A modified Langmuir Schaefer method for the creation of functional thin films
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Chapter 2

Highly ordered organo-clay nanostructures

2.1 Context
As described in the introduction, this thesis focuses on the study of a hybrid Langmuir-Blodgett or Langmuir-Schaefer deposition mechanism and its use for material science. This study started by the investigation of a rather basic topic: the use of the Langmuir-Schaefer (LS) method as a means to control the structure of hybrid organo-clay thin films consisting of montmorillonite and dimethyldioctadecylammonium (DODA) cations. We observed a significant modification of the compression isotherms as a function of clay mineral concentration in the subphase, implying clay interaction with the alkylammonium monolayer. For a particular range of clay concentrations, LS hybrid monolayers could be readily prepared on a hydrophobic substrate. The structure of hybrid multilayers of DODA and clay platelets, prepared by repeated LS deposition, was found to be governed by the synthetic route: when the multilayer is fabricated by transferring the hybrid Langmuir films from the surface of the clay dispersion, the DODA–clay particles were found to “flip over” while passing through the meniscus during the even cycles of the deposition, as demonstrated through the elemental analysis of the surface by x-ray photoelectron spectroscopy (XPS). In our new model for these multilayers, the structural building block consists therefore of two interdigitated DODA layers and two clay layers held together by Na+. Additionally, a minority phase forms, probably differing from the majority one in the conformation of the alkylammonium cations; this minority phase can be eliminated by annealing. This deposition procedure leads to a less ordered structure than an alternative route which combines LS deposition and self assembly (SA) to produce a multilayer consisting of two interdigitated DODA layers and one clay layer: here the hydrophilic surface of the transferred hybrid Langmuir film is converted to a hydrophobic surface by dipping into a solution of DODA cations before proceeding with the LS deposition of the next layer.

2.2 Motivation
Smectite clays are layered minerals, consisting of nanometer-sized aluminosilicate nanoplatelets, with a unique combination of swelling, intercalation, and ion exchange properties that make them valuable nanostructures in diverse fields of application such as catalysis, templates in organic synthesis, nano-fillers of engineering polymers or building blocks for composite materials. Their structure consists of two tetrahedral silica layers sandwiching a central octahedral alumina sheet (scheme 2-1). The thickness of such an elementary sheet is 0.96 nm. Due to the partial substitution of Al$^{3+}$ by Mg$^{2+}$ in the octahedral sites and of Si$^{4+}$ by Al$^{3+}$ in the tetrahedral sites, a negative lattice charge is created, which is compensated by exchangeable hydrated cations located in the interlamellar space. The intercalation process in these systems is equivalent to ion exchange and, in contrast with graphite intercalation compounds, does not necessarily involve charge transfer between guest and host species. These materials have the natural ability to absorb organic or inorganic cationic guest species (and even neutral molecules) from solutions. It is this cation “storage” behaviour that gives unique properties to clay minerals. Much attention has been focused on the interaction and organization of clay minerals and organic compounds resulting in the formation of the so-called “organo-clays”. Due to their unique structure and properties, these organic–inorganic hybrid materials can be utilized in a wide variety of analytical and biological applications including adsorbents of organic pollutants in soil, water and air, rheological control agents, paints, cosmetics and personal care products, refractory varnishes, thixotropic fluids, etc. Moreover, organo-clays are essential to develop polymer nanocomposites which constitute one of the most developed areas of nanotechnology. A critical challenge in the organic-inorganic hybrid fabrication is the preparation of materials where the spatial and orientational arrangement of the clay platelets is controlled at the nanoscale and this order is retained at the macroscale. Towards this aim, this chapter reports on the layer-by-layer assembly of montmorillonite nanoplatelets and cationic organic molecules by means of a modified Langmuir-Schaefer (LS) technique, where alkylammonium cations are used in the ion exchange. We follow up on the work of Umemura et al. who

Scheme 2-1 Montmorillonite clay structure. Black dots are silicon or aluminium (in their respective layer), the white dots represent oxygen sites.
employed a monolayer of cationic surfactant floating at the air-water interface as a template for adsorbing clay particles dispersed in an aqueous subphase. In fact, when amphiphilic organic cations are spread onto a diluted dispersion of negatively charged clay platelets, the latter are electrostatically adsorbed onto the bottom face of the buoyant cations and will follow the movement of the surfactants when lateral pressure is applied to induce packing and ordering in the floating layer. In this way a hybrid monolayer can be formed at the air-dispersion interface. This hybrid Langmuir film of clay platelets and amphiphilic cations can be deposited on a solid hydrophobic surface by horizontal lift (referred to as the LS method).

In the present work, we shed new light on the preparation of highly ordered alkylammonium organo-clay multilayer films, prepared following the two synthetic routes schematically presented in Figure 2-1. In the first route the hybrid monolayers of the clay platelets and the DODA cations were deposited by LS deposition one after another (Fig. 1 (a)), while in the second route after each horizontal lift, a surface modification of the clay platelets was performed by bringing the surface of the transferred Langmuir film in contact with a DODA-bearing solution (Fig. 1 (b)). The quality and structure of the films was investigated for different clay concentrations in the subphase and the effect of heating the samples below the melting point of DODA was also studied. Our goal was to identify which method gave the better ordered multilayers and to verify, with the help of Fourier Transform Infrared (FTIR) and XPS spectroscopies as well as by x-ray diffraction (XRD), whether the structure of the layers was actually the one sketched in Figure 2-1(a). In fact, the conventionally accepted model for LS deposition of surfactant molecules foresees a “flip over” of the molecules of the second layer (and all successive even ones) while passing through the meniscus, because this converts

Figure 2-1 Preparation scheme of hybrid multilayers of amphiphilic DODA cations and clay platelets prepared by (a) Langmuir Schaefer method (Route one), and (b) a modified Langmuir Schaefer approach exploiting self-assembly (Route two).
the interaction between hydrophilic head of the first layer and hydrophobic tails of the second layer into an interaction between hydrophilic heads. This same model was applied by Umemura et al.\textsuperscript{13} to the case of hydrid organo-clay multilayers deposited by LS following route 1, assuming that in this case only part of the surfactant molecules flip over and suggesting that the films do not contain double layers of clay as sketched in Figure 2-1(a) but single layers alternating with single layers of surfactants with part of the tails pointing up and part pointing down.

2.3 Method

2.3.1 Clay mineral.
The smectite clay used in this work was a natural dioctahedral montmorillonite, obtained from Kunimine Industries Co. (Japan), Kupipa F (KUN), with structural formula $\text{Ca}_{0.11}\text{Na}_{0.891}\text{(Si}_{7.63}\text{Al}_{0.37})\text{(Al}_{3.053}\text{Mg}_{0.65}\text{Fe}_{0.245}\text{Ti}_{0.015})\text{O}_{20}(\text{OH})_{4}$ and cation-exchange capacity (CEC) 1.18 meq g$^{-1}$ of clay. The stock dispersion of the clay was prepared by stirring 1 g of clay for 12 hours in 1 liter of Millipore ultrapure water. The dispersion was diluted to a given concentration with pure water before use as subphase.

2.3.2 Surfactant.
Dimethyldioctadecylammonium (DODA) bromide of 99+ % purity (Sigma-Aldrich) was used as received. DODA was dissolved in a mixed solvent of HPLC-grade chloroform and methanol (9:1 in volume) to prepare a spreading solution of 0.1 mg ml$^{-1}$. For the surface modification, a mixed solvent of ethanol and pure water (8:2 in volume) with 0.5 mg ml$^{-3}$ of DODA was used.

\begin{center}
\begin{tikzpicture}
\draw[->] (0,0) -- (2,0) node[below] {\textsim 20.7\AA};
\draw[->] (2,0) -- (5,0) node[below] {\textsim 20.7\AA};
\draw (3.5,0) -- (3.5,1.2) node[right] {\textsim 1.2\AA};
\draw (3.5,0) -- (3.5,-1.2) node[right] {\textsim 1.2\AA};
\end{tikzpicture}
\end{center}

Scheme 2.2 structure of Dimethyldioctadecylammonium (DODA) bromide and estimated dimension.

2.3.3 Substrate preparation.
Calcium fluoride (CaF$_2$) plates, rendered hydrophobic by rubbing with molten ferric stearate, were used as substrates for FTIR measurements while hydrophobic glass plates, modified with dodecyltrichlorosilane (from ABCR GmbH & Co), were employed for Atomic Force Microscopy (AFM) and mylar of 0.125 mm
thickness (from GE Polymershapes HiFi Snij-Unie) for X-Ray Diffraction (XRD) measurements.

2.3.4 Film preparation.
LS films were prepared on a Nima Technology thermostated 612D LB trough at a temperature of 21 ± 0.5°C. The pressure sensor employs a Wilhemly plate (small length of chromatography paper) to measure surface pressure (reduction in surface tension). Pure water and clay dispersions in Milipore Q-grade water were used as subphase. The clay concentration in the dispersion ranged from 5 to 500 mg l⁻¹. A microsyringe was utilised to spread the DODA dissolved in chloroform-methanol onto the aqueous subphase. After 15 min, the film was compressed at a rate of 30 cm² min⁻¹. Films were deposited by horizontal lift onto a hydrophobic surface, at a constant surface pressure of 10 mN m⁻¹ (with downward and lifting speeds of 4 and 2 mm min⁻¹, respectively). The hydrophilic surface of the transferred film was rinsed with pure water several times and dried with a flow of N₂ gas. A multilayer film was fabricated by repeating this procedure (route one, Figure 2-1a). The second family of multilayer films was fabricated following route two (see Figure 2-1b). For each layer, after the LS deposition, the surface of the film was rinsed with pure water and dipped into an ethanol-water solution of DODA to induce a change in surface property from hydrophilic to hydrophobic, due to the exchange of metal cations (Na⁺) on the outer side of the clay nanoplatelets with alkylammonium cations. Finally, the surface was rinsed copiously with pure water and dried with a flow of N₂ gas. Multilayer films were constructed by repeating this procedure.

2.3.5 Film characterization.
AFM images of the films were obtained using a Scientec 5100 equipped with Si n-type cantilever with a tip radius <10 nm and ~25-75 N/m of force constant. All the images were recorded in tapping mode. Data treatment was performed using WSXM freeware developed by Nanotec. The experimental data were fitted using a Gaussian distribution. XRD patterns of the films deposited on mylar were collected with a Philips PANanalytical X’Pert MRD diffractometer (Bragg-Brentano geometry) with a Cu Kα radiation (λ=1.5418 Å) using an anode voltage of 40 kV and a current of 40 mA, a 0.25° divergent slit and a 0.125° anti-scattering slit. The patterns were recorded in a 2θ range from 1 to 10°, in steps of 0.01° with a counting time of 15 s each. Infrared spectra of the multilayer films on hydrophobic CaF₂ plates (15 mm x 10 mm x 1 mm) were measured in transmission mode with a Bruker IFS 66v/S vacuum FTIR spectrometer operating at 10⁻² mbar. The FTIR spectrometer was equipped with a liquid nitrogen cooled Mercury Cadmium Telluride (MCT, HgCdTe) detector and a KBr beam splitter. Each spectrum was the average of 150 scans collected with 2 cm⁻¹ resolution. XPS data were collected using a Scienica R4000 spectrometer equipped with a monochromatic Al Kα X-ray source (hv = 1486.6 eV); the photoelectron take off angle was 70°; an electron flood gun was used to compensate for sample charging; the base pressure during
Highly ordered organo-clay nanostructures. The measurement was $5 \times 10^{-10}$ mbar. Mylar was used as substrate. All binding energies were shifted to match to the Si 2p core level of montmorillonite clay reference$^{15}$ at 102.9 eV. Data were normalized to the carbon peak area.

2.4 Results and discussion

2.4.1 Surface Pressure versus Molecular Area ($\Pi$-a) Isotherms of Langmuir Films on Clay Dispersions.

Figure 2-2 shows $\Pi$-a isotherms of DODA monolayers on pure water and on montmorillonite dispersions for clay concentration in the subphase ranging from 5 to 500 mg $^{-1}$. For each isotherm, the lift-off area was calculated by either extrapolating the linear section of the isotherm or, if the isotherm lacks a straight section, as in the case of pure water and high clay concentration, from the linear section of the derivative of the isotherm$^{10}$ as illustrated in Figure 2-2 (right panel).

![Figure 2-2. $\Pi$-a isotherms of floating monolayers of DODA on pure water and on clay mineral dispersions of different concentration (5-500 mg $^{-1}$) (left). $\Pi$-a isotherm of DODA on pure water and its derivative. The lift-off area is determined as 90 Å$^2$ by extrapolation of the linear section of the derivative (right).](image)

In the absence of clay, the surface pressure of the floating DODA monolayer increases smoothly over the entire area range, with a lift-off area of 100 Å$^2$, which correspond to the dimension of the fully extended DODA as depicted in scheme 2-2, and does not show a clear collapse point. This indicates that the DODA monolayer on pure water is in an expanded state, as already described in the literature.$^{16}$

When DODA is spread onto a subphase containing clay nanoplatelets (from 5 to 80 mg $^{-1}$) the overall shape of the $\Pi$-a isotherms is altered, showing a steeper increase
in surface pressure. The lift-off area increases when rising the clay concentration in the subphase, reaches a maximum of ca. 260 Å² at 100 mg l⁻¹ and then decreases for higher clay concentrations (Table 1). In addition, for clay concentrations above 80 mg l⁻¹, the shape of the isotherm changes again, showing a more gradual increase in surface pressure.

This behaviour indicates that the density of DODA molecules in the Langmuir film varies with clay concentration: increasing the amount of clay particles in the dispersion, the number of molecules per unit film area first increases reaching a maximum for 7 mg l⁻¹ and then gradually decreases to a minimum value at 100 mg l⁻¹ and increases again for higher clay concentrations (up to a maximum of 500 mg l⁻¹, which was the highest clay concentration investigated). The increase in molecular density at low clay concentration is most likely due to a phase transition from an expanded to a condensed surfactant phase which corresponds to a more dense packing of the DODA molecules than on pure water. This effect arises from the adsorption of the negatively charged clay platelets onto the positively charged monolayer. The interaction of the clay platelets with the surfactant compensates partly the electrostatic repulsion between DODA head groups, allowing for a higher molecular density at a given surface pressure (for clay concentrations lower then 10 mg l⁻¹).

An increased clay concentration augments the probability of interaction at the air-water interface; therefore the surfactant hybridizes in a less compact fashion as compared to low clay concentration. Indeed, at high clay concentrations, the clay mineral/surfactant hybridization process occurs at a higher rate (because of a higher interaction probability) than the reorganization of the surfactant molecules into domains of higher density. On the contrary, at low clay concentrations, the surfactant molecules less likely to interact with clay and therefore interact with each other to reorganize into more compact domains before (and while) the clay platelets adsorb. As a consequence, when the clay concentration in the subphase increases, the surfactant density decreases (molecular area increases). An additional increase in the clay concentration will generate a second decrease in the molecular density, and an alteration in the isotherm shape, which can be attributed to the presence of an important amount of clay aggregates in the subphase. This picture agrees with the AFM images (figure 2-5) where one can always see a small amount of clay aggregates, which however increases with clay concentration.

2.4.2 Apparent Compressibilities
We analysed the Langmuir films with regards to the compressibility C’ or the elasticity C’⁻¹. The apparent compressibility, C’, is defined in equation 1, where a₁ and a₂ correspond to the area per molecule at surface pressures of Π₁ and Π₂, respectively. Π₁ and Π₂ have been chosen in the relatively straight section of the isotherms (10 mN m⁻¹ and 15 mN m⁻¹, respectively).
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\[ C' = -\frac{1}{a_1 \Pi_2 - \Pi_1} \frac{a_2 - a_1}{\Pi_2} \] 

(1)

The values are reported in Table 1 together with the resulting lift-off areas and plotted as a function of clay concentration in Figure 2-3. These data indicate that the apparent compressibility of the DODA film is highest in the absence of clay nanoplatelets. Addition of clay results in a decrease in the apparent compressibility until a minimum value of \(~10\text{ m N}^{-1}\) is reached. This suggests that the monolayer of DODA on pure water is elastic and the presence of clay particles hardens the film. For clay concentrations between 10 and 200 mg l\(^{-1}\) in the subphase, the apparent compressibility oscillates around a value of \(~11\text{ m N}^{-1}\), reaching 15 m N\(^{-1}\) for the maximal clay concentration of 500 mg l\(^{-1}\). The same trend of film hardening with

### Table 1 Lift-off areas and apparent compressibilities for floating monolayers of dimethyloctadecylammonium cations and natural montmorillonite.

<table>
<thead>
<tr>
<th>Clay concentration / mg l(^{-1})</th>
<th>Lift-off area / Å(^2)</th>
<th>Apparent compressibility (C' / \text{m N}^{-1}) (error bar ± 1 m N(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (pure water)</td>
<td>90</td>
<td>22.9</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
<td>22.8</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>15.8</td>
</tr>
<tr>
<td>7</td>
<td>64</td>
<td>9.1</td>
</tr>
<tr>
<td>10</td>
<td>82</td>
<td>12.4</td>
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<tr>
<td>15</td>
<td>137</td>
<td>10.5</td>
</tr>
<tr>
<td>20</td>
<td>131</td>
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<td>178</td>
<td>10.6</td>
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<td>11.6</td>
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<td>250</td>
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<td>100</td>
<td>260</td>
<td>10.8</td>
</tr>
<tr>
<td>200</td>
<td>243</td>
<td>9.6</td>
</tr>
<tr>
<td>500</td>
<td>196</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Figure 2-3 Apparent compressibility \(C'\) determined from \(\Pi-a\) isotherms of the DODA monolayer on clay mineral dispersions of montmorillonite.
the increasing clay concentration was also observed for Langmuir films of alkylammonium cations and natural saponite.\textsuperscript{9}

\subsection*{2.4.3 AFM Observation of Hybrid Monolayers on Glass Plates.}

The hybrid Langmuir films of DODA and the clay platelets formed at the surface of the 10 mg l\textsuperscript{-1} dispersion were transferred onto glass plates at 0 mN m\textsuperscript{-1} (before compression), 10 mN m\textsuperscript{-1} and 15 mN m\textsuperscript{-1}, and the resulting surface morphology was investigated by AFM. As shown in Figure 2-4, clay platelets are easily observed in the AFM micrograph, testifying to the formation of a hybrid Langmuir film at the air-dispersion interface. When the Langmuir film was not compressed (0 mN m\textsuperscript{-1}, Figure 2-4a), the clay platelets in the transferred layer appear isolated with empty space between them. When the Langmuir film was compressed before lift-off (10 mN m\textsuperscript{-1}, Figure 2-4b) the clay platelets in the transferred layer contact each other, with small voids between them. Upon further compression (15 mN m\textsuperscript{-1}, Figure 2-4c) the platelets are closely packed. These micrographs reveal that the hybridization of the DODA cations and the clay platelets occurred before the compression and that the floating platelets were gathered as the film was compressed until they touched each other. An increase in the film roughness is also observed when the pressure is increased from 0 mN m\textsuperscript{-1} (2.0 nm) to 15 mN m\textsuperscript{-1} (4.1 nm). As illustrated in Figure 2-5, similar results were obtained for the hybrid monolayers transferred from the surface of the dispersions with 40 mg l\textsuperscript{-1} of clay, with the difference that for each transferred film (at different surface pressures) the amount of clay particles deposited on the glass plates is larger than the corresponding samples prepared with 10 mg l\textsuperscript{-1} clay in dispersion. For example, even before the compression (0 mN m\textsuperscript{-1}, Figure 2-5 (a)), the glass substrate is about 60% covered with isolated clay.

![AFM micrographs for hybrid monolayers of DODA and montmorillonite clay particles transferred onto glass plates at the surface pressure of (a) 0 10 mN m\textsuperscript{-1} (before compression), (b) 10 mN m\textsuperscript{-1} and (c) 15 mN m\textsuperscript{-1}. The clay concentration in the dispersion was 10 mg l\textsuperscript{-1}.](image-url)
Figure 2-5 AFM images for hybrid monolayers of DODA and clay particles transferred onto glass plates at a surface pressure of (a) 0 and (c) 10 mN m$^{-1}$. Roughness analysis for (b) 0 10 mN m$^{-1}$ and (d) 10 mN m$^{-1}$: (○) experimental; (−) best-fit (see text). The clay concentration in the dispersion was 40 mg l$^{-1}$.

platelets. If one assigns the lowest pixel on the image to height zero, from the micrograph, one can calculate the height distribution (Figure 2-5(b)): two peaks can clearly be distinguished; the first one mirrors the fact that the substrate (visible where not covered by clay platelets) is not flat and the full width at half maximum of this peak represents the roughness of the substrate. The second peak stems from the clay platelet layer. The spacing between these peaks (3.4 nm) gives a rough estimate of the layer thickness. Upon further compression (10 mN m$^{-1}$, Figure 2-6(c)), the platelets in the transferred layer form a nearly continuous, closely packed array and their edges are more difficult to distinguish. Large particles formed by two or three stacked clay lamellas are also visible (brighter spots). The height analysis (Figure 2-5(d)) of the AFM micrograph reveals the presence of 3 contributions: peak I corresponds to the single clay-DODA hybrid layer height (majority), peaks II and III testify to the presence of two and three swollen, aggregated clay mineral lamellas (an average thickness per lamella of 2.6 nm). From these findings one can conclude that the alkylammonium cations can adsorb one single clay mineral lamella or several clay platelets when the clay
concentration in the dispersion is increased; this indicates that for these concentrations the exfoliation of the clay into single platelets is incomplete.

### 2.4.4 Infrared Analysis of the Hybrid Films.

With transmission FTIR spectroscopy we studied the $\nu$(CH) region of the alkyl chains and the $\nu$(Si-O) vibrations of the montmorillonite as a function of the number of dipping cycles (every 10 cycles) and clay concentration in the subphase (10 mg l$^{-1}$, 60 mg l$^{-1}$ and 200 mg l$^{-1}$, respectively). The IR spectra of the different LS films deposited at 10 mN m$^{-1}$ on CaF$_2$ are very similar. Figure 2-6 (a) shows the IR spectrum of a 20 layer LS film of DODA-clay prepared from a subphase with a clay concentration of 10 mg l$^{-1}$. The peaks at 2915, 2848 and 1466 cm$^{-1}$ correspond to the symmetric and asymmetric stretching or scissoring vibrations of the methylene groups of dimethyldioctadecylammonium, while the bands at 1116 and 1035 cm$^{-1}$ are assigned to the in-plane and out-of-plane $\nu$(Si-O) vibrations of the clay.

![Figure 2-6](image)

**Figure 2-6.** (a) Infrared spectrum of a 20-layer hybrid DODA-montmorillonite film transferred onto CaF$_2$ plates at a surface pressure of 10 mN m$^{-1}$ and for a clay concentration in the subphase of 10 mg l$^{-1}$. (b) $\nu$(CH) and (c) $\nu$(Si-O) regions for different number of DODA-clay layers (from 10 to 60 layers) (the two insets show the relation between the IR intensity and the number of layers).
montmorillonite clay. As the number of hybrid layers increases, the $\nu$(CH) and $\nu$(Si-O) peaks become more intense, as illustrated in Figures 2-6 (b) and (c), respectively, and their amplitude grows linearly with the number of layers (insets Figure 2-6 (b) and (c)), which indicates that the LS multilayer film of DODA and montmorillonite is built in a layer-by-layer fashion. The same IR characteristics have been observed for the multilayer films of DODA-montmorillonite transferred at a surface pressure of 10 mN m$^{-1}$ from clay dispersions of 60 and 200 mg l$^{-1}$, respectively.

2.4.5 XRD Patterns of Hybrid Multilayers.
XRD measurements were carried out on 40-layer hybrid films prepared from different clay concentrations in the subphase according to the two routes described previously: route one where the hybrid LS films are deposited one layer after the other and route two where each hybrid LS film is deposited after having changed the hydrophilicity of the previously transferred monolayer through self-assembly. The XRD patterns of the hybrid films prepared following route one for clay concentrations in the subphase ranging between 5 to 500 mg l$^{-1}$ and following route two for clay concentrations in the subphase of 5, 10, 15 and 40 mg l$^{-1}$ are shown in figure 2-7. The XRD pattern of the multilayer prepared following the route one from clay dispersion of 5 mg l$^{-1}$ (figure 2-7 top curve-left panel) shows diffraction peaks around $2\theta = 2.7^\circ$, $4.2^\circ$ and $6.9^\circ$. As observed in figure 2-7 (left), increasing the clay concentration in the subphase leads to a decrease in the intensities of the peaks.

![Figure 2-7 XRD patterns for 40-layer hybrid films of DODA-clay platelets prepared from different clay dispersions (5-500 mg l$^{-1}$) by transferring the Langmuir films at a surface pressure 10 mN m$^{-1}$ one layer after the other (route one)(left panel). XRD patterns for 40-layer hybrid films of DODA-clay...](image)
platelets prepared from different clay dispersions (5, 10, 15 and 40 mg l$^{-1}$) by depositing the floating films at a surface pressure of 10 mN m$^{-1}$ after changing the surface properties by dipping in DODA solution (route two) (right panel).

around 2.7° and 4.2° until these peaks almost disappear for clay concentration higher than 60 mg l$^{-1}$, while the third peak at 6.9° gradually increases. The peak positions, which are also reported in Table 2, show a different behaviour: while the position of the third reflection stays strictly constant at $2\theta = 6.9°$ for the whole range of clay concentrations, the first peak moves back and forth around $2\theta = 2.6°$, while the second peak shifts toward bigger angles for higher clay concentrations. A detailed analysis if this peak including background removal and fitting is to be found in appendix 2. If the deposited films have a layered structure, the thickness of the periodically repeated unit can be calculated from the position of the first diffraction peak. Assuming that this peak corresponds to the (001) reflection, the value estimated from the XRD data amounts to ~35 Å. It is highly probable that this periodically repeated structure corresponds to a DODA-clay-clay-DODA building block and not only to a DODA-clay layer. In fact, after a first lift, the outer surface of the transferred hybrid DODA-clay monolayer is the hydrophilic clay. The Langmuir film is terminated by alkyl-chains and hence hydrophobic. When the substrate is again lowered into the trough for the transfer of the next layer, the hydrophilic clay surface of the hybrid film is supposed to interact with the hydrophobic alkyl-chains of the Langmuir film, and therefore a hydrophilic-hydrophobic interaction should hold together the two layers and all other consecutively deposited layers, in order to give rise to the X-type structure.\cite{17} However, this kind of film is stable only for non-dipolar molecules.\cite{12} For this reason, Umemura \textit{et al.}\cite{13} postulated, as already briefly mentioned in the introduction, that the molecules in the second layer “flip over” to cancel out their dipolar moments, affording a more stable Y-type structure. In Figure 2-8 we suggest a different, more probable “flip over” mechanism of the hybrid DODA-clay platelets which could occur when the substrate is lifted up for the second time and the newly deposited layer passes through the meniscus formed the water surface \cite{18} (further experimental evidence for this model are given below). This mechanism repeats in every even cycle of the deposition and indeed affords multilayers with DODA-clay-clay-DODA building blocks. Similar mixed-ion heterostructured clays hydrophilic inorganic ions (Na$^+$) and lipophilic organic cations have been extensively reported in the literature.\cite{19,20} The “flip over” of the hybrid monolayer during the horizontal lifting may provoke disorder within the alkyl chain (mixture of gauche-trans conformation of the alkyl chain) and this could be responsible for the second peak at $2\theta \sim 4.23°$. The second peak can in fact
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not be the (002) reflection which should be observed at approximately \(2\theta = 5.3^\circ\). We therefore tentatively attribute the second peak to the (001) reflection of a minority phase arising from a different phase conformation of the DODA cations within the multilayer films. The multitude of possible conformations of surfactant molecules within the interlayer space between clay platelets was already discussed in the past and is illustrated in figure 2-11. The third one at \(2\theta \sim 6.9^\circ\) arises from the presence of the clay platelets that are not intercalated with DODA molecules and thus bear Na+ as exchangeable cations, a phase which was already mentioned in the discussion of the AFM micrographs above. To gather information on the stability of the multilayers prepared following route one, the XRD patterns of the layered structures were collected during a heating cycle from room temperature up to 60°C (below the melting point of DODA). Figure 2-9 shows the XRD patterns of a film prepared with a clay concentration in the subphase of 12 mg l\(^{-1}\), heated at different temperatures (R.T., 28°C, 40°C, 60°C and after cooling down to 28°C). Increasing the temperature up to 60°C, the intensity of the first peak increases (position stays steady), while the second peak assigned to the second conformation is reduced. The peak corresponding to the (002) reflection appears more clearly around \(2\theta \sim 5^\circ\) (quantitative analysis for each temperature step in appendix). The latter indicates that annealing leads to enhanced film order. Moreover, the intensity change of the peak at \(2\theta \sim 4.23^\circ\) reinforces our hypothesis that it corresponds to the (001) reflection of a minority phase arising from a different phase conformation of the DODA cations within the multilayer films. Throughout the experiment the peak attributed to the basal clay spacing at \(2\theta \sim 6.9^\circ\) remains constant, as one would

![Figure 2-8 Most probable “flip over” mechanism for the hybrid DODA-clay platelets during the even cycles of the LS deposition following route one.](image-url)
Figure 2-9 XRD patterns of 40-layer hybrid films of DODA-clay platelets by depositing the floating films at a surface pressure of 10 mN m\(^{-1}\) from a clay dispersion of 12 mg l\(^{-1}\): initial (25°C); during heating at 40°C and 60°C; after slow cooling to 28°C.

expect for non-exfoliated clay particles. The lineshape and width remain constant over the temperature range. The XRD patterns of the multilayer film prepared from a clay dispersion of 5 mg l\(^{-1}\) following route two which combines the LS method with self-assembly, show three diffraction peaks around 2\(\theta\) = 2.4°, 4.6° and 7° (Figure 2-7 right). For the film prepared with an increased clay concentration in the subphase of 10 mg l\(^{-1}\), no significant change in the position of the first peak occurs, while instead for films prepared from clay dispersions with concentrations amounting to 15 mg l\(^{-1}\) and 40 mg l\(^{-1}\), a minor displacement towards larger angles is observed. As far as the second peak is concerned, its position stays rather constant. (see appendix for fit of the data set)

The intensity of the first two peaks is independent of the clay concentration in the subphase. The position (2\(\theta\) ~ 6.9°) and intensity of the third peak remains constant for the first three samples, while for the film prepared from a subphase with a clay concentration of 40 mg l\(^{-1}\) the peak is moved to 2\(\theta\) ~ 7° and its intensity is increased (Table 2). For samples prepared from subphases with clay concentrations amounting to 5 mg l\(^{-1}\), 10 mg l\(^{-1}\) and 15 mg l\(^{-1}\) the second and the third peak correspond, *grosso modo*, to the (002) and (003) reflections, respectively. However, for the sample prepared with a clay concentration of 40 mg l\(^{-1}\) the third peak is broader and more intense, pointing again to the increased presence of non-exfoliated, swelled sodium-clay platelet aggregates (around 12.4 Å). This reflection peak is expected to be very close to the (003) reflection of the DODA intercalated clay and thus contributes to the enhanced intensity around 2\(\theta\)=7°. This hypothesis is supported by the AFM micrographs discussed above.
2.4.6 XPS Spectra; probing the Surface of Hybrid Multilayers.

To support our model, we additionally performed XPS on samples prepared following route 1. Photoelectron spectroscopy is a direct method for identifying the surface elemental composition of a material (quantitative analysis). Using a 70° take off angle, 95% of the XPS signal is calculated to come from a depth of ~ 1.8 nm, the remaining 5% comes from deeper in the sample. Therefore this technique was used to investigate the nature of the topmost surface of hybrid clay DODA thin films in order to confirm the “flip over” of the clay layer. Figure 2-10 shows representative XPS spectra of the C1s (left hand side), as well as Si2p, Si2s and Al2p, Al2s (right hand side) core level regions collected from hybrid films with odd and even number of layers (from 3 to 7 layers). One clearly sees a large variation in the Si and Al peak intensities, which are the signature of the presence of clay. This variation is directly correlated with the layer parity: samples with an even number of layers display a low amount of silicon and aluminium on the topmost surface; on the contrary, samples with an odd number of layers display a high quantity of those elements at the surface. This observation confirms clearly the “flip over” of the clay-DODA layer like illustrated in figure 2-8, where every second will be flipped and therefore carbon (from surfactant) or silicon-aluminium (from clay) will dominate the topmost surface for alternate layer numbers. Our finding rules out the previously proposed model of flipping of the surfactant only since the latter would result in a constant ratio between the Si-Al and C peak.

![Figure 2-10](image)

Figure 2-10. X-ray Photoemission spectra of the carbon (1s) and Al(2s,2p),Si(2s,2p) regions for samples covered from 3 to 7 layers. Schematic representation of observed effect (XPS surface sensitivity) (left panel). Schematic models of layered structures of the hybrid multilayers prepared from a clay dispersion at low concentration: (a) a hybrid multilayer prepared by route one (b) a hybrid multilayer prepared by route two which involves a surface modification step (right panel).
Figure 2-11: Ideal film structures A (route 1) and B (route 2). Possible alternative conformations C-D paraffin type arrangement, E pseudo trimolecular layer and F bilayer. REF

(from clay) will dominate the topmost surface for alternate layer numbers. Our finding rules out the previously proposed model\(^{13}\) of flipping of the surfactant only since the latter would result in a constant ratio between the Si-Al and C peak intensities, regardless of the layer number (or parity).

2.5 Conclusion

Our findings link the structure of the hybrid multilayers of DODA and clay platelets to the synthetic route as follows: when the multilayer is fabricated following route one, a “flip over” of the hybrid DODA–clay particles during the even cycles is observed. This leads to a layered structure with a DODA-clay-clay-DODA periodically repeating building block; this structure consists of a majority and a (more defective) minority phase and thus entails two interlayer spacings (Figure 2-10a). If the multilayer is build up following route two, a more ordered structure composed of stacked clay nanosheets coated on both sides with DODA cations results. Here the charge of the clay platelets is compensated by the formation of the hybrid floating monolayer (Langmuir film) and the addition of a second DODA layer self-assembled on the bottom surface of the clay particles (Figure 2-10b). Additionally, a minority phase, which probably differs from the majority one in the conformation of the alkylammonium cations, forms and can be eliminated by annealing. In general route one leads to a less ordered structure than route two.

2.6 References

Highly ordered organo-clay nanostructures.

Appendix 2

Complementary X-ray diffraction analysis

Here is given a more detailed analysis of the XRD diffractogram illustrated above. The fits were performed on the line after background substraction. The backgraound used, as suggested by Reynolds (1986) for to best fit of clay minerals sample was \((1 + \cos^2 2\theta)/(\sin 2\theta \sin^{0.8} \theta)\). For the peak fitting a linear combination of Lorentzian and Gaussian lineshape with a 25-75% ratio was used.

Figure A2-1: XRD patterns for 40-layer hybrid films of DODA-clay platelets prepared from different clay dispersions (5-500 mg l\(^{-1}\)) by transferring the Langmuir films at a surface pressure 10 mN m\(^{-1}\) one layer after the other (route one) with fitting after background removal. Corresponding d(00l) spacing for the observed components (right).
Figure A2-2 XRD patterns for 40-layer hybrid films of DODA-clay platelets prepared from different clay dispersions (5, 10, 15 and 40 mg l$^{-1}$) by depositing the floating films at a surface pressure of 10 mN m$^{-1}$ after changing the surface properties by dipping in DODA solution (route two). Corresponding d(00l) spacing for the observed components (right).

The most obvious information from this more detailed analysis regards the full width at half maximum (FWHM) of the 001 peak for the sample prepared following route two (A2-2) is smaller pointing to a higher crystallinity (thinner peaks). Secondly, observing the 001 and 001’ peak positions in figure A2-1 left and right, an evolution of two phases/conformations developing as a function of clay loading becomes visible. It appears that the d(001) spacing of the first conformation varies around a value of 35 Å. While the 001’ position shifts to lower values as a function of loading. These observations are not yet perfectly understood.

The figure A2-3 shows XRD patterns of a film prepared with a clay concentration in the subphase of 12 mg l$^{-1}$, heated at different temperatures, the most striking feature as discussed in the main text is the decrease of the intensity of the 001’ reflection from the assumed second conformation.
Figure A2-3 XRD patterns of 40-layer hybrid films of DODA-clay platelets by depositing the floating films at a surface pressure of 10 mN m⁻¹ from a clay dispersion of 12 mg l⁻¹: initial (25°C); during heating at 40°C and 60°C; after slow cooling to 28°C.