Langmuir–Blodgett Multilayer Assembly by a Continuous Process Using a Steadily Flowing Subphase

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A continuously operating Langmuir–Blodgett (LB) trough was developed and set up using two basins of different fluid levels connected by a ramp. Water as subphase was circulated by a tube pump to generate a steady laminar flow film on the ramp and thereby compressing the molecules on the surface to form a monolayer. Spreading, compressing, and transferring occurred simultaneously at three spatially separated regions. The surface pressure in the monolayer was measured as a function of the flow conditions. Parameters were the volumetric flow rate of the subphase, the difference of fluid level in the two basins, and the slope of the connecting ramp. The flow conditions were modeled with the purpose of predicting the surface pressure in the monolayer. The theoretical predictions agree reasonably well with the experimental results. LB films of more than 100 layers of LB forming rigid-rod polymers were transferred onto solid substrates using this continuous processing mode.

Introduction

The Langmuir–Blodgett (LB) technique provides an excellent method to prepare ultrathin films of controlled thickness and well-defined molecular order. LB films have potential for applications in optical and microelectronic devices, as sensors, or as claddings to modify solid surfaces. These applications require uniform film quality at low production costs. Novel technologies have to be developed for reducing the processing time. Maximum automatization will guarantee constant and defined process parameters over expanded time periods.

Commercially available film balances operate in the batch processing mode. The number of layers which can be transferred to a solid substrate per batch is determined by the ratio of substrate surface to monolayer area. Therefore, when a new monolayer must be prepared. This involves the time-consuming processes of expanding the surface area, cleaning the water surface, spreading new material to the water surface, and compressing it to form a new transferable monolayer. Also, the start-up conditions for each batch may produce transient ordering phenomena in the first deposited layers of the substrates which are conserved in the layered assemblies and cause a deterioration of, e.g., the optical properties.

A continuously operating LB trough can overcome these problems. The sequence of steps needs to be decoupled spatially so that spreading, compressing, and transferring can take place simultaneously. In addition, operation at constant flow geometry minimizes the variation of process parameters during the transfer.

A concept to achieve continuous LB processing has been reported in the literature. It suggests to use rotating rollers to transfer molecules from one into another basin and hereby compress them into a monolayer. However, the rollers have the disadvantage that they may induce turbulence at the water surface and thus mix the LB forming molecules into the subphase or put water molecules on top of the monolayer.

In a related concept, surface pressure is created by a constant flow of the water subphase in a basin whereby the monolayer on the air–water interface is compressed by pushing it against a stationary surface barrier. Re- alizing this concept, a trough has been recently constructed in which the entire subphase volume participates in the flow and thereby creates interesting orientation phenomena in the compressed monolayer.

In this study, a continuously operating LB trough was developed with two separate basins, one for spreading the molecules onto the water surface and one for transferring the monolayer onto the substrate. Both are connected by a ramp on which a constantly flowing subphase compresses the molecules to a monolayer. A model has been proposed in order to predict the flow-induced surface pressure in the monolayer film.

Experimental Section

The experimental setup consists of two basins connected by a ramp; see Figures 1 and 2. The lower basin (basin 2) is a commercial Lauda film balance FW1 fully equipped with dipping gear and movable barrier. The ramp (30 mm wide and 100 mm long) enters sideways. It is made out of Teflon side walls and a hydrophilic glass bottom. This choice of materials allows the use of very thin water films as flowing subphase.

Upstream of the ramp is a 300 × 100 mm² basin (basin 1) which is made entirely out of Teflon. The water level in basin 1 is higher than in basin 2. However, the level difference is very small (2–10 mm). It is adjustable by mechanically raising basin 1.

A steady flow of subphase on the ramp was generated by a tube pump (lamatic Instruments, Model MV-CA) which steadily pumps subphase from basin 2 into basin 1. Constant volumetric rates between 0.18 and 0.45 L/min could be chosen while avoiding pulsations in flow.

The temperature of the subphase and the environment was kept at 20°C. The thermostat of the Lauda film balance allowed adjusting the temperature of the laminar flow box. The feedback system for constant surface pressure of the Lauda film balance was used to maintain a constant surface pressure in the monolayer in basin 2. Flow conditions were assumed to be steady when the

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surface tension measured with the Langmuir system on the Lauda trough was constant over a period of at least 5 min.

Rodlike polymers such as poly(bis(butoxyphenyl)silane)\(^8\) or poly(glutamates)\(^9\) were used as model compounds to form monolayers. These molecules form transferable monolayers at surface pressures of typically 5–30 mN m\(^{-1}\).

LB multilayers were assembled by transferring the monolayers with a Lauda FL-1E film lift at the position in basin 2 depicted in Figure 1 at transfer rates between 25 and 400 mm/min.

**Flow Model**

In order to generate a surface pressure, the flowing film on the ramp has to be covered with a monolayer film. The flowing substrate exerts a shear stress on the monolayer which pushes the monolayer toward basin 2 and, hence, generates a surface pressure in the monolayer. The highest surface pressure is reached at the bottom of the ramp where the flowing film merges with the main fluid volume in basin 2. This surface pressure \(\sigma\) depends on the shear stress and the active length of the ramp which is covered by a monolayer film. The Reynolds number of the flow is kept very low.

In the following we will estimate the flow induced surface pressure \(\sigma\) by modeling the flow in the active flow region of the ramp; see Figure 3. The connected area of the monolayer is \(WL\), where \(W\) is the width of the ramp and \(L\) is the active length. The flowing substrate film has a height \(H\).

The momentum balance for the flowing subphase reduces to

\[
0 = \eta \frac{\partial^2 u}{\partial y^2} + \rho g \sin \alpha
\]

(1)

when assuming unidirectional flow (neglecting inlet and outlet disturbances, assuming constant layer height \(H\)) and accounting for constant normal stress on the surface equal to the atmospheric pressure. The properties, viscosity \(\eta\) and density \(\rho\), are constant throughout the flow region.

The flow is shown schematically in Figure 3. The flowing subphase is bounded by the stationary ramp on the bottom and the LB film on the top. This monolayer will be treated as a solid boundary which moves very slowly in comparison to the average velocity \(\bar{v}\) of the subphase, \(\bar{v} \ll \bar{v}\).

Integrating eq 1, together with the zero velocity condition on both boundaries, gives the velocity distribution

\[
v(y) = 6\left(\frac{v}{H}\right)^2 \left(\frac{y}{L}\right)^2
\]

(2)

with an average velocity

\[
\bar{v} = \frac{\rho g H^2}{12 \eta} \sin \alpha
\]

(3)

The volume flow rate of the pump

\[
Q = \bar{v} WH
\]

(4)

determines the height of the subphase region \((H)\):

\[
H = \left(\frac{1}{W \rho g \sin \alpha}\right)^{1/3}
\]

(5)

The viscous force on the monolayer \(F_v\)

\[
F_v = LW\eta \frac{\partial u}{\partial y}_y=H = \frac{1}{2} LWHg \sin \alpha
\]

(6)

is equal to half the \(x\)-component of the subphase weight in the active region. Under the condition that the monolayer covers the entire ramp, the active length

\[
L = h/\sin \alpha
\]

(7)

is given by the slope of the ramp and the level difference \(h\) between the two basins.

The viscous force gives rise to the surface pressure

\[
\tau = F_v/W
\]

(8)

Combining eqs 3–7, we can express the surface pressure \(\tau\) as a function of volume flow rate \((Q)\) and ramp geometry \((L, W, \alpha)\)

\[
\tau = L(\rho g \sin \alpha)^{2/3} \left(\frac{2Q}{W}\right)^{1/3}
\]

(9a)

where \(L\) is the active length of the ramp. In the limiting case where the monolayer covers the entire ramp, \(\sin \alpha\) may be substituted (eq 7). This gives the upper limiting value of the surface pressure

\[
\tau = \left[\frac{3QH}{2W} \rho g h\right]^{1/3}
\]

(9b)

The inertial forces in the subphase are kept small compared to the viscous forces by choosing flow conditions with small...
Table I. Calculated and Experimental Values of the Surface Pressure (σ) at Various Height Differences (h) between the Surface Levels in Basins 1 and 2 at a Constant Flow Volume of 0.18 L/min

<table>
<thead>
<tr>
<th>h (mm)</th>
<th>Hcalc (mm)</th>
<th>σcalc [10^3 N/m]</th>
<th>σexp [10^3 N/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.84*</td>
<td>18.0</td>
<td>10.0</td>
</tr>
<tr>
<td>3.0</td>
<td>1.60</td>
<td>23.4</td>
<td>12.5</td>
</tr>
<tr>
<td>4.0</td>
<td>1.45</td>
<td>28.5</td>
<td>15.0</td>
</tr>
<tr>
<td>5.0</td>
<td>1.25</td>
<td>33.1</td>
<td>18.0</td>
</tr>
<tr>
<td>6.0</td>
<td>1.27</td>
<td>37.3</td>
<td>20.5</td>
</tr>
<tr>
<td>7.0</td>
<td>1.20</td>
<td>41.2</td>
<td>23.0</td>
</tr>
<tr>
<td>8.0</td>
<td>1.15</td>
<td>45.1</td>
<td>25.0</td>
</tr>
</tbody>
</table>

* Confirmed by measurement.

Reynolds numbers

\[
Re = \frac{\dot{v}H \rho}{\eta} = \frac{Q \rho}{W \eta}
\]  

A typical operating condition

\[
Q = 0.18 \text{ L/min} \\
W = 0.03 \text{ m} \\
L = 0.1 \text{ m} \\
h = 0.002 \text{ m} \\
\eta = 10^{-3} \text{ Pa s (water at 20 °C)}
\]

at an inclination angle α = 1.15° results in an average velocity \( \dot{v} = 0.055 \text{ m/s} \), a layer thickness \( H = 1.85 \text{ mm} \), a Reynolds number \( Re = 100 \), and a maximum surface pressure in the monolayer of \( \sigma = 17.9 \times 10^3 \text{ N/m} \).

Results and Discussion

The operation was started by spreading molecules onto the substrate in basin 1 from where they were convected toward the ramp and down onto the basin 2. There, they accumulated and eventually formed a dense surface layer. A low initial surface pressure was chosen by appropriately setting the feedback loop of the Lauda trough. The pressure setting in the feedback system was then gradually increased until more and more of the ramp region was covered with a monolayer. Coverage of at least part of the ramp is essential for the functioning of the continuous LB process since compression of LB molecules occurs in the ramp region.

To find the surface pressure which corresponds to the actual level difference between the two surfaces in basin 1 and basin 2, the pressure setting of the feedback system was increased step by step. Measurements of the surface pressure were carried out in steps of 0.5 \times 10^{-3} \text{ N/m}. Above a certain value of the surface pressure, the movable barrier started to push the monolayer over the ramp into basin 1 without further increasing the surface pressure in the film. These values of the surface pressure corresponding to the level difference \( h \) in both basins are given below.

Table I shows the experimental values for the surface pressure obtained at various level differences (\( h \)) and a constant substrate flow volume of 0.18 L/min as well as the theoretical values according to eq 9b. The height of the flow layer (\( H \)) was calculated using eq 5. The height \( H = 1.85 \text{ mm} \) of the film at a level difference between the two basins of \( h = 2 \text{ mm} \) was confirmed by direct measurement as well as by the decreasing value of \( H \) with increasing level difference \( h \).

In addition, the surface pressure was measured at a constant layer thickness \( H = 1.85 \text{ mm} \) varying the heights \( h \) between the basins and the flow volume (Q). The values for the surface pressure were determined as described above; see Table II.

Table II. Calculated and Experimental Values of the Surface Pressure (σ) at Various Height Differences (h) between the Surface Levels in Basins 1 and 2 and a Constant Thickness (H = 1.85 mm) of the Fluid Layer on the Ramp

<table>
<thead>
<tr>
<th>h (mm)</th>
<th>Q (L/min)</th>
<th>σcalc [10^3 N/m]</th>
<th>σexp [10^3 N/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.18</td>
<td>18.0</td>
<td>10.0</td>
</tr>
<tr>
<td>3.0</td>
<td>0.27</td>
<td>27.3</td>
<td>14.5</td>
</tr>
<tr>
<td>4.0</td>
<td>0.36</td>
<td>36.4</td>
<td>19.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.45</td>
<td>45.4</td>
<td>24.5</td>
</tr>
</tbody>
</table>

Based on the assumptions of our flow model and our operating conditions, the surface pressure will be lowered by 1% when the level between the basins is changed by 0.03 mm. This corresponds to a change in the area of friction (2L(W + H)) of about 3%. The statistical fluctuations in surface pressure measured with the Langmuir balance are in the range of ±0.5 \times 10^{-3} \text{ N/m} as found for plain water surfaces. The fluctuations in the temperature control of ±2 K give a relative error for the viscosity (\( \eta \)) of about ±3% resulting in a 1% statistical deviation of the surface pressure. A maximum relative error of the volumetric flow rate of 10% would result in a relative error for the surface pressure of 3%. The accuracy of the measured level differences \( h \) is about 0.5 mm resulting in a relative error for the surface pressure of ±16% or an error of ±3.0 \times 10^{-3} \text{ N/m} at \( h = 2 \text{ mm} \). The experimentally obtained values of the surface pressure have about half the predicted value. Nonideal behavior of the flow film due to incomplete coverage by molecules on the ramp could explain this observation. For example, a flow film with an increasing thickness toward the lower basin would account for a significantly reduced friction on the covering monolayer. Also inhomogeneities in the flow conditions at the beginning and the end of the ramp could contribute to the same effect. Further, the monolayer on top of the flow film may not behave as an ideal stationary wall in the complete area of contact. In the upper region of the ramp the surface pressure in the LB film converges to zero so that the molecules do not form a densely packed monolayer in this region. This reduces the friction coefficient in this region as well as the effective area of friction on the whole ramp.

Monolayers, prepared as described above, were transferred onto solid substrates using the Langmuir–Blodgett technique. The desired surface tension was applied to the monolayer using the feedback system of the Lauda film balance. The height between the basins was chosen so that half of the ramp was covered by the monolayer according to eq 9.

During the transfer of monolayer material onto the solid substrate, the movable barrier adjusted the surface area in basin 2 in order to maintain the surface pressure. As a result, the active area on the ramp covered by the film was kept constant. Thus, fluctuations induced by either removing part of the monolayer on basin 2 for LB assembly or by adding new material to basin 1 were buffered by the motion of the movable barrier. More than 100 layers of poly(glutamate) at a surface tension of 20 \times 10^{-3} \text{ N/m} were transferred with a rate of 25 mm/min onto a solid substrate of about 20 cm² size in a continuously operating mode. Multilayers of rodlike poly(di-m-butoxyphosphylsilane) transferred at 12 \times 10^{-3} \text{ N/m} and a rate of 100 mm/min with the continuous process showed the same orientation of the molecules on the substrate as samples prepared by the conventional LB method. In other words, the molecules are aligned with their long axes in the dipping direction of the substrate. This orientation is different
from the one obtained in the experiment by Nitsch et al.\textsuperscript{7} discussed above.

**Conclusions**

The formation of the monolayer in the apparatus of Figure 1 occurs by convection. New molecules are convected toward the edge of the existing monolayer where they become integrated and compressed as further molecules join the assembly. The compression of the monolayer is due to the shear flow in the ramp region. The experiments show that the moving substrate is able to generate a sufficiently high shear stress on the monolayer. The shear stress results in a surface pressure in the monolayer which is of the right order for the usual LB applications. Constant coverage of the ramp region is necessary and it is achieved by maintaining a constant surface pressure with the LB feedback system in basin 2.

The flow down the ramp region is driven by gravity and the substrate is recirculated by a pulsation-free pump. The flow model predicts an upper limit of the surface pressure. Only about 50\% of this ideal value could be reached in the actual experiments.

It is demonstrated that the preparation of LB multilayers can be carried out in a continuous mode, by spreading, compressing, and transferring at the same time in spatially different regions. LB multilayers prepared in the continuously operating mode show the same quality and same molecular orientation as multilayers prepared in the conventional batch process. The problem of going through the unfavorable startup conditions which are naturally connected to batch processes are avoided since many different LB assemblies can be produced once the process has been started.