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Morphological Changes of Monolayers of Two Polymerizable Pyridine Amphiphiles upon Complexation with Cu(II) Ions at the Air–Water Interface

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The monolayer behavior of two amphiphilic, diacetylenic units containing pyridine ligands at the air–water interface is studied by measuring the surface pressure–area isotherms and by Brewster angle microscopy (BAM). Both amphiphiles form stable monolayers at the air–water interface. The amphiphile containing an ester group shows a well-defined liquid-expanded (LE) to liquid-condensed (LC) phase transition, while the amphiphile with the amide group forms only a condensed monolayer film at 9.4 °C. For both amphiphiles, addition of CuCl₂ to the subphase causes an increase of the surface pressure (Π_c) at which the phase transition appears, suggesting the formation of a coordination complex at the air–water interface. Addition of Cu(ClO₄)₂ to the subphase instead of CuCl₂ causes an even larger increase in Π_c , indicating that more copper ions bind to the monolayer which results in a more charged monolayer. On a pure water subphase, Brewster angle microscopy of the monolayer of the ester-containing ligand shows the formation of spiral dendritic crystalline domains at the plateau in the isotherm near the solid state region. The formation of spiral crystalline domains indicates that the LC phase is L₁'. The amide-containing ligand, however, forms two-dimensional crystalline domains directly after spreading at the air–water interface, which are pushed together upon compression. No chiral crystalline domains were observed for this amphiphile indicating that the ester and amide amphiphile have a different LC phase. Both amphiphiles spread uniformly when the subphase contains CuCl₂, and upon compression crystalline domains are formed which grow when the area per molecule is reduced further, until a condensed monolayer film is formed. The shape of the crystalline domains on a Cu(II) ion containing subphase changes by replacing the Cl⁻ counterion by a ClO₄⁻ anion. The size of the crystalline nuclei decreases when the Cu(II) concentration increases.

Introduction

Several reports have been published on the incorporation of transition metal ions in Langmuir–Blodgett (LB) films, describing all kinds of interesting properties.^{1–7} Until recently, metal ions were added to the subphase to stabilize a fatty acid monolayer by salt formation with the fatty acids. For instance, Katherine Blodgett^{8,9} already described the stabilizing action of the metal ions dissolved in the subphase (like Pb(II), Ca(II), Cd(II), etc.) on a stearate monolayer, due to the cross-linking action of the metal ions.

Nowadays, there is a growing interest in functional LB films, in which the metal ions, incorporated in these films,

introduce all kinds of special properties into these multilayer films. Depending on the kind of metal ion, semiconductive, magnetic, or quantum physical properties are introduced in the LB films. In this way, these films have potential applications as sensors, catalytical systems, and membranes and in microelectronic devices.^{10,11}

In principle, metal ions can be incorporated into LB films by means of salt formation (like in the case of fatty acids) or by means of coordination of the metal ions with amphiphilic ligands. The latter approach has a growing interest, and several papers have been published in which the monolayer behavior of amphiphilic ligands upon complexation with metal ions at the air–water interface has been described. For instance, van Esch et al.¹² have studied the complexation behavior of imidazole amphiphiles with different metal ions (Cu(II), Co(II), Zn(II), and Ni(II)) at the air–water interface by measuring the surface pressure–area isotherms and by means of fluorescence microscopy. Caminati et al.^{2,13} have built up multilayers of an aliphatic pyridine amphiphile from Ni(II) ions containing subphase, and X-ray photoelectron

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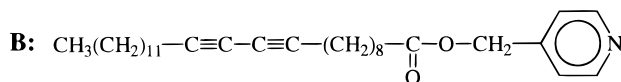
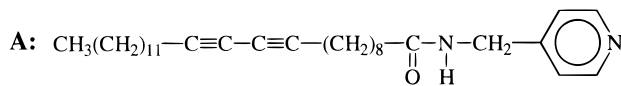
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spectroscopy (XPS) measurements confirmed the presence of Ni(II) ions in these multilayers. Furthermore, porphyrins¹⁴ and phthalocyanines^{15,16} have frequently been used as ligands.

Recently, we published an investigation on the monolayer characteristics of 4-(10,12-pentacosadiynamidomethyl)pyridine at the air–water interface at different subphase temperatures on an aqueous subphase by measuring the surface pressure–area isotherms.¹⁷ Furthermore, we also studied the complexation behavior of the amphiphile with Cu(II) ions at the air–water interface in this publication. We showed that the amount of complexation could be tuned by the proper choice of metal ion concentration, complexation time, temperature, ionic strength of the subphase, and the type of counterion. In a later study, more or less the same complexation behavior was found for the amphiphile 4-(((10,12-pentacosadiynoyl)oxy)methyl)pyridine (an ester).¹⁸ Moreover, it was shown that the liquid-expanded (LE) to liquid-condensed (LC) phase transition appeared already at much lower subphase temperatures for the ester amphiphile compared to the amide amphiphile. XPS measurements confirmed the presence of Cu(II) in the multilayers of this ester. It was shown that the Cu(II) ions of the metal complex in this multilayer were coordinated to two amphiphiles when the multilayers were built up from a 5 mM Cu(II) ion containing subphase. This coordination number for the Cu(II) ions was also found for the amide pyridine amphiphile in another publication¹⁹ at these Cu(II) ion concentrations. The formed multilayer films had a regular layer structure and could easily be polymerized by means of UV irradiation.

Brewster angle microscopy (BAM) allows direct visualization of changes in the morphology of the monolayers during compression at the air–water interface.^{20–26} Unlike fluorescence microscopy no additional probe has to be introduced in the monolayer which may cause artifacts.^{27,28} The domains of the condensed (C) phase surrounded by the liquid-expanded (LE) or gas (G) phase, have been observed by Brewster angle microscopy with a great variety of sizes and shapes²⁹ like circular, spiral, and dendritic structures. These shapes depend on a variety of parameters such as the type of amphiphilic molecule, temperature, modification of the water subphase, impurity content, spreading technique, and compression rate.

In this paper we present a morphology study on the monolayer behavior of two polymerizable amphiphilic ligands: 4-(10,12-pentacosadiynamidomethyl)pyridine (**A**) and 4-(((10,12-pentacosadiynoyl)oxy)methyl)pyridine (**B**).



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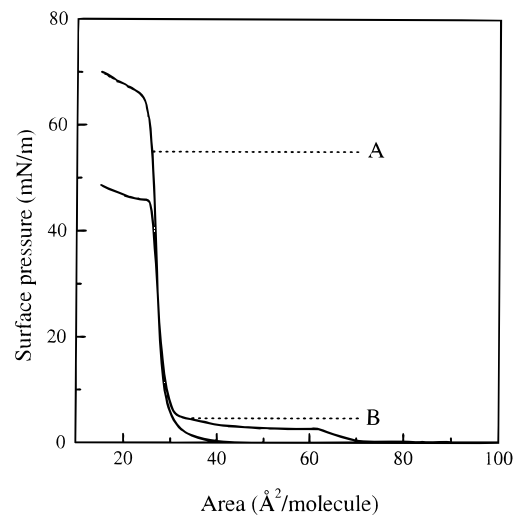


Figure 1. Surface pressure–area isotherms of the amide (**A**) and the ester (**B**) amphiphiles on an aqueous subphase at 9.4 °C.

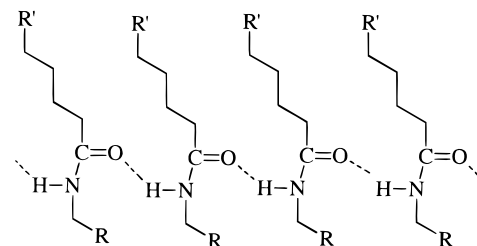


Figure 2. Schematic representation of the hydrogen bonds between the neighboring amide amphiphiles in a monolayer.

It is known from the literature that amphiphilic amides form much more stable monolayers than ester compounds³⁰ due to additional stabilization by hydrogen bonding. In the present study we investigate the effect of hydrogen bonding upon the stability and morphology of the monolayer and the influence of Cu(II) ions dissolved in the subphase. To investigate the influence of the Cu(II) ions dissolved in the subphase on the monolayer characteristics and morphology of amphiphile **A**, isotherms and BAM images were recorded at a subphase temperature of 19.8 °C. At lower subphase temperatures no phase transition from the LE to LC phase could be observed. So, at lower subphase temperatures the crystallization process of the formed Cu(II) complex of the amphiphile **A** could not be studied. At a subphase temperature of 19.8 °C, amphiphile **B** forms a totally expanded monolayer film. At a subphase temperature of 9.4 °C a clear phase transition from the LE to LC phase could be observed. For this reason all experiments for amphiphile **B** were carried out at a subphase temperature of 9.4 °C.

It appeared that on a Cu(II) ion containing subphase the crystalline domains have a different shape than on a

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pure water subphase. Upon complexation with the Cu(II) ions, amphiphile A spreads homogeneously at the air–water interface, while on a subphase without Cu(II) ions, crystalline domains were formed, which moved toward each other upon compression. At high Cu(II) concentration more but smaller crystalline domains were formed at the liquid-expanded to liquid-condensed (LC) phase transition. Also the type of counterion had a great influence on the shape of the crystalline domains.

Experimental Section

The synthesis and characterization of both amphiphiles will be discussed elsewhere.^{18,19} Cu(ClO₄)₂ (Across, 98%) and CuCl₂ (Merck, 99%) were used as received. The 5 mM Cu(II) ion containing subphases had a pH of 4.9 irrespective of the counterion used and the 10 mM Cu(II) ion containing subphases had a pH of 4.7.

The monolayer properties were studied by measuring surface pressure–area isotherms on a computer-controlled (temperature ± 0.1 °C) Lauda-Filmbalance (FW 2) with water, purified by a Milli-Q filtration system, as the subphase. A Langmuir trough (custom made by Riegler & Kirstein (GmbH), Ultrathin Organic Film Technology) equipped with a Brewster angle microscope was used to study the morphology of the monolayers. The light source of the BAM was a small diode laser (LaserMax MDL-200-680-35, 34 mm long, 11 mm diameter), which emitted 35 mW at 680 nm. The BAM setup is described elsewhere in more detail.³¹ The surface pressures and surface areas were recorded with accuracies of $0.5 \text{ mN}\cdot\text{m}^{-1}$ and $0.2 \text{ \AA}^2\cdot\text{molecule}^{-1}$.

The amphiphiles were dissolved in chloroform (Merck, spectroscopic quality), with a concentration of 0.1 wt %, and the isotherms were recorded at a barrier speed of $10 \text{ \AA}^2\cdot\text{molecule}^{-1}\cdot\text{min}^{-1}$. Lowering the compression speed until $2 \text{ \AA}^2\cdot\text{molecule}^{-1}\cdot\text{min}^{-1}$ had no influence on the shape of the isotherms.

For all complexation experiments a complexation time of 1 min was used.

Results and Discussion

Isotherms. The surface pressure–area isotherms of the two amphiphiles at 9.4 °C are shown in Figure 1. It can be seen that the amide (compound A) forms a condensed monolayer at the air–water interface with a limiting area of approximately $29 \text{ \AA}^2\cdot\text{molecule}^{-1}$ and a collapse pressure of about $60 \text{ mN}\cdot\text{m}^{-1}$, whereas the ester (compound B) shows a phase transition from the LE to the LC phase. The ester has a limiting area of approximately $30 \text{ \AA}^2\cdot\text{molecule}^{-1}$ and a collapse pressure of about $45 \text{ mN}\cdot\text{m}^{-1}$, so the monolayer of the ester is less stable than the monolayer of the amide, probably because in the amide monolayer hydrogen bonds are formed between the molecules (Figure 2) which stabilize the monolayer^{30,32,33} additionally.

4-(10,12-Pentacosadiynamidomethyl)pyridine. Figure 3 shows surface pressure–area isotherms of the amphiphile at a temperature of 19.8 °C on a subphase with (5 and 10 mM) and without Cu(ClO₄)₂. On a subphase with Cu(ClO₄)₂, a phase transition from LE to LC state can be observed, indicating that complexation occurs because charged molecules are formed, which start to repel each other.¹⁷ The surface pressure starts to rise at about $59 \text{ \AA}^2\cdot\text{molecule}^{-1}$.

At a Cu(ClO₄)₂ concentration of 10 mM, the surface pressure at which the phase transition occurs (Π_c) increases from about 7 to about $13 \text{ mN}\cdot\text{m}^{-1}$, indicating

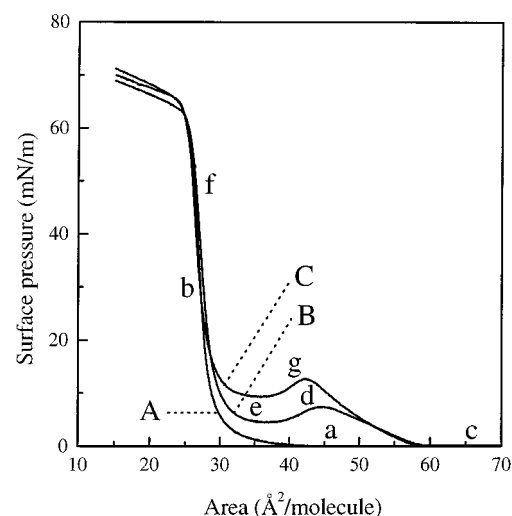


Figure 3. Surface pressure–area isotherms of the amide amphiphile at 19.8 °C on an aqueous subphase (A) and a 5 mM (B) and a 10 mM Cu(ClO₄)₂ subphase (C).

that the monolayer becomes more charged at this higher Cu(II) concentration, probably because more Cu(II) ions bind to the pyridine group of the amphiphiles.¹⁹

The isotherms were recorded simultaneously with the BAM imaging. The BAM images are shown in Figure 4. The pictures correspond to the points indicated in Figure 3. When the subphase does not contain Cu(II) ions, no homogeneous monolayer is formed (Figure 4a), but the molecules formed crystalline domains at the air–water interface, probably due to hydrogen bond formation between the molecules. Upon compression, the domains are pushed toward each other and the surface pressure starts to rise. In panel b of Figure 4, a homogeneous condensed monolayer is formed, and when the area per molecule is decreased further the monolayer starts to collapse.

The amphiphile spreads well at the air–water interface when the subphase contains 5 mM Cu(ClO₄)₂. No crystalline domains are formed, but the gas and liquid-expanded phase coexist (image c of Figure 4). Upon compression a LE monolayer is formed. The surface pressure rises gradually until the point is reached where crystalline nuclei appeared and the surface pressure decreased again (image d of Figure 4). The whole air–water interface was covered with nuclei, so the dip in the isotherm corresponds to a crystallization process in the monolayer. The formed crystalline nuclei have a dendritic structure. Dendritic structures are metastable structures formed by a diffusion-limited growth of the crystalline phase as is shown by various research groups by means of fluorescence microscopy or BAM.^{29,31,34–36}

The nuclei grow as the area per molecule is decreased (image e of Figure 4) and the surface pressure starts to rise. At high surface pressures (about $50 \text{ mN}\cdot\text{m}^{-1}$) a pure condensed film is formed (image f of Figure 4). When the Cu(ClO₄)₂ concentration is increased up to 10 mM, more crystalline nuclei are formed at the dip in the isotherm (image g in Figure 4), but the nuclei are smaller in size as compared to the nuclei formed on a 5 mM Cu(ClO₄)₂ subphase.

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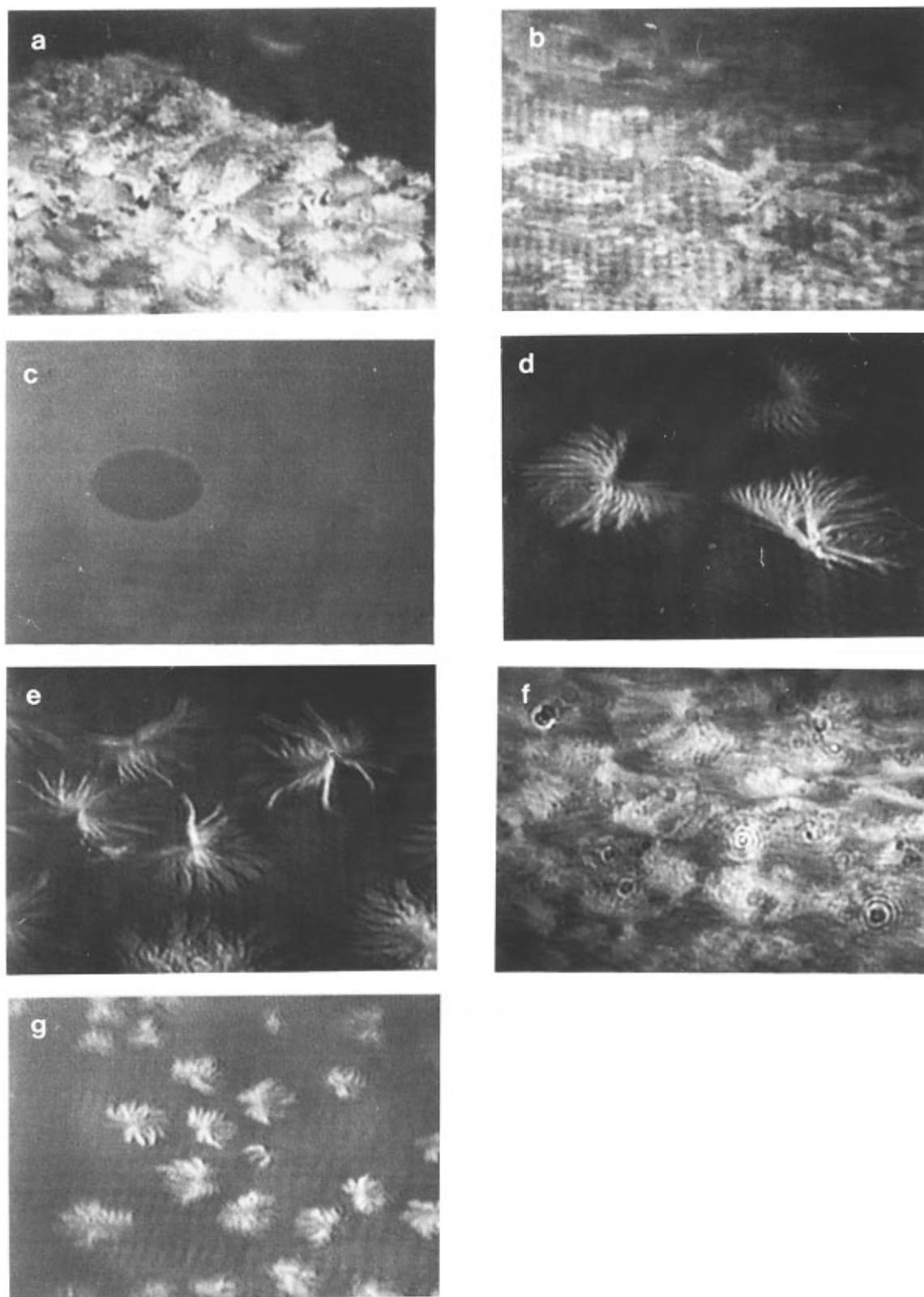


Figure 4. BAM images of the amide monolayer at 19.8 °C corresponding to the points of the Π - A isotherms for the amide compound (Figure 3). Image size was $350 \times 480 \mu\text{m}^2$.

At a higher Cu(II) ion concentration in the subphase, Π_c increases (Figure 3). This increase in Π_c causes a decrease in nucleation energy as is shown by Helm et al.^{37,38} They found that Π_c increases for different phos-

pholipids when the subphase temperature increased or when the NaCl concentrations of the subphase of the subphase increased. At higher subphase temperatures or higher NaCl concentrations of the subphase, fluorescence microscopy showed that more and smaller crystalline

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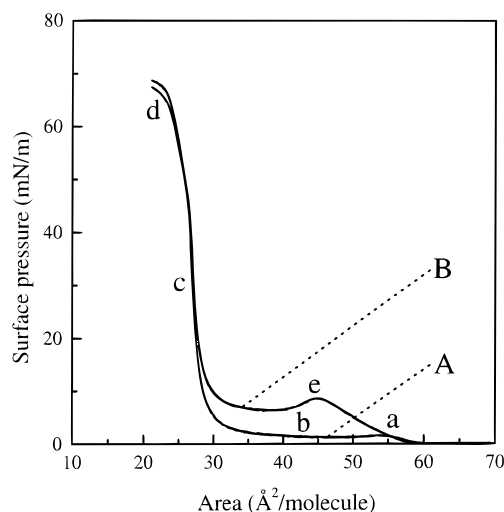


Figure 5. Surface pressure–area isotherms of the amide amphiphile at 19.8 °C on a subphase with 5 mM (A) and 10 mM (B) CuCl_2 .

domains were formed due to a decreased nucleation energy at higher values of Π_c .

Figure 5 shows the surface pressure–area isotherms of the amide amphiphile at a temperature of 19.8 °C on a subphase containing 5 and 10 mM CuCl_2 . Both isotherms exhibit a LE to LC phase transition suggesting complexation has occurred. At higher copper concentrations the surface pressure at which the phase transition LE to LC phase (Π_c) appears increases again, indicating that more copper ions bind to the monolayer film.¹⁹ The BAM images of Figure 6 represent the points indicated in Figure 5. At large areas (more than $63 \text{ \AA}^2 \cdot \text{molecule}^{-1}$) the monolayer appears to be homogeneous. The reflectivity of the monolayer changes when Π_c is reached (image a of Figure 6). Crystalline nuclei are formed here also, and upon further compression of the monolayer the nuclei grow (image b of Figure 6). In this case we see crystallization of the amphiphiles in dendritic structures which may originate from a diffusion-limited growth mechanism. The nuclei differ in shape from the nuclei formed on a $\text{Cu}(\text{ClO}_4)_2$ subphase. At a surface pressure of $30 \text{ mN} \cdot \text{m}^{-1}$ a homogeneous condensed monolayer is formed without any pinhole. At surface pressures of about $60 \text{ mN} \cdot \text{m}^{-1}$, the monolayer starts to collapse (image d of Figure 6). At higher copper concentrations (10 mM) much more nuclei are formed at the phase transition (image e of Figure 6) with more arms but smaller in size as in the case of a $\text{Cu}(\text{ClO}_4)_2$ subphase, probably due to a decreased nucleation energy at higher values of Π_c . Moreover, these nuclei grow upon decreasing the area per molecule until a complete condensed film is formed.

So, by using ClO_4^- as a counterion instead of Cl^- , more complexation takes place in the monolayer as indicated by the higher Π_c at the same $\text{Cu}(\text{II})$ ion concentration¹⁷ (Figures 3 and 5). Furthermore, the shape of the crystalline domains is changed when ClO_4^- is used as an anion instead of Cl^- .

4-((10,12-Pentacosadiynoyl)oxy)methylpyridine. As can be seen from Figure 7, the collapse pressure of the monolayer film of the ester increases drastically (from 45 to about $70 \text{ mN} \cdot \text{m}^{-1}$) on a $\text{Cu}(\text{ClO}_4)_2$ containing subphase in contrast to the amide where only a slight increase in collapse pressure can be observed. Moreover, the Π_c of the ester increases from 3 to $12 \text{ mN} \cdot \text{m}^{-1}$ upon complexation with $\text{Cu}(\text{II})$, forming a much more stable monolayer film. When the subphase contains CuCl_2 , also

an increase in collapse pressure (from 45 to about $58 \text{ mN} \cdot \text{m}^{-1}$) is observed, compared to the pure aqueous subphase, but this value is lower than the collapse pressure on a $\text{Cu}(\text{ClO}_4)_2$ containing subphase. Also the Π_c increases compared to the pure aqueous subphase, but again its value is lower than the Π_c of the monolayer on a $\text{Cu}(\text{ClO}_4)_2$ subphase, indicating that on a $\text{Cu}(\text{ClO}_4)_2$ subphase more $\text{Cu}(\text{II})$ ions bind to the pyridine group of amphiphile **B** at the air–water interface at the same $\text{Cu}(\text{II})$ ion concentration.

Figure 8 shows BAM images of the ester compound upon compression on a water subphase at 9.4 °C. The images correspond to the points in Figure 7. At low surface pressure the LE and G phases coexist (image a of Figure 8). When the monolayer is compressed, a homogeneous LE phase is formed. At Π_c no nuclei can be seen, probably because the dimensions of the crystallites of the newly formed condensed phase do not exceed the lateral resolution of the BAM (about $5 \mu\text{m}$). At the beginning of the solid state region of the isotherm, however, suddenly big dendritic crystals are formed ($>200 \mu\text{m}$) (image b of Figure 8). Again these dendritic structures suggest a diffusion-limited growth mechanism as in the case of amphiphile **A**. Upon further compression these nuclei grow very fast in a circular way (image c of Figure 8). The spiral growth of the crystalline domains is somewhat surprising because it suggests that these domains are chiral, although amphiphile **B** is achiral. This behavior was also observed by other research groups^{39–42} for achiral fatty acids and their esters. The spiral effects can only be accounted for when it is assumed that the liquid-condensed phase is the so-called L_1' phase. This phase is a tilted mesophase in which the molecules have a tilt azimuth in a direction intermediate between the nearest neighbor and next-nearest neighbor.^{40,42} The L_1' phase has a broken reflection symmetry³⁹ which causes the spiral structures observed by fluorescence microscopy^{39,40} and BAM⁴² for achiral compounds.

At high pressures, of $30 \text{ mN} \cdot \text{m}^{-1}$, a homogeneous condensed phase (image d of Figure 8) is reached. At $45 \text{ mN} \cdot \text{m}^{-1}$ the monolayer starts to collapse and the monolayers start to shift over each other, which can nicely be seen in image e.

When $\text{Cu}(\text{ClO}_4)_2$ is added to the subphase again at large surface areas ($>61 \text{ \AA}^2 \cdot \text{molecule}^{-1}$), the LE and G phases coexist, but at Π_c (image f of Figure 8) circular domains are formed, which grow when the surface area is decreased (image g of Figure 8). Again, the appearance of chirality identifies the LC phase as L_1' .⁴⁰ Following the growing process, we observe that the point on the edge is the nucleus of the domain. Upon further compression the domains start to deform, and at high surface pressures ($30 \text{ mN} \cdot \text{m}^{-1}$) crystalline domains with different orientations are formed (image h of Figure 8).

When the subphase contains 5 mM CuCl_2 , crystalline nuclei start to grow at Π_c (image i of Figure 8), but again these nuclei differ in shape from the nuclei formed on a $\text{Cu}(\text{ClO}_4)_2$ subphase. The nuclei formed on a CuCl_2 subphase have a dendritic structure. On this subphase no chiral crystalline domains are formed, which indicates that the LC phase is not L_1' .⁴⁰ So by changing the counterion of the $\text{Cu}(\text{II})$ ions, the LC phase is changed.

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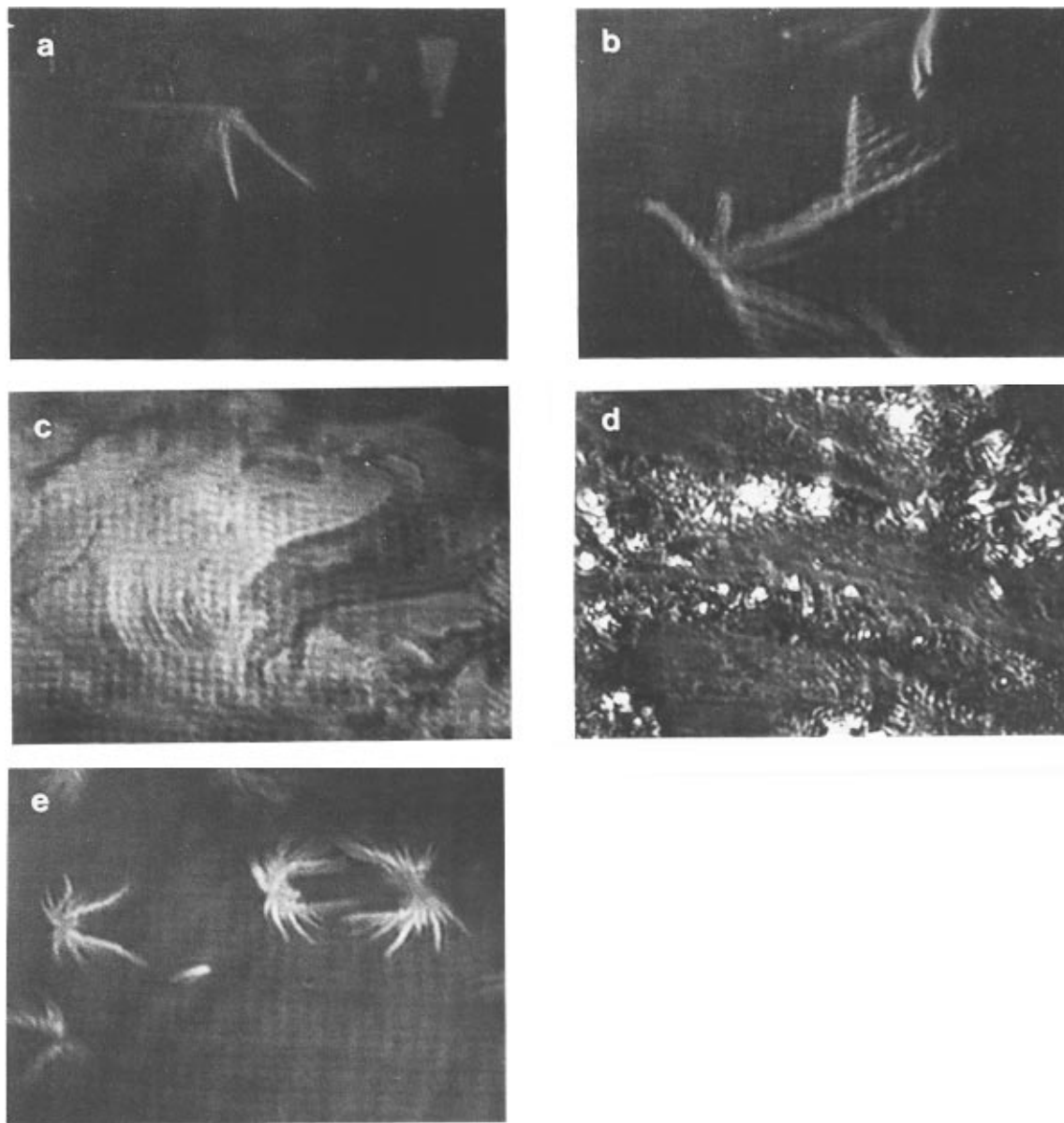


Figure 6. BAM images of the amide monolayer at 19.8 °C corresponding to the points of the Π - A isotherms for the amide compound (Figure 5). Image size was $350 \times 480 \mu\text{m}^2$.

Upon further compression these nuclei grow (image j of Figure 8), and at high surface pressures a homogeneous LC phase was formed again.

Therefore, both the presence of Cu(II) ions and the type of the used counterion have an enormous influence on the shape of the crystalline domains formed during the compression of the monolayer.

Conclusions

The two pyridine amphiphiles form stable monolayers at the air-water interface. Amphiphile **A** (the amide) forms the most stable monolayers, as was expected, because hydrogen bonds can be formed between the molecules.

Both compounds form complexes when Cu(II) ions are present in the subphase, which can clearly be seen from the surface pressure-area isotherms by the presence (compound **A**) or increase of Π_c (compound **B**). The stability of the ester monolayer is greatly enhanced upon complexation, while the stability of the amide monolayer is hardly affected by the complexation process.

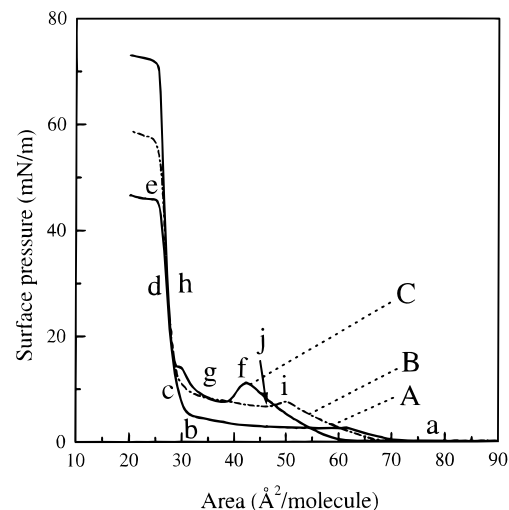


Figure 7. Surface pressure-area isotherms of the ester amphiphile at 9.4 °C on an aqueous subphase (A) and a 5 mM CuCl₂ (B) and a 5 mM Cu(ClO₄)₂ (C) subphase.

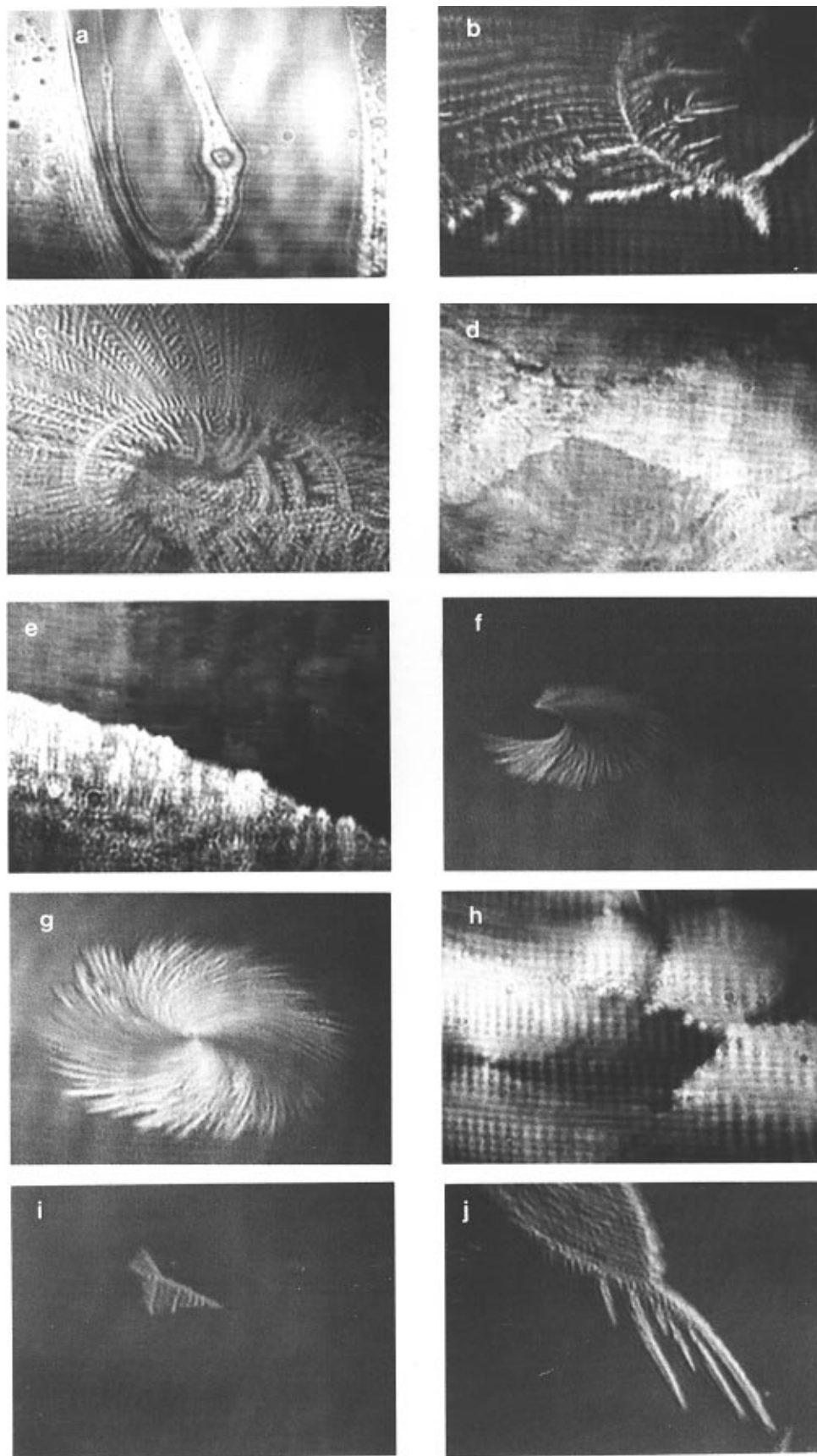


Figure 8. BAM images of the ester monolayer at 9.4 °C corresponding to the points of the Π - A isotherm of the ester compound (Figure 7). Image size was $350 \times 480 \mu\text{m}^2$.

The morphology of the monolayer can nicely be studied by means of BAM. It shows that upon complexation the amide amphiphile is spread homogeneously at the air-

water interface, but when the subphase does not contain Cu(II) ions crystalline domains are formed and a homogeneous condensed film is obtained upon further com-

pression. Moreover, it can be seen that for both amphiphiles crystalline nuclei start to appear at Π_c , which grow upon further compression. The shapes of these crystalline nuclei depend strongly on the counterion, whereas the size of these nuclei can be varied by changing the Cu(II) ion concentration of the subphase. Furthermore, it is shown that amphiphile **B** forms chiral crystalline domains on an aqueous subphase and on a 5 mM $\text{Cu}(\text{ClO}_4)_2$ subphase which identifies the LC phase as L_1' . When the counterion is changed from ClO_4^- to Cl^- , the LC phase changes from a phase with a broken reflection symmetry to a phase with a reflection symmetry, and no

chiral crystalline domains could be observed. Moreover, also the crystalline domains of amphiphile **A** had no chirality on an aqueous subphase as well as on a Cu(II) ion containing subphase. This indicates that the two amphiphiles have different LC phases.

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