Langmuir-Blodgett film formation of polymerisable amphiphilic metal complexes

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Chapter 7

An investigation on the formation of mono- and multilayers of metal complexes of N-(10,12-pentacosadiynamidopropyl)imidazole at the air-water interface

Abstract

The monolayer characteristics of N-(10,12-pentacosadiynamidopropyl)-imidazole have been studied at the air-water interface by measuring surface pressure-area isotherms. The amphiphile forms stable monolayers with a well-defined liquid-expanded (LE) to liquid-condensed (LC) phase transition. The liquid-expanded (LE) phase of this monolayer film is thermodynamically not stable. As can be seen by changes in the isotherms metal complexes at the air-water interface are formed even when the subphase has a metal ion concentration as low as 5·10⁻⁷ M. The extent of complexation can easily be tuned by variation of metal ion concentration, the counter ion, the temperature and ionic strength of the subphase. Transmission electron microscopy (TEM) revealed that the monomer monolayer has a smooth appearance while upon UV irradiation at the air-water interface, the red form of the polymer is formed, which has a striated structure.

Multilayers with a regular layer structure can be built up when the subphase contained CuCl₂, with a Z-type transfer. These multilayers, however, have a Y-type structure as was shown by small angle X-ray reflection (SAXR) measurements, therefore the molecules have “turned over” to form a Y-type structure. XPS measurements confirmed the presence of Cu(II) ions in these multilayers, giving a direct proof of the formation of metal complexes at the air-
The structure of the multilayers was examined more closely by FT-IR measurements. The multilayers can easily be polymerised by exposure to UV light. SAXR and FT-IR measurements revealed that the layer structure is preserved during the polymerisation process, although the alkyl side chains loose their all-trans conformation.

Introduction

In the Chapters 3, 5 and 6 [1-3] the monolayer behaviour of 2, diacetylene group containing amphiphilic ligands, with a pyridine group as ligand, linked with an amide or ester bond to the aliphatic tail, has already been studied. The amide formed the most stable monolayers, due to hydrogen bonding between the amide bonds of the molecules. Both amphiphiles formed metal complexes at the air-water interface and multilayers of these metal complexes could also be built up. XPS measurements confirmed the presence of metal ions in these multilayer films. The multilayers preserved their regular layer structure upon irradiation with UV light.

Furthermore, van Esch et al. [4] studied the monolayer behaviour of imidazole group containing amphiphiles upon coordination with metal ions at the air-water interface by measuring surface pressure-area isotherms and by means of fluorescence microscopy. They found that metal complexes were most easily formed with Cu(II) ions, already at concentrations as low as $10^{-6}$ M CuCl$_2$ complexation took place at the air-water interface.

In this Chapter, the complexation behaviour of N-(10,12-pentacosadiynamidopropyl)imidazole (Scheme 7.1) at the air-water interface, with various metal ions dissolved in the subphase, is studied by measuring the surface pressure-area isotherms.

\[
\text{CH}_3\text{(CH}_2)_11\text{C}=\text{C} \equiv \text{C}=\text{C}-(\text{CH}_2)_8\text{C}-\text{N}-(\text{CH}_2)_3\text{N}^\text{O}\text{H}
\]

Scheme 7.1

An imidazole headgroup was used as a ligand because imidazole has a much greater equilibrium constant for the formation of metal complexes than pyridine, mainly due to the larger basicity of the imidazole ligand [5]. The imidazole headgroup is linked to the aliphatic
Mono- and multilayer formation of an imidazole amide amphiphile

tail via an amide bond, and therefore hydrogen bonds can be formed between the molecules which increases the monolayer stability. The aliphatic tail contains a diacetylene functionality, so the mono- and multilayers can be polymerised [6-8]. The amphiphiles indeed forms metal complexes at the air-water interface and the extent of complexation can easily be controlled by the proper choice of the complexation conditions. Regular multilayers can be built up when the subphase contained CuCl₂. The structure of the multilayers is studied by means of SAXR and FT-IR measurements. XPS measurements gave direct proof for the incorporation of Cu(II) ions into the multilayers. The monolayers at the air-water interface and the multilayer films can easily be polymerised by means of UV irradiation, which results in the formation of the red form of the polymer.

Experimental

Materials

10,12-pentacosadiynoic acid (Hüls-Petrarch, 99%) was reacted with thionyl chloride (Merck, > 99%) to obtain the corresponding acid chloride. The amide derivative, N-(10,12-pentacosadiynamidopropyl)imidazole, was obtained in good yields (about 60%) by reaction of 1-(3-aminopropyl)imidazole (Acros, 98%) with the acid chloride in dry benzene (Merck p.a.) under nitrogen atmosphere. Triethylamine (Merck, > 99%), distilled under nitrogen atmosphere from CaH₂ (Acros), was added as a HCl scavenger. The crude product was purified by a twofold crystallisation from n-hexane (Merck p.a.).

Elemental analysis: Calc. for C₃₁H₅₁N₃O: C 77.29; H 10.67; N 8.72. Found: C 76.98; H 10.55; N 8.78.

IR: ν (cm⁻¹) 3300 (ν NH), 2920 (νₐ CH₂), 2850 (νₛ CH₂), 1640 (Amide I), 1548 (Amide II), 1508 (ν C=Н, imidazole ring), 1466 (δ CH₂).

¹H NMR (200 MHz): δ 0.87 (t, 3H), 1.26-1.55 (м, 32Н), 2.00 (м, 2Н), 2.11-2.27 (м, 6Н), 3.27 (м, 2Н), 4.00 (т, 2Н), 5.58 (т, 1Н) 6.96 (т, 1Н), 7.07 (т, 1Н), 7.50 (т, 1Н).

Tₘ = 54.9 °C, Tₖ = 35.4 °C.

All metal salts (BHD Chemicals, Ltd., Merck, Acros and Fluka) were used as received.

The general procedures have been outlined in the experimental sections of the Chapters 2 and 4.
Electron microscopy

Samples for transmission electron microscopy (TEM) were prepared by a horizontal lifting method of a monolayer, stabilised at a constant surface pressure of 30 mN·m⁻¹, onto a carbon-coated copper grid, which was made hydrophilic by glow discharge in air under reduced pressure. The samples were Pt shadowed at an angle of 20°. The samples used for electron diffraction (ED) were not Pt shadowed. TEM micrographs and ED patterns were recorded with a Philips EM300 instrument using an acceleration voltage of 80 kV and for the TEM micrographs a magnification of 10000× was used.

Results and discussion

Monolayer behaviour

Figure 7.1A: Surface pressure-area isotherms of the amphiphile on an aqueous subphase at 4.8 °C (A), 9.3 °C (B), 13.8 °C (C) and 18.3 °C (D).
Figure 7.1B: Isobaric stabilisation curve of the amphiphile on an aqueous subphase at 4.8 °C and a surface pressure of 3 mN·m⁻¹. In the inset the result of the Avrami analysis of the isobaric stabilisation experiment is shown.

By measuring the surface pressure-area isotherms, the monolayer characteristics of the imidazole amphiphile, at the air-water interface were studied at different temperatures (Fig. 7.1A) and pH (Fig. 7.2) values of the subphase.

The amphiphile already has a phase transition from the liquid-expanded (LE) to the liquid-condensed (LC) state at subphase temperatures as low as 4.8 °C, with a limiting area in the condensed state of approximately 32 Å²·molecule⁻¹ (Fig. 7.1A). The liquid-expanded (LE) state is thermodynamically not stable. When the monolayer is stabilised at a surface pressure of 3 mN·m⁻¹ and a subphase temperature of 4.8 °C, the area per molecule decreases from about 73 Å²·molecule⁻¹ to about 31 Å²·molecule⁻¹ as is shown in Figure 7.1B. This decrease in area per molecule is probably caused by a slow crystallisation process forming a condensed monolayer film at a surface pressure of 3 mN·m⁻¹. The crystallisation process can be studied by using the well-known Avrami analysis [9-13] of the conversion-time plots. Avrami proposed the following equation for the time dependence of the crystalline fraction during isothermal crystallisation [9-11]:

\[ 1-\alpha = \exp(-Kt^p) \]

(7.1)
in which $\alpha$ is the fraction of crystalline material, $K$ is a constant, $t$ is the time and $n$ is the so-called Avrami exponent. When isobaric and isothermal conditions are used, the Avrami equation is expected to describe the crystallisation process of the amphiphile at the air-water interface. The fraction of crystalline material can easily be calculated by calculating the area loss, referred to the beginning of the crystallisation process, divided by the area loss associated with the completed crystallisation process. The result of the Avrami analysis is shown in the inset of Figure 7.1B. From the slope of the straight line the Avrami exponent can be calculated. This Avrami exponent ($n$) has a value of approximately 1.3, indicating that probably two crystallisation processes take place at the same time. One in which the nucleation is simultaneous and where disc-like crystals are formed with a diffusion-controlled growth ($n = 1$) [12,13]. In the other process, the nucleation is sporadic, so during the whole crystallisation process new nuclei are formed. In the latter process, there are also disc-like crystals formed with a diffusion-controlled growth ($n = 2$) [12,13].

Upon raising the temperature of the subphase, the pressure at which the phase transition occurs ($\Pi_c$), increases while the collapse pressure decreases, indicating that a less stable, more expanded monolayer is formed. At a temperature of 18.7 °C a totally expanded monolayer is formed.

**Figure 7.2:** Surface pressure-area isotherms of the amphiphile at 9.3 °C on an aqueous subphase at pH values of 9.00 (A), 5.70 (B), 4.15 (C) and 3.00 (D).
The pH of the subphase also influences the monolayer characteristics of the amphiphile (Fig. 7.2). Increasing the pH from 5.70 (normal pH of the water used as subphase) up to 9.00 does not alter the monolayer properties but when the pH was decreased to 4.15, the monolayer became more expanded, indicating that protonation of the monolayer takes place, which is consistent with the observations of van Esch et al. [4]. Upon protonation a charged monolayer is formed leading to an enhanced repulsion between the charged amphiphiles, causing an increase in $\Pi_c$ and an increase in the onset of the LE phase ($A_{\text{fl}}$). At even lower pH values (3.00), the monolayer becomes totally protonated forming a totally expanded monolayer film without a LE to LC phase transition. Also the $A_{\text{fl}}$ increases upon protonation from about $83 \text{ Å}^2\text{-molecule}^{-1}$ at pH = 5.70 to about $87 \text{ Å}^2\text{-molecule}^{-1}$ at pH = 4.15 to very large values at lower pH values of the subphase.

Complexation behaviour in the monolayer

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.3}
\caption{Surface pressure-area isotherms of the amphiphile at 9.3 °C on a subphase without CuCl$_2$ (A) and with CuCl$_2$ at concentrations of $5\cdot10^{-7}$ M (B), $5\cdot10^{-6}$ M (C) and $5\cdot10^{-5}$ M (D).}
\end{figure}
Figure 7.4A/B: Surface pressure-area isotherms of the amphiphile at 9.3 °C on a subphase without CuCl₂ and on a 5·10⁻⁶ M Cu(II) subphase with different counter ions.
Even small amounts of CuCl2, dissolved in the subphase, have an enormous effect on the isotherms of the amphiphile, as can be seen in Figure 7.3. Upon addition of Cu(II) ions to the subphase, Πc increases, suggesting that complexation has occurred, while upon complexation charged molecules are formed which results in an increased repulsion between neighbouring molecules which may retard the crystallisation process, causing the increase in Πc. At Cu(II) concentrations as high as 5·10^-5 M, a totally expanded monolayer is formed. Also Afl is shifted from about 83 to about 78 Å²·molecule⁻¹. Apparently, upon complexation a thicker monolayer film is formed in which the amphiphiles have a different orientation compared to a pure water subphase.

The effect of the counter ion on the complexation process can be seen clearly in the Figures 7.4A and B. When the Cl⁻ counter ion is replaced by the bigger more easily polarisable Br⁻ anion, an increase in Πc can be observed (Fig. 7.4A), and the monolayer becomes more expanded. This counter ion effect was also observed for the pyridine amphiphiles and more extensively described in the Chapter 3 and 5. The increase in Πc follows the series: Cl⁻ ≅ NO₃⁻ < CH₃COO⁻ ≅ Br⁻ < ClO₄⁻.

Also other metal ions do form metal complexes with the amphiphile at the air-water interface, as can be seen in Figure 7.5. Addition of 5·10^-4 M metal chlorides to the subphase causes an increase in Πc. The isotherm of CuCl2 is not shown in Figure 7.5, because at concentrations of 5·10^-5 M CuCl2, the monolayer is already totally expanded, which is not the case for the other metal chlorides. The increase in Πc depends on the metal ion dissolved in the subphase and follows the series: Mn(II) < Ni(II) < Cd(II) ≅ Co(II) < Zn(II) < Cu(II). This is the same order of binding of the metal ions to the amphiphiles as was found by van Esch et al. [4].

The ionic strength of the subphase has an enormous influence on the monolayer characteristics, as can be seen in Figure 7.6. The ionic strength of the subphase was increased by adding KCl to the 5·10^-6 M CuCl2 subphase, which causes an increase in Πc indicating that the extent of complexation is increased at higher ionic strengths of the subphase. At higher ionic strengths of the subphase, the metal ions and amphiphiles are more shielded from each other by the electrolytes and complexation can occur more easily [15].
Figure 7.5: Surface pressure-area isotherms of the amphiphile at 9.3 °C on a subphase without metal ions and on a 5·10⁻⁴ M subphase of different metal chlorides.

Figure 7.6: Surface pressure-area isotherms of the amphiphile at 9.3 °C on a subphase without CuCl₂ (A) and on a 5·10⁻⁶ M CuCl₂ subphase with different ionic strengths: 1.5·10⁻⁵ (B), 3.0·10⁻⁵ (C), 6·10⁻⁵ (D) and 1.5·10⁻⁴ (E).
Morphology of the monolayers

The monolayers could be stabilised at the air-water interface in the condensed phase at surface pressures up to 40 mN·m⁻¹ on a subphase containing water without Cu(II) ions at a temperature of about 5 °C, forming a stable monolayer within 60 minutes with an area of about 28.0 Å²·molecule⁻¹. These monolayers could easily be polymerised at the air-water interface after 40 minutes of a constant flow of argon, by means of a small UV lamp (254 nm, 1.6 W) for 2 minutes, resulting in a small contraction of the monolayer (about 8%). The polymerised monolayer of the amphiphiles appeared as the red form of the polymer, as could be seen by the naked eye. In Figure 7.7 the TEM micrographs of the monomer (7.7A) and polymerised (7.7B) monolayer can be seen, which were picked up at a surface pressure of 30 mN·m⁻¹ on an aqueous subphase.

![TEM micrographs of monomer (A) and polymer (B) monolayer](image)

**Figure 7.7:** Transmission electron micrographs of a monomer (A) and polymer (B) monolayer of the amphiphile at 9.3 °C on an aqueous subphase at a surface pressure of 30 mN·m⁻¹. The polymer monolayer was formed after UV irradiation of the monomer monolayer at the air-water interface for 2 minutes under argon atmosphere. The scale bar corresponds to 0.2 μm.

The monomer monolayer has a very smooth appearance while the polymer monolayer on the other hand has a striated texture which is often observed for polydiacetylene monolayers [16,17]. The crack in the middle of the micrograph of the polymer monolayer (7.7B) has to be ascribed to the preparation of the sample. Apparently, this crack is formed
along the direction of the fibres, indicating the chain direction of the polymer backbone [16]. From picture 7.7B it is possible to estimate the thickness of one polymer monolayer, by measuring the length of the shadow. From the equation $h = l \times \tan \alpha$, in which $h$ is the thickness of the polymer monolayer, $l$ is the length of the shadow and $\alpha$ is the angle at which the samples were Pt-shadowed, a monolayer thickness of $34 \text{ Å} \pm 8 \text{ Å}$ can be calculated.

**Figure 7.7C:** *ED pattern of the polymerised monolayer of the amphiphile at the air-water interface at 9.3 °C on a aqueous subphase at a surface pressure of 30 mN·m⁻¹ by means of UV irradiation for 2 minutes under argon atmosphere.*
Figure 7.7D: Schematic representation of the deduced plane group from the ED pattern of Figure 7.7C. Plane group cm.

Figure 7.7C shows the electron diffraction (ED) pattern of the polymer monolayer. The streaking in the c* direction can be attributed to the limited number of unit cells (5-10) within a crystalline fibre in the direction perpendicular to the fibre axis. The fibres are stabilised by an intramolecular hydrogen bonding network between the amide bonds nearly parallel to the polydiacetylene backbone [18,19]. From the ED pattern the lattice of Figure 7.7D is deduced. It shows a cm plane group symmetry with b = 4.84 Å and c = 8.85 Å. The lattice has 3 mirror planes and 2 glide planes over which the polydiacetylene backbones are shifted parallel to the chain direction with respect to each other by 1/2b. The surface area of the unit cell is 42.83 Å² with 2 molecules per unit cell. So, every molecule in the crystalline state occupies about 21.4 Å². From these data and in analogy with Kanetake et al. [18], the molecular packing shown in Figure 7.8 is proposed, in which the separated sheets are shifted with respect to each other, parallel to the direction of the polymer backbone.
Figure 7.8: Schematic representation of the polymerised monolayer of the amphiphile.

Multilayer formation

Multilayers of the amphiphile were built up when the subphase contained $5 \times 10^{-5}$ M CuCl$_2$ at a subphase temperature of 4.5 °C and a surface pressure of 30 mN·m$^{-1}$. Upon stabilisation the area decreases very rapidly from the LE phase, of about 36 Å$^2$·molecule$^{-1}$ (Fig. 7.3) to an area of about 29 Å$^2$·molecule$^{-1}$, because crystallisation takes place and a homogeneous condensed monolayer is formed which can be transferred onto solid substrates. Z-type transfer is observed with transfer ratios of 0.0-0.1 on the downstroke and 1.0 on the upstroke. When other metal ions or counter ions were used, a more Y-type transfer was observed with transfer ratios of 0.2-0.6 on the downstroke and 1.0 on the upstroke, so these multilayers had no regular layer structure. Also the polymerised monolayers could be
deposited onto solid substrates, again a more or less Y-type transfer was observed (transfer ratio on the downstroke: 0.5-0.7; transfer ratio on the upstroke: 0.9-1.0). In this way, irregular multilayers were built up.

Therefore only multilayers consisting of 16 layers, built up from a $5 \times 10^{-5}$ M CuCl$_2$ subphase, will be discussed in the present work.

**Structural investigation of the multilayers**

![Figure 7.9](image)

**Figure 7.9:** The copper region of XPS spectra of a multilayer consisting of 16 layers of the amphiphile on silicon, built up from a $5 \times 10^{-5}$ M CuCl$_2$ subphase at 4.5 °C and 30 mN·m$^{-1}$.

XPS measurements were performed on these multilayers in order to confirm the presence of Cu(II) ions in the multilayers and to give some quantitative information about the formed metal complexes. In Figure 7.9, XPS spectra of the copper region of a multilayer consisting of 16 layers, built up from a $5 \times 10^{-5}$ M CuCl$_2$ subphase can be seen. After 1 hour of exposure to the soft X-rays, the presence of the copper peaks located at 936.5 eV (Cu 2p$_3$) and 956.5 eV (Cu 2p$_1$) and their satellites which are characteristic for Cu(II), can be seen clearly. Also Cu(I) peaks can be observed (934.5 eV Cu 2p$_3$ and 954.6 eV Cu 2p$_1$). As is already pointed out in Chapter 4 [2], upon longer exposure times of the multilayers to soft X-rays
(Fig. 7.9), the Cu(I) peaks increase in intensity while the Cu(II) peaks and their satellites decrease in intensity and finally after 20 hours of exposure to X-rays almost all Cu(II) is reduced to Cu(I). This phenomena is commonly observed in the literature [20-24] for transition metal ions and in the case of copper it is called X-ray induced copper reduction. From the ratio between the areas of the N and Cu 2p3 peak (including the satellite peak), the amount of Cu(II) ions incorporated into the multilayers could be calculated. The ratio N to Cu was approximately 7:1, because every amphiphile contained 3 nitrogen atoms, the ratio of amphiphile to copper in these multilayers is approximately 2:1. Furthermore the ratio Cu to Cl is 1:2, as expected.

![Figure 7.10: Small angle X-ray reflection curve of a multilayer consisting of 16 layers of the amphiphile on silicon, built up from a 5·10⁻⁵ M CuCl₂ subphase at 4.5 °C and 30 mN·m⁻¹.](image)

SAXR measurements were performed on the multilayers in order to establish if these multilayers had a regular layer structure. The SAXR curve of a multilayer consisting of 16 layers, built up from a 5·10⁻⁵ M CuCl₂ subphase (Fig. 7.10) has one clear Bragg peak which corresponded to a bilayer spacing of about 54.6 Å. Very weak second an third order Bragg peaks can also be seen. Because the multilayers were built up with a Z-type transfer, a Bragg peak corresponding to monolayer distance (about 27 to 37 Å, depending on the tilt angle with
Mono- and multilayer formation of an imidazole amide amphiphile

respect to the surface normal) was expected. Apparently the molecules have “turned over” to form a Y-type structure, which is the thermodynamically most favourable structure [25,26].

![Graph showing infrared spectra](image)

**Figure 7.11:** Bulk (scale factor: 0.0310×), transmission and GIR (scale factor: 0.432×) infrared spectra of the amphiphile. Samples: In the case of the transmission spectrum, 16 layers of the amphiphile transferred onto silicon from a $5\cdot10^{-5}$ M CuCl$_2$ subphase and in the case of GIR, 16 layers of the amphiphile transferred onto a gold coated glass slide from a $5\cdot10^{-3}$ M CuCl$_2$ subphase. Subphase temperature was 4.5 °C and the surface pressure was 30 mN·m$^{-1}$. The bulk and transmission spectra were y-shifted by 0.06 and 0.03 absorbance units, respectively.

In order to examine the structure of the multilayers in more detail, FT-IR measurements were performed as shown in Figure 7.11. The band assignments are listed in Table 7.1. The same scaling factors were used for the bulk, transmission and GIR spectra as in Chapter 4 [2] for a proper comparison of the 3 spectra.
Table 7.1: The IR band assignments [27-32].

| Wavenumber (cm\(^{-1}\)) | Assignment | Transition dipole moment, M
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3300</td>
<td>v (NH)</td>
<td>(\parallel) N–H bond</td>
</tr>
<tr>
<td>2954</td>
<td>v(_a) (CH(_3))</td>
<td>(\perp) C–CH(_3)</td>
</tr>
<tr>
<td>2920</td>
<td>v(_a) (CH(_2))</td>
<td>(\perp) C–C–C chain plane</td>
</tr>
<tr>
<td>2871</td>
<td>v(_s) (CH(_3))</td>
<td>(\parallel) C–CH(_3)</td>
</tr>
<tr>
<td>2850</td>
<td>v(_s) (CH(_2))</td>
<td>(\parallel) H–C–H plane, bisecting HCH angle</td>
</tr>
<tr>
<td>1640</td>
<td>Amide I</td>
<td>(\parallel) C=O bond</td>
</tr>
<tr>
<td>1548</td>
<td>Amide II</td>
<td>(\perp) C=O bond</td>
</tr>
<tr>
<td>1508</td>
<td>v (C=N(_{\text{imid}}))</td>
<td>(\parallel) ring</td>
</tr>
<tr>
<td>1466</td>
<td>(\delta) (CH(_2))</td>
<td>(\parallel) H–C–H plane, Bisecting HCH angle</td>
</tr>
</tbody>
</table>

As is shown in Figure 7.11, a bulk infrared spectrum of an uncoordinated amphiphile is recorded, powdered in KBr, in which the individual groups have no preferred orientation. Also transmission and GIR spectra were recorded of multilayer films consisting of 16 layers of the amphiphile, built up from a 5·10\(^{-5}\) M CuCl\(_2\) subphase. In the transmission mode, the electrical field vector is parallel to the substrate surface, so, all individual group vibrations with a transition dipole moment parallel to the substrate surface will absorb maximally in this mode while in the GIR mode, the electrical field vector is perpendicular to the substrate surface, so, all individual group vibrations with a transition dipole moment perpendicular to the substrate surface will absorb maximally in the GIR mode. In Figure 7.11, it can clearly be seen that the N-H (3300 cm\(^{-1}\)) and amide I (1642 cm\(^{-1}\)) bands are strongly present in the transmission spectrum while their intensity is much weaker in the GIR spectrum. The amide II band (1552 cm\(^{-1}\)) is strongly present in the GIR spectrum. The integrated area of the amide I peak in the transmission spectrum is larger than the integrated area of the amide I peak in the bulk spectrum. From these observations it can be concluded that the amide bond has a small tilt angle with respect to the surface normal. Closer examination (Fig. 7.11) of the amide I vibration reveals that there is also a vibration at 1671 cm\(^{-1}\) of much smaller intensity. From this second, much weaker, vibration it can be concluded that there is a small number of free amide groups which are not hydrogen bonded to their neighbouring molecules [27]. The
imidazole vibration is shifted completely to 1527 cm\(^{-1}\), indicating that free ligands are no longer present \cite{27,28} and all imidazole headgroups are involved in the complexation process because a free imidazole ligand shows a vibration at 1508 cm\(^{-1}\) (Fig. 7.11 bulk spectrum). The imidazole vibration can be seen in both the transmission and GIR spectra, although its intensity is somewhat stronger in the GIR spectrum, indicating that the imidazole group also makes a rather small tilt angle with respect to the surface normal. Major differences between the 2 IR methods can be observed in the CH stretching region, in which the symmetric methylene stretch (\(\nu_s (\text{CH}_2)\) at 2850 cm\(^{-1}\)) is strongly present in the transmission spectrum but has a weak intensity in the GIR spectrum and the asymmetric methylene stretch (\(\nu_a (\text{CH}_2)\) at 2920 cm\(^{-1}\)) appears relatively strong in the GIR mode. These observations in the CH stretching region suggest, as is already pointed out in Chapter 4 \cite{2}, that the C–C–C plane of the all-trans alkyl chain has a preferred orientation around the chain director, because when the all-trans alkyl chain can freely rotate around the C–C–C plane the ratio of the intensities of \(\nu_a (\text{CH}_2)\) and \(\nu_s (\text{CH}_2)\) will be about 2 in both the transmission and GIR spectrum. This is not the case for the multilayers of the imidazole amphiphile, so, the orientation of the all-trans alkyl chain is not random.

From Figure 7.11 it can be deduced that \(\nu_s (\text{CH}_2)\) has a preferred orientation nearly parallel to the substrate surface, because it appears strong in the transmission spectrum and relatively weak in the GIR spectrum. On the other hand, \(\nu_a (\text{CH}_2)\) is relatively strong in the GIR spectrum, compared to the transmission spectrum, indicating a large tilt angle (\(\alpha\)) of the chain director with respect to the surface normal. Furthermore, the transition dipole moment of the \(\nu_s (\text{CH}_2)\) vibration must lie nearly parallel to the substrate surface because this vibration strongly absorbs in the transmission spectrum but has a very weak intensity in the GIR spectrum. These results were also found by Walsh and Lando \cite{33} for alternating multilayers of diacetylene group containing amphiphiles.

From the SAXR and FT-IR measurements a model (Fig. 7.12) is proposed for the multilayer film of the imidazole amphiphile, built up from a 5·10\(^{-5}\) M CuCl\(_2\) subphase. From the experimental data, a value of about 45\(^{\circ}\) has been found for \(\alpha\), taking into account a bilayer spacing of 54.6Å, a length of about 37 Å for the amphiphile in a fully stretched conformation and a large tilt angle of the aliphatic tail as is deduced from the IR spectra.
Polymerisation in the multilayers

The LB films were polymerised by means of exposure to UV light ($\lambda = 254$ nm) under argon atmosphere. The polymerisation process was followed by UV/Vis spectroscopy as can be seen in Figure 7.13A. After several minutes of UV irradiation a red form of the polymer is formed with $\lambda_{\text{max}} = 540$ nm and after 30 minutes of exposure to UV light a maximum degree of polymerisation is reached because the absorption at 540 nm does not increase anymore. This can also be seen in Figure 7.13B, where the integrated absorbance, between 400 and 800 nm, is plotted as function of UV irradiation times. Apparently, a maximum conversion is reached after 30 minutes of exposure to UV light.

Figure 7.12: Schematic representation of the structure of the amphiphiles inside the multilayers.
Figure 7.13: A, UV/Vis absorption spectra of a multilayer of the amphiphile on glass, consisting of 16 layers, built up from a $5 \times 10^{-5} \text{ M CuCl}_2$ subphase at 4.5 °C and 30 mN·m$^{-1}$, at different UV irradiation times. B, Integrated absorbance, between 400 and 800 nm, from the UV/Vis spectra of Figure 7.13A at different times of exposure to UV light.
Figure 7.14: Small angle X-ray reflection curves of a LB film consisting of 16 layers of the amphiphile on silicon, built up from a 5·10^{-5} M CuCl_2 subphase at 4.5 °C and 30 mN·m^{-1}, before and after 30 minutes of exposure to UV light.

The layer structure of the multilayer, consisting of 16 layers of amphiphile, built up from a 5·10^{-5} M CuCl_2 subphase is preserved during the polymerisation process, as can be seen in Figure 7.14, although the bilayer distance decreases from the original 54.6 to 53.5 Å.
Figure 7.15: A, GIR infrared spectra of a LB film consisting of 16 layers of the amphiphile, built up from a 5·10⁻⁵ M CuCl₂ subphase at 4.5 °C and 30 mN·m⁻¹, before and after 30 minutes of exposure to UV light. B, transmission infrared spectra of a LB film consisting of 16 layers of the amphiphile, built up from a 5·10⁻⁵ M CuCl₂ subphase at 4.5 °C and 30 mN·m⁻¹, before and after 30 minutes of exposure to UV light. The CH₂ and CH₃ stretching vibration region.
During the polymerisation process, only in the CH stretching region major structural changes can be observed, as is shown in Figure 7.15A and B. The vibrations, due to \( \nu_s (\text{CH}_2) \) (2850 cm\(^{-1}\)) and \( \nu_a (\text{CH}_2) \) (2920 cm\(^{-1}\)) stretching vibrations, reveal a small shift to higher wavenumbers: 2852 and 2921 cm\(^{-1}\) for \( \nu_s (\text{CH}_2) \) and \( \nu_a (\text{CH}_2) \) respectively, indicating that the all-trans alkyl chain is partly converted to a more irregular one containing gauche conformations as was already described by Saito et al. [34] for the polymerisation of LB films of Cd(II) salts of 10,12-pentacosadiynoic acid. Furthermore, the intensity of the \( \nu_a (\text{CH}_2) \) vibration decreases in the GIR spectrum, while the intensity of the \( \nu_s (\text{CH}_2) \) vibration increases upon polymerisation (Figure 7.15A). This fact, together with the slight shift of the methylene stretch vibrations to higher wavenumbers, can be explained by considering a partial conversion of the all-trans alkyl chain during the polymerisation process into a more irregular alkyl chain containing gauche conformations, thereby loosing the orientation of the C−C−C plane of the aliphatic tail around the chain director.

Conclusions

The diacetylene group containing amphiphile N-(10,12-pentacosadiynamidopropyl)-imidazole, with an imidazole group as ligand, forms metal complexes at the air-water interface with all kinds of metal ions dissolved in the subphase at concentrations as low as 5·10\(^{-7}\) M. The complexation process can easily be controlled by variation of the metal ion concentration, the counter ion, the temperature and ionic strength of the subphase.

The amphiphile forms stable monolayers at the air-water interface at surface pressures up to 40 mN⋅m\(^{-1}\). But only when the subphase contained CuCl\(_2\), multilayers with a regular layer structure can be built up, which is confirmed by SAXR and FT-IR measurements. XPS measurements revealed the presence of Cu(II) ions in the multilayers, giving a direct proof that complexation in the monolayer at the air-water interface has occurred. The multilayers can be polymerised by means of UV irradiation, forming the red form of the polymer. During the polymerisation process, the regular layer structure is preserved, although FT-IR measurements show that the all-trans alkyl chains are partly converted to more irregular alkyl chains containing gauche conformations.
References


