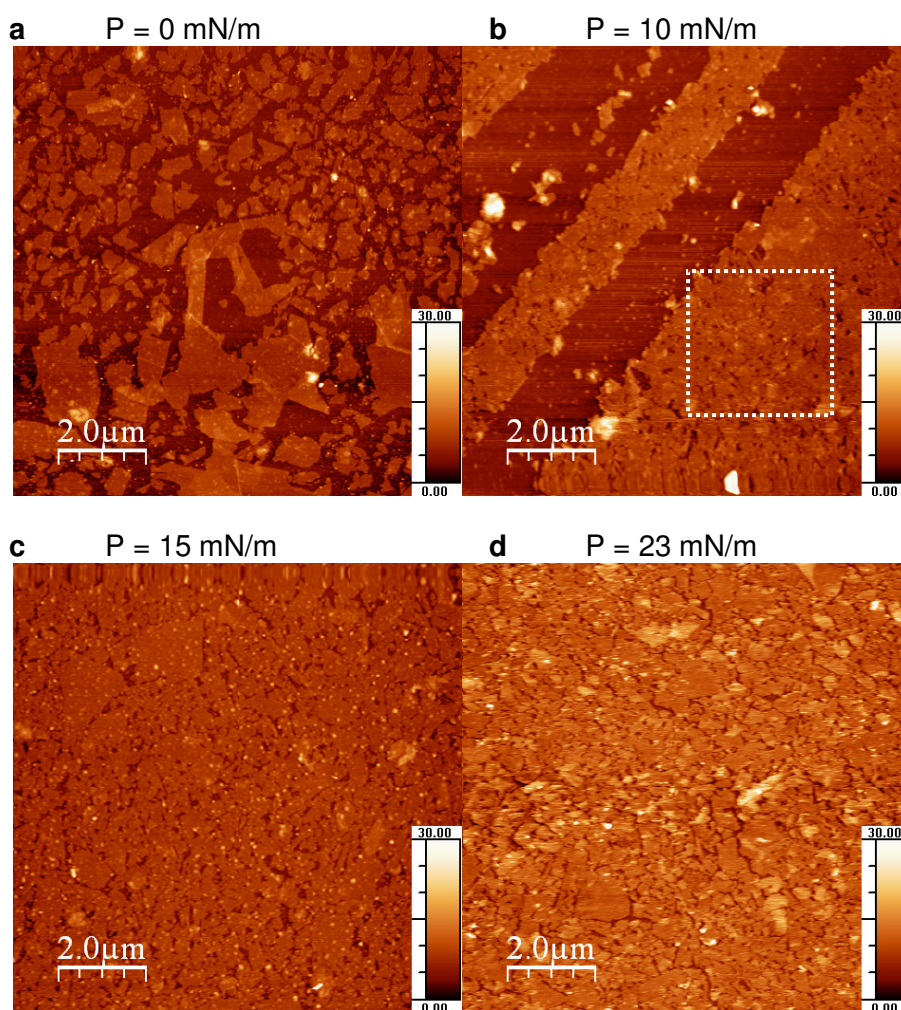the substrate. Image (d) also shows a light surface with dark gaps.

Figure 4.3-4 *AFM height images of hybrid films of DODA and clay minerals
(40 ppm) transferred onto a glass substrate. Film transfer was done at a
surface pressure of 0 mN/m (a), 10 mN/m (b), 15 mN/m (c) and 23 mN/m (d)
The colour scale is given by the bar at the side of each image, with a range
from 0 to 40 nm.*

The image of the hybrid monolayer of DODA before compression
shows large domains of the clay-DODA layer transferred. Compared
to the similar AFM image of the film deposited off clay suspension of

10 ppm, much more clays particles have attached to the substrate. This is explained by the fast hybridization at high clay concentrations.

The AFM image for the monolayer deposited onto the glass substrate at 10 mN/m shows domains as expected with clays particles attached to the substrate and some small gaps, but also diagonal dark areas which we interpret as two scratches. Other images of the same sample showed these scratches as well. They might result from dropping the sample before the AFM measurement was performed. For later analysis a region where the hybrid DODA-clay platelets monolayer was successfully transferred was used to determine the coverage in that region. This has been shown as a white dotted square in the image.

The images for the hybrid monolayer deposited onto the glass substrate at 15 and 23 mN/m surface pressure are quite similar, indicating that most of the surface is covered by the hybrid clay-DODA monolayer. Compared to the image of the layer prepared from the 10 ppm clay concentration transferred at 23 mN/m, the clay platelets are not as closely packed.

As for the LB monolayers prepared from a montmorillonite dispersion with a clay concentration of 10 ppm, two types of statistics have been performed: the roughness analysis and the coverage measurements for the hybrid DODA-clay platelets monolayer on glass substrate.

Figure 4.3-5 shows the roughness analysis for one of the AFM pictures of the monolayer deposited at 0 mN/m. Two distinct peaks can be observed, the first one at approximately 4 nm and the second one at approximately 8 nm. The spacing between these peaks is attributed to the hybrid clay-DODA monolayer.
The roughness analysis for 10 and 15 mN/m are not included, but the spacing between the peaks is given in table 4-2. At pressure 23 mN/m the analysis gave only one peak (the amount of substrate events was too low to give a clear peak in the analysis).
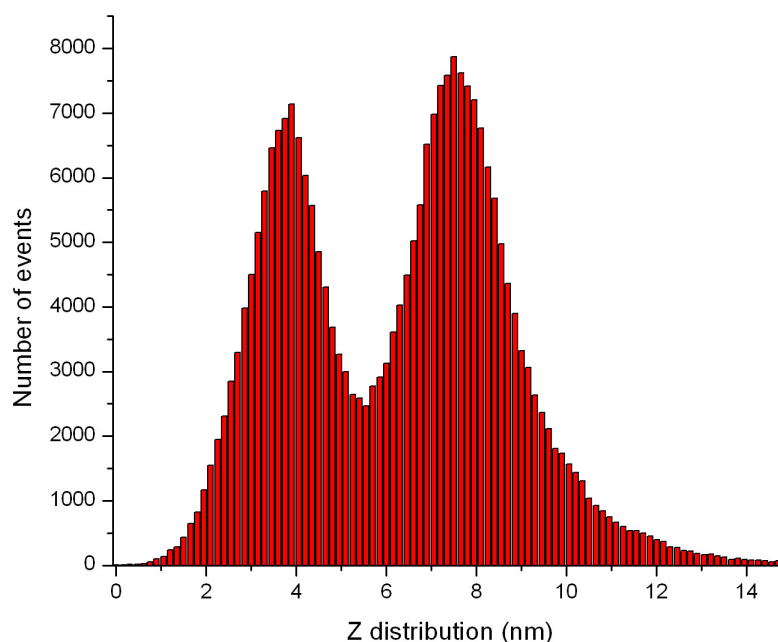
Figure 4.3-5 *Roughness analysis made for the hybrid DODA-clay platelets (40 ppm) monolayer transferred onto a glass substrate at pressure 0 mN/m.*

As explained above, the coverage of the clay platelets on the substrate can be measured by 'flooding' the images. Figure 4.3-6 shows the flooding of the AFM image at pressure 0 mN/m. As was the case for 10 ppm the background has been flooded and the coverage calculated. For the different pressures the average coverage calculated from all images (even the ones not included in the thesis) are given in table 4-2. In the case of the monolayer transferred at pressure 10 mN/m the coverage was lower because of the scratches on the image. To analyse the coverage of regions were the transfer of the hybrid monolayer was successful, the coverage of the region highlighted in the picture has been calculated and was given in table 4-2.
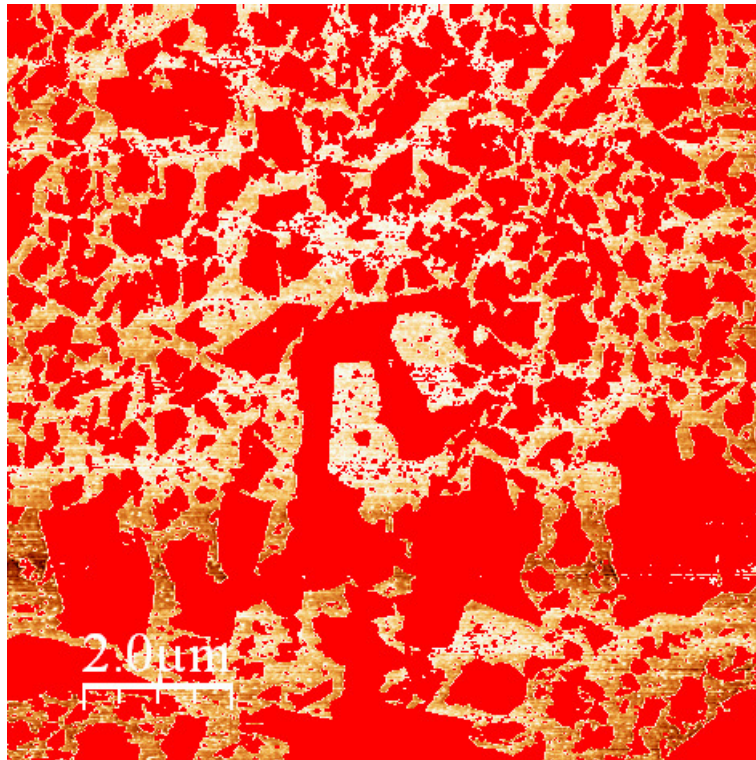
Figure 4.3-6 *Flooding of AFM image of the hybrid DODA-clay particles (clay concentration 40 ppm) monolayer deposited at pressure 0 mN/m: the flooded parts (the clay platelets) are in red.*

From pressure (mN/m)	Distance between peaks with roughness analysis (nm)	Coverage (%)
0	4	56.44
10	3.2	83.60
15	4	88.50
23	Only 1 peak	93.68

Table 4.2 *Coverage of the hybrid DODA-clay particles (clay concentration 40 ppm) monolayer deposited onto the glass substrate at different surface pressures.*

5   Conclusions

In this project the Langmuir Schäfer technique has been used for the preparation of monolayers. Clay mineral platelets were hybridized with amphiphilic molecules, namely alkylammonium cations. The morphology of these hybrid monolayers deposited onto a glass substrate was studied by atomic force microscopy.

By measuring the π-A isotherms and AFM images, clay particles in a aqueous subphase are found to stabilize a monolayer of water-insoluble alkylammonium cations.

Hybrid clay-alkylammonium cation particles are formed at the air-water interface immediately after the chloroform solution of the surfactant salt is spread onto the surface of an aqueous clay suspension. The DODA monolayer on pure water is clearly in an expanded state as demonstrated by its compression isotherm. When clay particles are introduced in the subphase, a more condensed monolayer at the air-clay suspension is formed.

The film formation is governed by the competition between domain formation of water-insoluble DODA molecules at the air-water interface and the adsorption rate of clay particles.

In absence of surface pressure, the film consists of randomly oriented clay mineral particles giving rise to a submonolayer coverage. A monolayer of nicely ordered clay mineral particles can be obtained by applying lateral pressure. In this way, hybrid films can be obtained and transferred onto a substrate.

The images obtained by atomic force microscopy clearly show the clay platelets for all depositions. These clay platelets are approached during the compression of the film until they contact each other and larger domains can be seen on the AFM images. For all depositions multiple images were collected and found to be the same for each sample, leading us to conclude that the depositions were uniform over the entire surface of the substrate. The the most close-packed monolayer, which corresponded to a coverage of 99,3%, was produced in a deposition made at a clay concentration of 10 ppm at a surface pressure 23 mN/m.

We can therefore conclude that using a clay suspension concentration of 10 ppm is the most suitable for future depositions where one wishes to incorporate functional molecules in the nanofilm using the clay platelets as template.

6   *Acknowledgements*

I would like to extend my gratitude to Prof. Dr. Petra Rudolf for the opportunity to work in her research group and to learn the Langmuir Blodgett technique. Furthermore I would really like to thank Régis Gengler and Luminita Toma for their help while doing the experiments and for correcting my thesis. Additionally I would like to thank the whole Surfaces and Thin Films group for all the fun during my time in the group.

Bibliography

1) Y. Umemura and E. Shinohara, Langmuir **21**, 4520-4525 (2005)

2) Y. Umemura, A. Yamagishi, R. Schoonheydt, A. Persoons and F. De Schryver, Thin Solid Films **388**, 5-8 (2001)

3) Y. Umemura, Y. Onodera, A. Yamagishi, Thin Solid Films **426**, 216-220 (2003)

4) G.L. Gaines, Jr., *Insoluble Monolayers at Liquid-Gas Interfaces*, John Wiley & Sons, Inc, 1966

5) C.N.C. Sobrala, M.A. Sotob and A.M. Carmona-Ribeiroa, Chemistry and Physics of Lipids **152**, 38-45 (2008)

6) Angelove and R. Ionov, Langmuir **12**, 5643-5653 (1996)

7) P. Martin and M. Szablewski, *Langmuir Blodgett Troughs operating manual,* Nima TechnologyLtd, 2001

8) B. Theng, *Clay-Organic Reactions*, A. Hilger, London, 1974

9) R.H.A. Ras, J. Németh, C.T. Johnston, E. Dimasi, I Dékány and R.S. Schoonheydt, Phys. Chem. Chem. Phys. **6**, 4174-4184 (2004)

10) R. H. A. Ras, Y. Umemura et al., Phyical Chemistry Chemical Physics **9**, 918-932 (2007)

11) Kunimine Industries, www.kunimine.co.jp

12) S. Yariv and H. Cross, *Organo-Clay Complexes and Interactions*, M. Dekker, New York, 2001

13) F. Bergaya, B. Theng and G Lagaly, *Handbook of Clay Science,* Elsevier, Amsterdam, 2006

14) Y. Umemura, J. Phys. Chem B **106**, 11168 (2002)

15) Y. Umemura and E. Shinohara, Chem. Commun., 1110 (2004)

16) D. Baselt, PhD thesis, California Institute of Technology, Caltech Library System, California, 1993

17) Pinnavaia, T. J. *Science* **1983**, *220*, 365; Konta, J. *Appl. Clay Sci.* **1995**, *10*, 275