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Wettability, Surface Morphology, and Stability of Long-Chain Ester Multilayers Obtained by Different Langmuir-Blodgett Deposition Types

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Methyl arachidate Langmuir-Blodgett multilayers, built up by X-, XY- and Y-type transfers, are characterized by means of contact angle measurements, and optical and atomic force microscopy under ambient conditions. Contact angle investigation shows identically high hydrophobicity of the surfaces produced by X- and Y-type depositions, implying molecular overturning during the X-type transfer. This overturning has not been detected in the previous X-ray study of small numbers of deposited fatty acid methyl ester monolayers. Molecular resolution AFM images of thin methyl arachidate LB films show a disordered surface structure. Scanning over larger film regions reveals a considerable difference in the surface morphology, corresponding to pure and mixed-type LB transfers. Reorganization of the multilayers occurs under ambient conditions in both cases. Larger aggregates, steps, and irregular islands are found with Y-type deposition. Ester LB films studied in an aqueous environment rearrange more easily than those stored in air. AFM imaging of the "contact line corrosion" of the multilayers shows a collective depletion of the whole LB film from the substrate at the wetting perimeter. The instability of the ester mono- and multilayers is explained on the basis of the intra- and interlayer molecular interactions within the spread and the deposited films, and by their weak adhesion to the substrate.

Introduction

Investigations of asymmetrical type (X- or Z-) Langmuir-Blodgett (LB) depositions are of fundamental and practical interest both for understanding the mechanism of multilayer transfer^{1–8} and for creation of noncentrosymmetric structures (e.g. for nonlinear optics applications⁹). X-type LB deposition (on dipping only) has been achieved with esters of long-chain acid monolayers by controlling the deposition speed, transfer pressure, and temperature.^{10–15} If the multilayers thus obtained are stable under ambient conditions, and may exist without molecular overturning, they could be utilized as matrices in which optically active components can be included in a noncentrosymmetrical arrangement. A single-layer repeated spacing has often been evaluated¹⁶ for multilayers prepared by X-type LB deposition. X-ray structure investigations¹³ of films built of a very large number of monolayers have shown that the overturning of the ester molecules to a symmetrical (head-to-head) arrangement is related to the number of the carbon atoms in their alkyl chain.

Previously, we have studied¹⁵ the deposition conditions corresponding to X- or Y-type transfer of methyl arachidate and methyl behenate monolayers. It has been shown that the increase of the withdrawal deposition velocity results in a transition from X- to Y-type transfer of the films. However, it has been difficult to establish by means of the small angle X-ray diffraction method whether overturning of the ester amphiphiles occurs during X- and XY-type transfer of the initial 20–30 monolayers. Owing to the peculiarities of the ester molecular structure (respectively, electron density profile), an asymmetrical (tail-to-head) ar-

rangement in the multilayers could be deduced on the basis of the X-ray patterns.¹⁵

In the present investigation, contact angle measurements are applied for a characterization of the outermost surface of methyl arachidate multilayers obtained by X-, XY-, and Y-type depositions. It has been well documented^{17–19} that wettability is dominated by the properties of the atoms and groups located within the last few angströms from the film surface. Since contact angles of methyl group-terminated and methyl ester group-terminated surfaces are rather different,^{19,20} wettability investigation should be more appropriate than X-ray diffraction to distinguish head-to-head from tail-to-head arrangement in the ester multilayers.

In addition, atomic force microscopy (AFM) and optical microscopy are employed here for a visualization of the surface morphology of the obtained methyl ester multilayers. Previous studies^{3,21} of pure and mixed-type fatty acid LB-film transfer have indicated the need for a direct comparison of the surface configurations of both kinds of multilayers, showing similar X-ray patterns. This need is supported also by the recent evidence^{22–26} for a dramatic influence of the environment on the morphology and structure of the deposited LB films.

The aim of the present work is to investigate the relationship between the type of methyl arachidate monolayer transfer and the surface perfection and surface hydrophobicity of the corresponding LB multilayers under ambient conditions.

Experimental Section

Langmuir-Blodgett Film Preparation. A Langmuir-Blodgett trough KSV-5000, operating in a sealed cabinet, was employed for preparation of the long-chain ester multilayers. Freshly spread methyl arachidate monolayers were compressed at a constant surface pressure, π , of 20 or 30 mN/m. The use of freshly compressed films was essential because of the stability limitations of the floating monolayers.¹⁵ Subphase temperature, providing

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stability of the spread films, was 17 °C, and deposition speeds up to 0.14 cm/s were used.

LB deposition was performed on different solid supports. Polystyrene and polypropylene films were commercial products. Silicon, glass, and mica plates were hydrophobized by LB deposition²⁷ of an octadecylamine monolayer. Vacuum-evaporated gold substrates were prepared by deposition of a 40 nm thick gold film on chromium-covered (15 nm thick film) glass plates. Transfer ratios were determined by averaging the results for three LB-film samples.

Methyl arachidate (Sigma, standard for gas chromatography) was dissolved to a concentration of 1×10^{-3} M in chloroform (Aldrich) for monolayer spreading. The aqueous subphase was prepared by dissolving NaCl (Merck, AnalaR grade) in MilliQ filtered water (Millipore Co.). The salt concentration was 1×10^{-3} M.

Contact Angle Determination. Surface hydrophobicity of methyl arachidate multilayers was probed under ambient laboratory humidity (normal for practical use).²⁸ Static maximum advancing, θ_A , and minimum receding, θ_R , contact angles were determined after the LB deposition, according to the procedure recommended by Ulman.³³ The experimental setup used has been described in detail previously.^{34,35} Contact angles were measured by a goniometer-microscope (Carl Zeiss, Jena). Most of the determinations were performed by means of the sessile drop technique at an ambient temperature of 25 °C. The captive bubble technique was also employed. However, the results obtained in this case were influenced by the instability of the ester films soaked in an aqueous environment. Contact angles were measured on both sides of at least three drops or bubbles. The values reported were mean quantities of about 16 readings. The experimental error was $\pm 1.5^\circ$. Pure water (MilliQ) was used as the probe liquid. Its surface tension (72.5 mN/m) has been repeatedly checked by means of a K12 tensiometer (Krüss).

Atomic Force Microscopy. Surface morphology of methyl arachidate LB multilayers was probed by means of a Park Scientific Instruments atomic force microscope (SA1/BD2). AFM measurements were performed with soft cantilevers with a force constant of 0.032 N/m. Commercially available pyramidal Pt/Ir tips were used. The lever deflection was monitored through an optical system allowing control of the repulsive force between the tip and the investigated surface in a contact mode. Typical forces applied were about 10 nN. Imaging was done with $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ (x,y) and $125 \mu\text{m} \times 125 \mu\text{m}$ (x,y) scanners. Molecular resolution images were obtained in a constant-height mode. A constant-force mode was used to record topographic images of larger surface regions. Calibration of the instrument was performed with freshly cleaved smooth mica sheets as well as with optical gratings.

Optical Microscopy. Optical microphotographs of the LB films were taken by means of an Olympus BH-2 microscope in a reflection mode. The microscope was equipped with an optical cable and a Panasonic color CCTV camera, Model WVCL310-G (Matsushita Communication Industrial, Ltd.). The maximum magnification of the system was about 3400 times.

All AFM and optical images were obtained in air (at room temperature and ambient relative humidity).

Results

Dependence of LB Deposition Type on the Transfer Pressure and the Number of Dipping Strokes. Methyl arachidate multilayers were deposited at a constant surface pressure, π , of 20 and 30 mN/m on different hydrophobic substrates. Figure 1 shows the dependence of the transfer ratios of dipping and withdrawal, α , on the number of the dipping strokes, N , for a polystyrene substrate. At both surface pressures, the transfer ratios of dipping are close to unity and almost constant with the increase of N . Transfer ratios of withdrawal are dependent both on π and N .

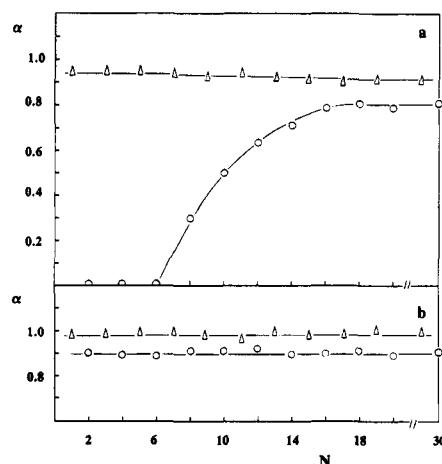


Figure 1. Dependence of the transfer ratios of methyl arachidate monolayers, α , of dipping (Δ) and withdrawal (\circ) on the number of the dipping strokes, N . Deposition pressure: (a) $\pi = 20$ mN/m; (b) $\pi = 30$ mN/m. Deposition velocity: 0.14 cm/s. Subphase temperature: 17 °C. Substrate: polystyrene.

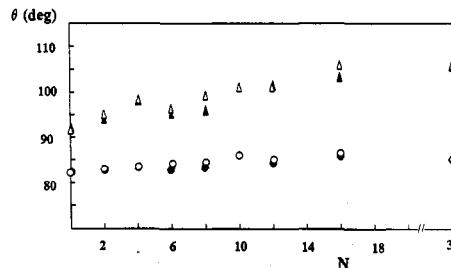


Figure 2. Dependence of the static advancing (Δ) and receding (\circ) contact angles of water drops on methyl arachidate multilayer surfaces, θ , on the number of the dipping strokes, N . Substrate: polystyrene. (a) open symbols, transition from X- to Y-type deposition ($\pi = 20$ mN/m); (b) full symbols, Y-type deposition ($\pi = 30$ mN/m).

A gradual transition from X- to Y-type deposition is found at $\pi = 20$ mN/m upon an increase in the number of dipping strokes (Figure 1a). Pure Y-type deposition occurs at $\pi = 30$ mN/m (Figure 1b).

Hydrophobicity of Methyl Arachidate LB Multilayers. Figure 2 shows static advancing and receding contact angles of water drops, θ , on methyl arachidate LB-film surfaces versus the number of dipping strokes, N . Two sets of data, corresponding to $\pi = 20$ mN/m and $\pi = 30$ mN/m, are presented. Multilayers are deposited on a polystyrene support. Contact angle values measured for the bare polystyrene substrate ($N = 0$) are in good agreement with the literature values.³⁶ Comparison of the wettability of the multilayer surfaces obtained by different LB-deposition types (Figure 1) shows almost identical results for a given N (Figure 2). The asymmetrical X-type (at $N \leq 6$), as well as the mixed XY-type transfer (at $N > 6$), does not produce more hydrophilic LB films than the symmetrical Y-type deposition. In both cases multilayers expose highly hydrophobic outer surfaces to the probe liquid. In general, the advancing static contact angles increase with the number of the deposited methyl arachidate monolayers. Saturation of the surface hydrophobicity is observed after about 16 deposition strokes. The increase of the receding contact angles with N was only slight.

A difference in the wettability of the multilayers transferred on different substrates was observed only for the initial deposition strokes. Table 1 compares static advancing, θ_A , and receding, θ_R , contact angles on methyl arachidate films at two constant values of N . Since the hydrophobicity of the films was independent of the investigated deposition pressure, only the data corresponding to $\pi = 20$ mN/m are presented. For all substrates studied, LB deposition at small N resulted in lower contact angle values as

TABLE 1: Static Advancing, θ_A (deg), and Receding, θ_R (deg), Contact Angles of Water Drops on Methyl Arachidate LB Films deposited at $\pi = 20 \text{ mN/m}$ on Different Hydrophobic Substrates^a

substrate	$N = 0$				$N = 2$				$N = 20$			
	θ_A	θ_R	$\Delta\theta$	R	θ_A	θ_R	$\Delta\theta$	R	θ_A	θ_R	$\Delta\theta$	R
mica, hydrophobic	93	62	31	0.1 ^b	86	59	27	0.3	104	70	34	
glass, hydrophobic	90	30	60	1.2 ^b	92	50	42		104	68	36	2.9
gold, hydrophobic	88	60	28	2.3 ^b	91	74	17	1.8				
polystyrene	91	82	9	9.3	95	83	12	9.3	106	87	19	18.5
polypropylene	103	86	17	18.6	97	72	25		105	90	15	

^a Contact angle hysteresis, $\Delta\theta = \theta_A - \theta_R$ (deg). N = number of dipping strokes of methyl arachidate monolayers. Root mean square (rms) surface roughness, R (nm), is determined by means of AFM over a $20 \times 20 \mu\text{m}^2$ scan area. ^b Rms roughness of pure nonhydrophobized substrate.

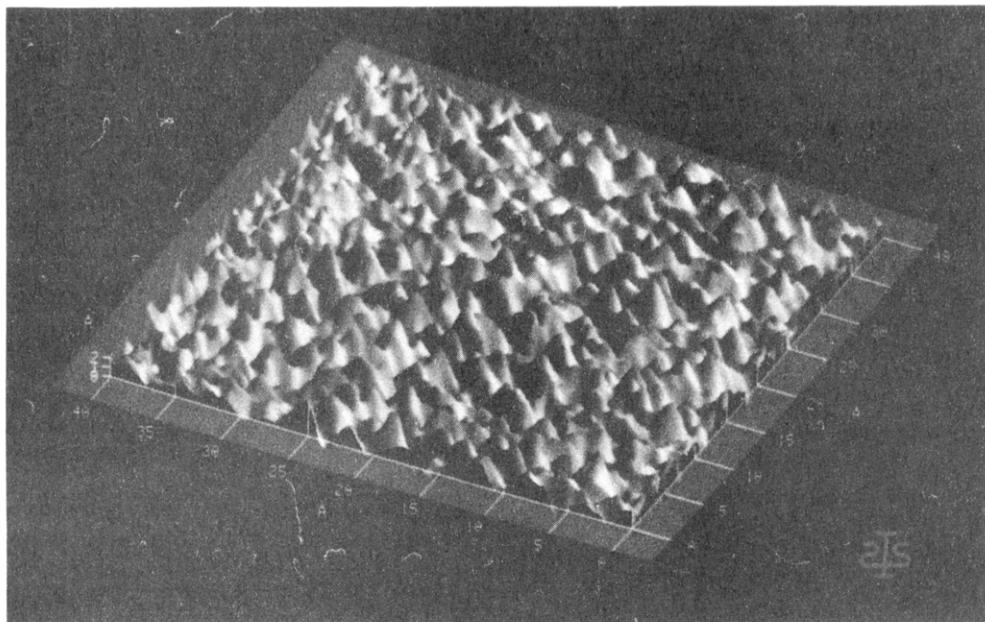


Figure 3. Molecular resolution AFM image of a methyl arachidate bilayer deposited at $\pi = 30 \text{ mN/m}$ on a hydrophobized gold substrate. Image size: $40 \text{ \AA} \times 40 \text{ \AA}$.

compared to those at large N . The values of θ_A at $N = 2$, as well as the contact angle hysteresis, $\Delta\theta$, were dependent on the hydrophobicity of the solid support (at $N = 0$). The films deposited on inorganic substrates showed lower advancing contact angles and larger hysteresis in comparison to those on polymers. The maximum θ_A values ($104\text{--}106^\circ$), found at $N = 20$, were not influenced by the characteristics of the solid supports. Surface roughness, determined by AFM, increases in the order from mica to polypropylene (Table 1). However, the observed wetting hysteresis does not correlate with the established roughness variation. Moreover, it is larger for the substrates of lower average roughness.

AFM Images of Methyl Arachidate LB-Film Surfaces. Figure 3 shows a molecular resolution image of a methyl arachidate bilayer deposited on a gold substrate. It is seen that the surface structure of the ester LB film is densely packed, but the packing of the molecules is not regular in a long range. A crystalline lattice structure is not observed on the molecular scale.

Figure 4 presents typical micrometer-scale AFM images of the surface morphology of methyl arachidate multilayers prepared by XY-, Y-, and X-type LB depositions. Figure 4a shows that the mixed XY-type deposition (performed at $\pi = 20 \text{ mN/m}$) results in a relatively flat methyl ester LB film. On inspection of the large scan area, the surface of the multilayer contains a number of holes (dark areas) ranging in diameter from 0.1 to about $2 \mu\text{m}$. The depth of the holes is divisible by the bilayer spacing of the film,³⁷ and it varies between the thicknesses of two and ten monolayers.

The multilayer deposited by means of pure Y-type deposition ($\pi = 30 \text{ mN/m}$) exhibits more irregular surface structure than that obtained by mixed XY-type transfer. Figure 4b shows a flat

methyl arachidate film interrupted by sharp and wide gaps or protrusions. Bare substrate areas are exposed at the bottom of the gaps formed due to a lateral contraction of the LB film. As a result, smooth film regions (RMS roughness of 0.5 nm on $1 \times 1 \mu\text{m}^2$ scan area) with smaller holes (about $0.1\text{--}0.5 \mu\text{m}$ in diameter) and large protruding islands and irregular gaps are simultaneously present on the imaged surface.

Figure 4c shows the surface morphology of a methyl arachidate LB film prepared under conditions of X-type deposition ($\pi = 20 \text{ mN/m}$, $N = 6$) on a polystyrene substrate. Island formation and lateral contraction are typical for the multilayers on this substrate as well. The height of the islands (about 60 nm) exceeds considerably the thickness of three methyl arachidate monolayers.

Optical Photomicrographs of the Ester Film Morphology. Topographical information about larger regions of the investigated ester multilayers was obtained by means of optical microscopy (Figure 5). The morphological features for the X- and Y-type LB depositions, observed in the AFM study, are distributed over the entire substrate area. Obviously, they do not appear as occasional defects. Reorganization and lateral contraction occur with the films on all substrates studied.

Figure 5a illustrates the aggregated island texture of methyl arachidate film prepared by X-type LB transfer. The islands tend to form elongated aggregates randomly distributed on the surface. The evaluated average island dimension ($1\text{--}2 \mu\text{m}$) agrees with the AFM data.

Inhomogeneities in the surface structure are found in the case of the Y-type transfer as well, showing a stronger tendency of the film molecules toward 3D-aggregation (Figure 5b). The aggregates are of irregular shape, and they are larger than those in Figure 5a. The gaps visible on the film surface vary in dimension

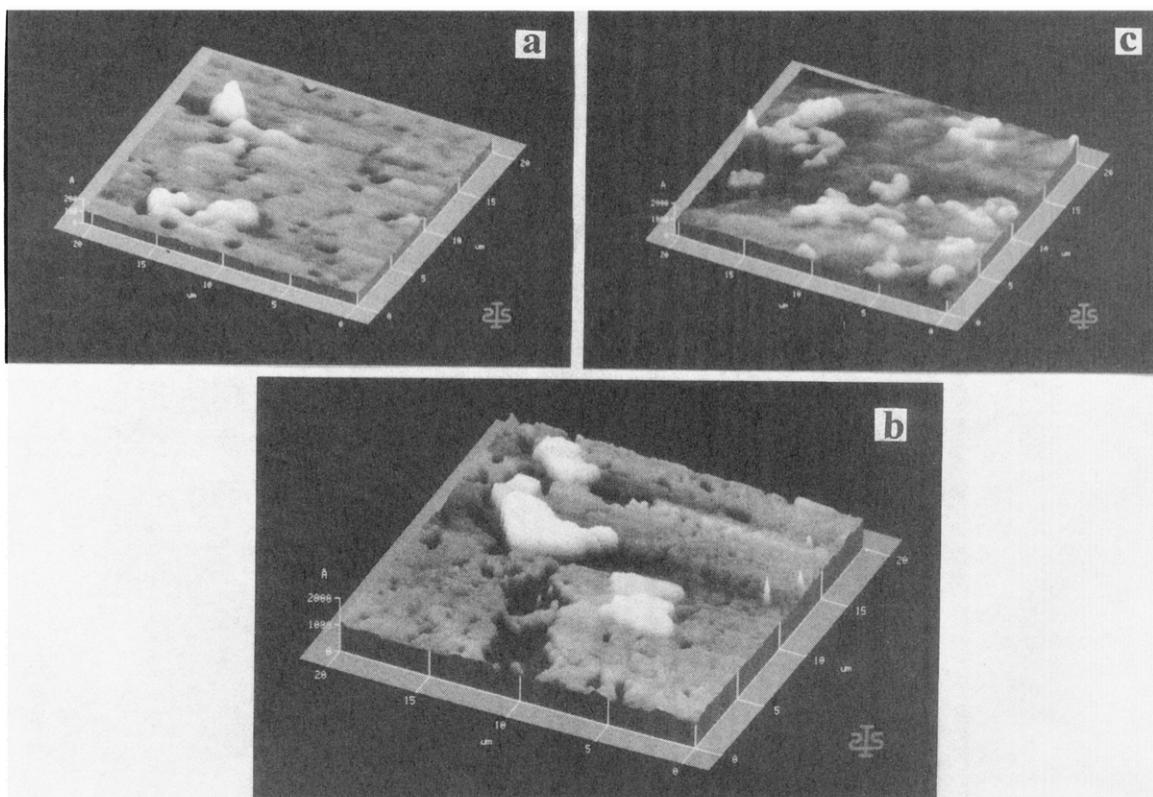


Figure 4. AFM images of the surface morphology of methyl arachidate multilayers transferred on hydrophobized smooth glass substrates by means of XY-type deposition ($\pi = 20 \text{ mN/m}$, $N = 20$) (a) and Y-type deposition ($\pi = 30 \text{ mN/m}$, $N = 20$) (b), and on a polystyrene substrate by means of X-type deposition ($\pi = 20 \text{ mN/m}$, $N = 6$) (c). Scan area: $20 \mu\text{m} \times 20 \mu\text{m}$.

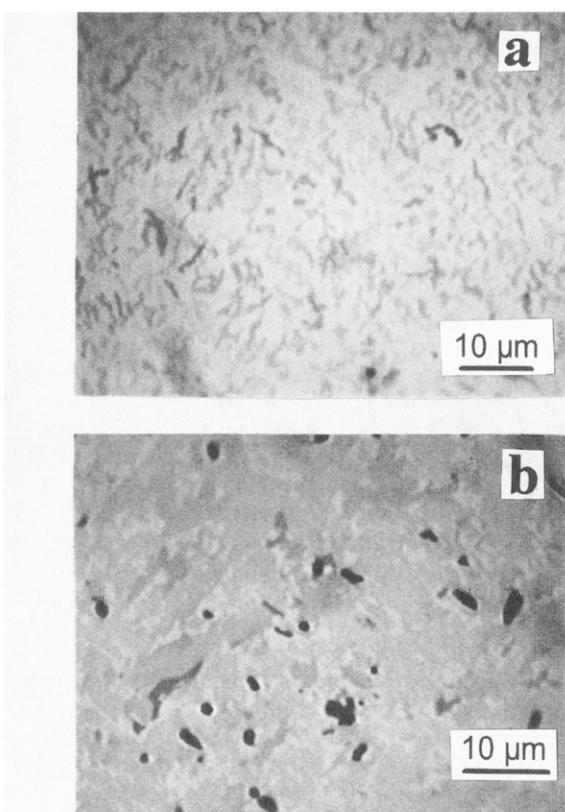


Figure 5. Typical reflection optical photomicrographs of methyl arachidate LB films deposited on hydrophobized polished silicon wafers. The dark areas correspond to aggregated material. The number of dipping strokes equals 6. (a) X-type transfer ($\pi = 20 \text{ mN/m}$). (b) Y-type transfer ($\pi = 30 \text{ mN/m}$). Gaps are seen as light areas.

between 1 and 5 μm . Gaps of this kind were observed only in the multilayers transferred at $\pi = 30 \text{ mN/m}$.

“Contact Line Corrosion” of the Fatty Acid Ester LB Films. After most of the contact angle hysteresis determinations on methyl arachidate LB-film surfaces, the three-phase contact line perimeter was seen on the samples. This so called “contact line corrosion” effect^{38,39} was observed more easily with the captive air bubble technique than with the sessile water drop technique. However, the ester multilayers were not depleted from the solid substrates during steady advancement (or retraction) of the probe liquid on their surfaces. This indicates that the observed “perimeter” effect is not due to dissolution of the films. It seems to be related to forced surface deformation in the three-phase contact zone when the contact angles under measurement approach their maximum (or minimum) static values at a fixed position of the wetting perimeter.

“Contact line corrosion” of the methyl arachidate multilayers owing to the wetting hysteresis measurements was directly visualized by means of the atomic force microscopy. Figure 6a,b presents AFM images of two portions of the circular “groove” made by a water drop three-phase contact line perimeter on an LB film with $N = 30$. The width of the gap evaluated from the image (a) is about 60 μm . The height of the step seen on the image (b) is about 80 nm. It corresponds to a cooperative depletion of the whole methyl arachidate multilayer from the substrate at the three-phase boundary.

“Contact line corrosion” produced by a captive air bubble three-phase contact line on a methyl arachidate LB film is illustrated in Figure 6c. As a result of the environmental influence (100% humidity and ambient temperature higher than the temperature for LB deposition), the thin bilayer film has transformed into 3D-islands. Aggregated ester material and bare substrate areas are seen on both sides of the three-phase contact line “groove”.

Discussion

Molecular Overturning during the Asymmetrical-Type LB Deposition. It is well-known that contact angles are average macroscopic characteristics of the surface wettability. However,

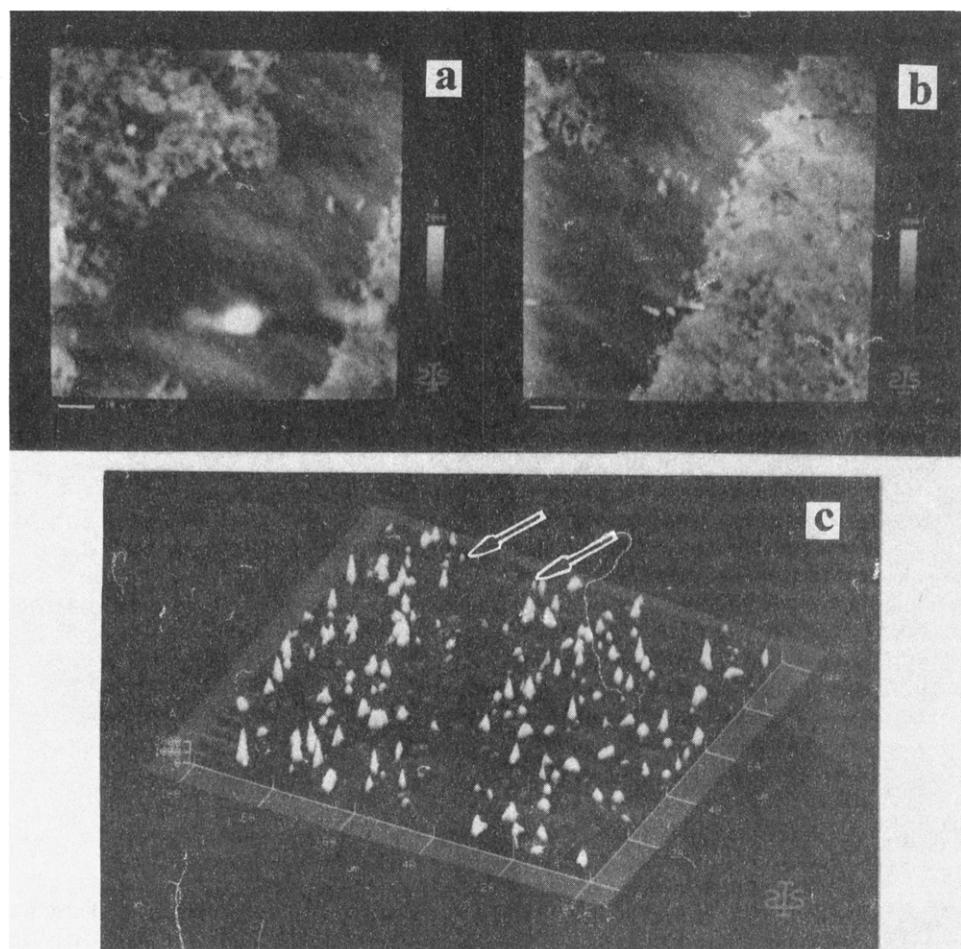


Figure 6. AFM topographic images of two sections (a and b) of the circular "groove" made by the sessile water drop wetting perimeter during a contact angle hysteresis determination on a 30-monolayer-thick methyl arachidate LB film ($\pi = 30 \text{ mN/m}$. Substrate: polystyrene). (c) Methyl arachidate bilayer kept in an aqueous environment (25°C) for a contact angle determination by means of the captive bubble technique. A part of the wetting perimeter "groove" is seen in the center of the image. It is surrounded on both sides by light areas of aggregated island film structure (substrate: gold). Image size: $100 \mu\text{m} \times 100 \mu\text{m}$.

it has been repeatedly proven^{17–20,29–33,40–44} that wetting is very sensitive to the variations of the microscopic structure, packing, surface order/disorder, and reorganization of the monolayer surfaces. Wettability investigations of self-assembled monolayers^{19,20,31} have established advancing static contact angles of 110° for surfaces exposing closely packed methyl groups, about $100\text{--}104^\circ$ for methylene groups, and $67\text{--}69^\circ$ for monolayers exposing methyl ester terminal groups.

Initially, it could be presumed that the surfaces of methyl arachidate LB films produced by X-type deposition will be composed of methyl ester groups, and those obtained by Y-type transfer will be terminated by hydrophobic methyl groups. Therefore, advancing angles of about 67 and 110° are expected for the two cases, respectively. On intermediate withdrawal transfer (XY-deposition), more disordered film surfaces, exhibiting simultaneously methyl and methylene groups, should be created. Hence, values of θ_A between 100 and 110° are anticipated.

The fact that the X-type LB deposition does not result in considerably more hydrophilic surfaces than the Y-type transfer (Figure 2) implies that the multilayer configuration with methyl ester head groups facing toward the air is energetically unstable. The same hydrophobicity (at a given N) of X-, XCY-, and Y-type deposited LB films is an indication for overturning of the ester amphiphiles to a bilayer structure during their asymmetrical transfer.

Cemel et al.¹¹ have also found identical hydrophobicity of vinyl stearate multilayers produced by X- and Y-type depositions. From this, overturning of the ester molecules during X-type transfer

has been inferred. In addition, these authors have reported a variation of the static advancing water contact angles with the number of the deposited monolayers—from 79° (at $N = 2$) to 101° (at $N = 32$). However, the reasons for this behavior have not been discussed in their publication.

Surface Morphology of Fatty Acid Ester Multilayers as a Result of the Reorganization and Instability of their Monolayer Structure. Comparison with the Fatty Acid Salt LB Films. The observed transition from X- to Y-type deposition of long-chain ester monolayers upon an increase of the number of dipping strokes differs essentially from the case of fatty acid soap films. The transfer of the latter develops X-type character when the deposition proceeds at lower transfer pressures, low subphase concentrations, or high pH values of the subsolutions. Several models have been proposed for an explanation of such a deposition mechanism.^{2–8} It has been shown experimentally⁴ and simulated theoretically²¹ that the XY-type deposition results in more defects and inhomogeneous structure than the Y-type transfer.

Methyl arachidate multilayers prepared by different LB-deposition types also show a difference in their surface morphologies (Figure 4). Surprisingly, symmetrically deposited ester films (Y-type) are less homogeneous and regular than the asymmetrical ones (XY-type). Both the AFM images and optical micrographs indicate that the Y-type transfer results in a higher degree of surface rearrangement and aggregate formation. The holes found in the XY-type transferred ester films are on average larger than those imaged by AFM in fatty acid soap multilayers.^{25,26,45,46}

The difference in the surface morphology of the ester multilayers deposited at $\pi = 20$ and $\pi = 30 \text{ mN/m}$ can be explained

by the different kinetics of the relaxation processes occurring in the corresponding spread monolayers. It has been established¹⁵ that floating methyl arachidate films show temperature- and surface pressure-dependent stability at the air/water interface.⁴⁷ The reported area relaxation at constant surface pressure can be considered as a nucleation-growth process in supersaturated monolayers⁴⁸ on the basis of the nucleation-growth-collision theory.⁴⁹⁻⁵¹

All methyl arachidate LB multilayers were transferred from subphases of reduced temperature providing no area relaxation of the monolayers at constant surface pressure. However, recent Brewster angle microscopy and Normarski microscopy studies of mono- and multilayers of fatty acids^{52,53} and their esters^{54,55} have confirmed that the small centers inducing the 3D-aggregate growth in the deposited films are present already in the spread monolayers. Once initiated at the air/water interface, the nucleation and growth process is accelerated by film transfer onto a solid support.⁵⁶ Thus, the entire film area is reconstructed at room temperature (Figures 4 and 5).

The morphological results obtained for the different types of LB transfer illustrate that the higher surface pressures and the higher deposition speeds induce larger 3D-clusters in the films. This is in agreement with the previous reports.^{52,53} There is also evidence (Figure 6c) that the ester film morphology is strongly influenced by the storage at elevated temperatures and in aqueous environments.

Rearrangement of monolayers and LB films under ambient conditions has been detected to occur in a number of cases.^{23-26,45,46,57,58} Surface reorganization has been possible even with close-packed monolayers chemically bonded to the substrate.³¹ It has been found that the modification of the surface morphology of fatty acid LB films is very quick in contact with solutions²³ but rather slow on aging of the films in air.⁴⁶ Due to the instability of their monolayer organization,¹⁵ ester films undergo faster spontaneous transformations as compared to the case for fatty acid soap films.

Forced Deformation of the LB Films. "Contact Line Corrosion". The instability of the methyl arachidate LB films is manifested not only in their spontaneous reorganization under ambient conditions but also in their forced modification during contact angle hysteresis measurements. The ester films studied proved to be soft, mechanically unstable, and weakly adhering to the solid supports used. They were completely removed from the substrates by the interfacial forces in the three-phase contact zone (Figure 6).

In his report³⁸ on the "contact line corrosion" effect, Bikermann has evaluated a depth of the circular "groove" of about three molecules and a width of about 10–20 μm for a barium stearate multilayer deposited on a chromium substrate. The depth of the "groove" imaged on Figure 6b corresponds to the total methyl arachidate multilayer thickness. This demonstrates that while fatty acid soap LB films are only partially depleted from the metal surface, the entire ester multilayers are displaced at the three-phase contact perimeter during the wettability investigation. Obviously, this difference results from the different mechanical stability of both kinds of multilayers, as well as from their different adhesion to the substrate surface. The collective desorption of the ester molecules at the three-phase line reflects the weak bonding of the ester multilayers to the solid support.

The instability of the LB films, weakly bonded to the substrate, due to structural rearrangement in an aqueous environment and irreversible degradation in the vicinity of the wetting line appears to be a general problem for the wetting investigations.^{29,59} It can result in unexpected large contact angle hysteresis, and in a misleading interpretation of the wetting results in the absence of morphological characterization of the investigated LB films.

Effect of the Surface Morphology and Instability of the Ester LB Films on Their Hydrophobicity and Wetting Hysteresis. Due

to the irreversible surface modification of the ester films on "contact line corrosion", only the water contact angles, determined initially on virgin portions of the investigated samples, can be compared. The maximum advancing static contact angle measurements were rather reproducible. The results obtained indicate that the increase of θ_A with the number of dipping strokes, N , is not due to a transition from X- to Y-type deposition (Figure 2, open symbols). An increase of the surface hydrophobicity occurs with the Y-type transfer as well (Figure 2, full symbols).

A possible explanation of this contact angle behavior is based on a consideration of the homogeneity and the degree of the hydrophobic surface coverage produced by the LB deposition. It follows from the present study that methyl arachidate LB films do not cover completely the real substrate surface area even at transfer ratios of unity. Areas of bare polystyrene surface (of lower $\theta_A \sim 91^\circ$) remain exposed to the probe liquid. A heterogeneous composite surface of more hydrophobic LB film and less hydrophobic substrate is formed as a result of the rearrangement of the multilayer structure (evidenced by AFM). The rise of θ_A with N might be related to a gradual screening of the substrate contribution to the wettability, owing to the improvement of the hydrophobic surface coverage with the number of transferred monolayers. However, this coverage cannot be characterized simply by the average transfer ratios measured (Figure 1) because of the spontaneous structural transformations of the ester films during and after the LB deposition.

Contact angle hysteresis on the investigated methyl arachidate LB-film surfaces is larger than expected for smooth and densely packed surfaces.⁴¹⁻⁴⁴ In the absence of "contact line corrosion", it could be explained^{43,44} by the disorder of the ester film surfaces (Figure 3) or by their heterogeneity (Figure 4). In fact, surface roughness (Table 1) is not of a macroscopic dimension, and it seems not to be the main reason for the established wetting hysteresis.

The slightly lower values of the observed maximum advancing contact angles ($104\text{--}107^\circ$) in comparison with those for methyl groups exposing surfaces (110°) might also reflect the disorder of the film's surface structure and its reorganization. The interpretation of the minimum receding static contact angles is not straightforward. These angles have usually been measured after the advancing angles. During these measurements (i) the contact of the film with water might induce significant surface change²³ and (ii) an uncontrolled amount of the film material could be depleted at the wetting perimeter as a result of "contact line corrosion".

LB-Film Stability as a Result of Inter- and Intralayer Molecular Interactions. Implication for Practical Application. It is well-known that the stability of the multilayered structures depends on the interlayer and intralayer bonds formed. More stable are structures involving ionic, coordination, and hydrogen bonds^{60,61} rather than pure van der Waals interactions. The symmetrical transfer of methyl arachidate monolayers is due to the hydrophobic interaction between their hydrocarbon chains on dipping and the methyl ester groups on withdrawal.^{62,63} The resulting inter- and intralayer interactions in the multilayers deposited on a solid support are predominantly of van der Waals type. Therefore, the established instability of the methyl arachidate thin film structure (revealed as a lateral contraction and easy displacement from the substrate) is related to these weak bonds between the adjacent monolayers within the multilayers and with the substrate. However, the cooperativity in the movement of the film molecules during the observed processes of "dewetting" implies that the interactions within the ester multilayers are stronger than those with the substrate.

Although by choosing ester films as neutral matrices one can avoid some electrostatic effects, the easy reorganization of their mono- and multilayer structures makes them unsuitable for certain applications under ambient conditions. The noncentrosymmetric

"tail-to-head" arrangement in these LB films appears energetically unfavorable. The perfection of the multilayers with "head-to-head" structure depends dramatically on the quality and integrity of the corresponding spread monolayers and the LB-deposition conditions.

The above results indicate also the essential need of stability studies of LB films in contact with water or solutions. Such studies will prove which LB films are appropriate for building up molecular devices functioning in humid or aqueous environments.

Conclusion

Wettability investigation of fatty acid methyl ester multilayers prepared by X- and XY-type LB depositions, for which X-ray diffraction patterns¹⁵ have yielded a single-layer repeated spacing (tail-to-head arrangement), shows molecular overturning to a bilayer (head-to-head) structure. This overturning is in agreement with the findings of Fukuda and Shiozawa.¹³ It results in highly hydrophobic outermost surfaces, indistinguishable in wettability from those produced by symmetrical Y-type deposition.

AFM comparison of the surface morphology of multilayers prepared by XY- and Y-type transfer shows, opposite of the expectation, less uniform surface structure in the second case. This can be attributed to different, surface pressure-dependent, relaxation kinetics in the corresponding spread monolayers.

Contact angle measurements on the deposited methyl arachidate LB multilayers show some peculiarities: (i) unexpected large static contact angle hysteresis; (ii) static advancing contact angles that are lower as compared to those for methyl groups exposing highly ordered and close-packed organic surfaces; (iii) an increase of the static advancing contact angles with the number of deposited monolayers and saturation of the surface hydrophobicity after about 16 dipping strokes; (iv) "perimeter" or "contact line corrosion" effect. All these effects are related to the irreversible restructuring and instability of the ester LB films under ambient conditions. A stronger environmental effect on the surface reorganization is found for samples kept in contact with water of elevated temperature.

Instability of the ester LB films in the absence of ionic and hydrogen bonds in their structure is manifested both in (i) spontaneous rearrangement of the films into islands and 3D-aggregates under ambient conditions and (ii) deformation and forced displacement of these soft films at the three-phase contact line perimeter during contact angle hysteresis determination. The depth of the "groove" produced by the wetting perimeter corresponds to a collective depletion of the whole LB multilayer from the substrate surface.

All results obtained indicate the necessity of systematic investigations of the environmental influence (humidity, temperature, contact with liquids, mechanical loading) on the stability of the deposited surfactant mono- and multilayers. Both the stability and the quality of the built-up LB films depend on the intra- and interlayer molecular interactions in the spread and deposited monolayers, and on their interaction with the underlying substrate (liquid or solid).

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References and Notes

- (1) Bikerman, J. J. *Proc. R. Soc. London* 1939, A170, 130.
- (2) Langmuir, I. *Science* 1938, 87, 493.
- (3) Peng, J. B.; Ketterson, J. B.; Dutta, P. *Langmuir* 1988, 4, 1198.
- (4) Peng, J. B. *Langmuir* 1990, 6, 1725.
- (5) Peng, J. B.; He, S.; Dutta, P.; Ketterson, J. B. *Thin Solid Films* 1991, 202, 351.
- (6) Honig, E. P. *J. Colloid Interface Sci.* 1973, 43, 66.
- (7) Honig, E. P. *Langmuir* 1989, 5, 882.
- (8) Binks, B. P. *Adv. Colloid Interface Sci.* 1991, 31, 343.
- (9) Roberts, G. G., Ed. *Langmuir-Blodgett Films*; Plenum Press: New York, 1990; Chapter 7.
- (10) Stenhagen, E. *Trans. Faraday Soc.* 1938, 34, 1328.
- (11) Cemel, A.; Fort, T., Jr.; Lando, J. B. *J. Polym. Sci., Part A*, 1972, 10, 2061.
- (12) Enkelman, V.; Lando, J. B. *J. Polym. Sci.* 1977, 15, 1843.
- (13) Fukuda, K.; Shiozawa, T. *Thin Solid Films* 1980, 68, 55.
- (14) Shiozawa, T.; Fukuda, K. *Thin Solid Films* 1989, 178, 421.
- (15) Angelova, A.; Ionov, R.; Reiche, J.; Brehmer, L. *Thin Solid Films* (LB Conf. Proc.) 1994, 242, 283.
- (16) Kato, T. *Jpn. J. Appl. Phys.* 1988, 27, L1358.
- (17) Schafrazi, E. G.; Zisman, W. A. *J. Phys. Chem.* 1960, 64, 519.
- (18) Whitesides, G. M.; Laibinis, P. E. *Langmuir* 1990, 6, 87.
- (19) Bain, C. D.; Troughton, E. B.; Tau, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1989, 111, 321.
- (20) Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* 1989, 5, 101.
- (21) Momose, A.; Hirai, Y. *Thin Solid Films* 1991, 204, 175.
- (22) Chen, Y. L. E.; Gee, M. L.; Helm, C. A.; Israelachvili, J. N.; McGuigan, P. M. *J. Phys. Chem.* 1989, 93, 7057.
- (23) Schwartz, D. K.; Viswanathan, R.; Zasadzinski, J. A. N. *J. Phys. Chem.* 1992, 96, 10444.
- (24) Schwartz, D. K.; Garnaes, J.; Viswanathan, R.; Zasadzinski, J. A. *N. Science* 1992, 257, 508.
- (25) Viswanathan, R.; Schwartz, D. K.; Garnaes, J.; Zasadzinski, J. A. *N. Langmuir* 1992, 8, 1603.
- (26) Schaper, A.; Wolthaus, L.; Möbius, D.; Jovin, T. M. *Langmuir* 1993, 9, 2178.
- (27) Scales, P. J.; Grieser, F.; Healy, T. W. *Thin Solid Films* 1992, 215, 223.
- (28) Drying of LB- and self-assembly monolayers in a nitrogen flow usually enhances their hydrophobicity and may reduce the contact angle hysteresis. 22,29-32.
- (29) Chen, Y. L.; Helm, C. A.; Israelachvili, J. N. *J. Phys. Chem.* 1991, 95, 10736.
- (30) Chen, Y. L.; Chen, S.; Israelachvili, J. N. *J. Colloid Interface Sci.* 1992, 153, 244.
- (31) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; *Adv. Colloid Interface Sci.* 1992, 39, 175.
- (32) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* 1991, 113, 1499.
- (33) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press, Inc.: London, 1991; p 50.
- (34) Kamusewitz, H.; Possart, W. *Int. J. Adhes. Adhes.* 1985, 5, 211.
- (35) Schulze, R.-D.; Possart, W.; Kamusewitz, H.; Bischof, C. *J. Adhes. Sci. Technol.* 1989, 3, 39.
- (36) Ellison, A. H.; Zisman, W. A. *J. Phys. Chem.* 1954, 58, 503. Good, R. J.; Kotsidas, E. D. *J. Colloid Interface Sci.* 1978, 66, 360.
- (37) A methyl arachidate monolayer thickness of 2.6 nm has been determined¹⁵ by means of small angle X-ray diffraction of the LB multilayers.
- (38) Bikerman, J. J. *Trans. Faraday Soc.* 1940, 36, 412.
- (39) McGuigan, P. M.; Pashley, R. M. *Colloids Surf.* 1987, 27, 277.
- (40) Ulman, A.; Evans, S. D.; Sharma, R. *Thin Solid Films* 1992, 210/211, 810.
- (41) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7155. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1989, 111, 7164.
- (42) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 5897.
- (43) Folkers, J. F.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* 1991, 8, 1330.
- (44) Evans, S. D.; Ulman, A. *Chem. Phys. Lett.* 1990, 170, 462.
- (45) Fuchs, H.; Chi, L. F.; Eng, L. M.; Graf, K. *Thin Solid Films* 1992, 210/211, 655.
- (46) Chi, L. F.; Eng, L. M.; Graf, K.; Fuchs, H. *Langmuir* 1992, 8, 2255.
- (47) Faster area relaxation of methyl arachidate monolayers occurs at a constant surface pressure of 30 mN/m.
- (48) Vollhardt, D. *Langmuir*, submitted for publication.
- (49) Vollhardt, D. *Adv. Colloid Interface Sci.* 1993, 47, 1.
- (50) Vollhardt, D.; Ziller, M.; Retter, U. *Langmuir* 1993, 9, 3208.
- (51) Vollhardt, D.; Retter, U. *J. Phys. Chem.* 1991, 95, 3723.
- (52) Morelis, R. M.; Girard-Egrot, A. P.; Coulet, P. R. *Langmuir* 1993, 9, 3101.
- (53) Girard-Egrot, A. P.; Morelis, R. M.; Coulet, P. R. *Langmuir* 1993, 9, 3107.
- (54) Gutberlet, T.; Vollhardt, D. *Colloids Surf.*, submitted for publication.
- (55) Angelova, A.; Ionov, R.; Vollhardt, D. To be published.
- (56) Gabrielli, G.; Guarini, G. G.; Ferroni, T. J. *Colloid Interface Sci.* 1976, 54, 424.
- (57) Chi, L. F.; Anders, M.; Fuchs, H.; Johnston, R. R.; Ringsdorf, H.; *Science* 1993, 259, 213.
- (58) Schwartz, D. K.; Garnaes, J.; Viswanathan, R.; Chirovolu, S.; Zasadzinski, J. A. N. *Phys. Rev. E* 1993, 47, 452.
- (59) Yaminsky, V. V.; Claesson, P. M.; Eriksson, J. C. *J. Colloid Interface Sci.* 1993, 161, 91.
- (60) Angelova, A.; Petrov, J. G.; Dudev, T.; Galabov, B. *Colloids Surf.* 1991, 60, 351.
- (61) Petrov, J. G.; Angelova, A. *Langmuir* 1992, 8, 3109.
- (62) Petrov, J. G.; Möbius, D.; Angelova, A. *Langmuir* 1992, 8, 201.
- (63) Petrov, J. G.; Angelova, A.; Möbius, D. *Langmuir* 1992, 8, 206.