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Langmuir−Blodgett Film Organization Resulting from Asymmetrical or Partial Types of Monolayer Transfer: Comparison for Amphiphiles of Different Geometrical Shapes

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The problem of whether the Langmuir-Blodgett (LB) technique is capable of producing ordered films of molecular arrangement different from a bulk phase one is addressed for amphiphiles of rod-like and disk-like geometrical shapes. Low-angle X-ray diffraction and morphological characterization are performed for LB films deposited by means of asymmetrical and partial types of monolayer transfer. The influence of thermodynamic parameters, steric molecular peculiarities, and intermolecular interactions on the efficiency and mechanism of the monolayer transfer is considered. Molecular overturning to a multibilayer ("bulk") arrangement is established for the case of Z-type (one-direction up-stroke) deposition of the rod-like amphiphile, and a crystalline body-centered orthorhombic ("bulk") structure for the case of partial ("mixed" XY type) LB transfer of the diskotic films. Symmetrical Y-type deposition is found to result in almost defect-free multilayers over large scales of film surface examination. For both kinds of amphiphiles studied, the asymmetrical and partial types of LB transfer are less effective, as compared to the Y-type, in inducing periodic thin film organizations, distinct from the bulk phase structures of the amphiphiles.

Introduction

By definition, the films obtained by successive transfer[1,2] of insoluble monolayers from a liquid onto a solid surface (Figure 1) upon application of an external force (constant deposition pressure and substrate dipping speed) have been referred to as Langmuir−Blodgett (LB) films.[3,4] Irreversible, multiple "dry"[5] monolayer transfer could be used for preparation of periodic multilayer structures on solid supports.[6] The degree of monolayer transfer is quantitatively characterized by the transfer ratio, α. At constant deposition surface pressure, it has been defined[7] as the ratio of the reduction of the monolayer area at the liquid surface to the geometrical area of the solid, over which the transfer has occurred. α can be either positive or negative, with values ranging from 0 to 1.[7−14] LB studies have shown[15−23] that higher transfer ratios can be achieved with close-packed, condensed-phase monolayers com-

pressed to surface pressures exceeding the main monolayer phase transition pressure. More appropriate for LB deposition are monolayers exhibiting a steep part in their surface pressure/area (π/A) isotherms. It allows high deposition surface pressures to be applied in order to achieve higher transfer ratios and in-plane closer molecular packings. However, the high-pressure phase states (e.g., LS, S, CS[24]) of the commonly studied (alkanoic acid) monolayers are usually metastable, since monolayers appear to be overcompressed.[25−27] Relaxation phenomena[25,28] are undesirable for the LB deposition process because of the possible accumulation of defects[17] in the films (e.g., 3D crystallites, holes, "collapse" structures) or reorganization of the multilayer structures into islands, causing in-plane inhomogeneities.[19]

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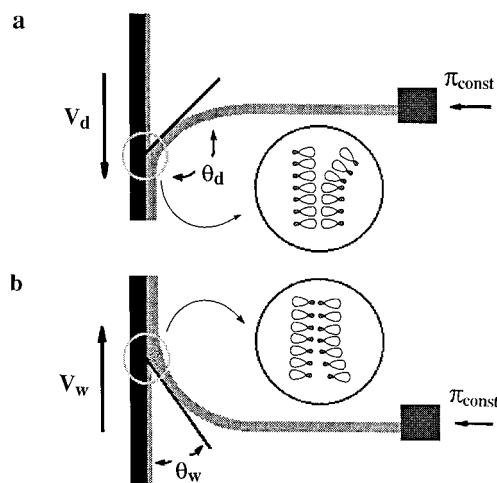(28) Kuri, T.; Oishi, Y.; Kajiyama, T. *Langmuir* **1991**, *11*, 366−368.

a

b

Figure 1. Schematic presentation of the Langmuir−Blodgett deposition process of transferring amphiphilic monolayers from a liquid onto a solid surface. Macroscopically, the deposition can be viewed as a (monolayer-covered) liquid meniscus moving along a (bare or monolayer-covered) solid substrate. The macroscopically observed contact angles θ_d and θ_w correspond to monolayer transfer on dipping (a) and on withdrawal (b) strokes. The apparent dynamic (during deposition) contact angles, θ_d and θ_w, can be influenced by the deposition velocity, $V_{d(w)}$, the deposition pressure, π_{const}, and the intermolecular interactions in the three-phase contact zone (denoted by a circle). Microscopically, the deposition requires irreversible molecular contact of the adjacent monolayers (insets) and maximum expulsion of the hydration water. Energetically stable configurations, corresponding to symmetrical "Y"-type LB transfer, are of a hydrophobic−hydrophobic (a, inset) and polar−polar type (b, inset).

In discussions of the advantages of the LB films, it has been usually presumed that they are transferred in a closed-packed state with $\alpha \sim 1$. $\alpha = 1$ implies that the two-dimensional (2D) density of the monolayer does not change upon its transfer onto a solid substrate.[29] For irreversible monolayer transfer, LB deposition experiments with various kinds of amphiphiles have established that the transfer ratios on dipping, α_d, may differ from those on withdrawal, α_w. Depending on the values of α_d and α_w, different types of monolayer transfer have been introduced into the terminology of the LB deposition:[30−32] (i) symmetrical "Y"-type of LB deposition, for which monolayer transfer occurs upon both dipping and withdrawal with $\alpha_d = \alpha_w = 1$; (ii) asymmetrical "X-" and "Z"-types of deposition, for which monolayers are transferred, respectively, only upon dipping ($\alpha_d = 1$, $\alpha_w = 0$) or only upon withdrawal ($\alpha_d = 0$, $\alpha_w = 1$). "Mixed" types of LB deposition, e.g., "ZY-" or "XY"-types, have also been possible,[15,19,20,23,33] with transfer ratios α_d and α_w taking intermediate values between 0 and 1, respectively. Thus, all types of monolayer transfer, for which α_d and/or α_w are less than unity, can be regarded as *partial LB deposition*. For fatty acid derivatives, diverse mechanisms of partial transfer have been proposed[8,32,34,35] leading, in most of the cases, to irregular film structures.[19,23,33]

Important questions to be answered toward understanding of the molecular organization of LB films built-

up by diverse types of monolayer transfer are as follows: (i) Is the LB technique capable of producing (e.g., through changing the deposition type) thin organic films of molecular arrangement different from that existing in the bulk phase of the investigated amphiphiles? (ii) Is it justifiable to regard the film structures obtained upon partial (asymmetrical or "mixed" type) monolayer transfer as "disordered"?[36] (iii) What is the reason for the lack of multilayer periodicity of some of the LB films despite of their preparation by successive deposition of distinct monolayers?

Classically, LB multilayer structures have been presented and designed[1−3] as sequences of individual, oriented monolayers of close-packed arrangement and high in-plane order. Possible interdigitation[4] of the layers, due to steric peculiarities of the selected amphiphiles, have not been initially[1,2] considered. Recent morphological studies[40−44] have demonstrated that it is difficult to achieve in-plane long-range molecular order over macroscopic film areas. Evidence for lateral rearrangement of the transferred mono- and multilayers has been obtained by means of atomic force microscopy.[19,26a] X-ray diffraction has been introduced[6,45−51] for characterization of the periodicity of the LB films in the *z*-direction to the solid substrate and the structure of the transferred layers. For LB films of rod like amphiphiles, e.g., fatty acid derivatives, X-ray diffraction has often shown the same X-ray peaks as those present in the bulk lipid phase.[46] Owing to the specificity of the electron density profiles of fatty acid alkylester LB films, overturning has been difficult for detection by means of standard X-ray diffraction[20,39] upon asymmetrical and "mixed" types of transfer.

While the LB deposition mechanism of rodlike (e.g., long-chain) molecules has received attention in several publications,[8,21,30−35] relatively little has been known about the deposition process of "exotic"-shaped amphiphiles. Recently, pyramidic, bowlic, starlike, disklike, spherical-shaped, and platelike amphiphilic molecules have been reported[52−66] as interesting for technical applications. With

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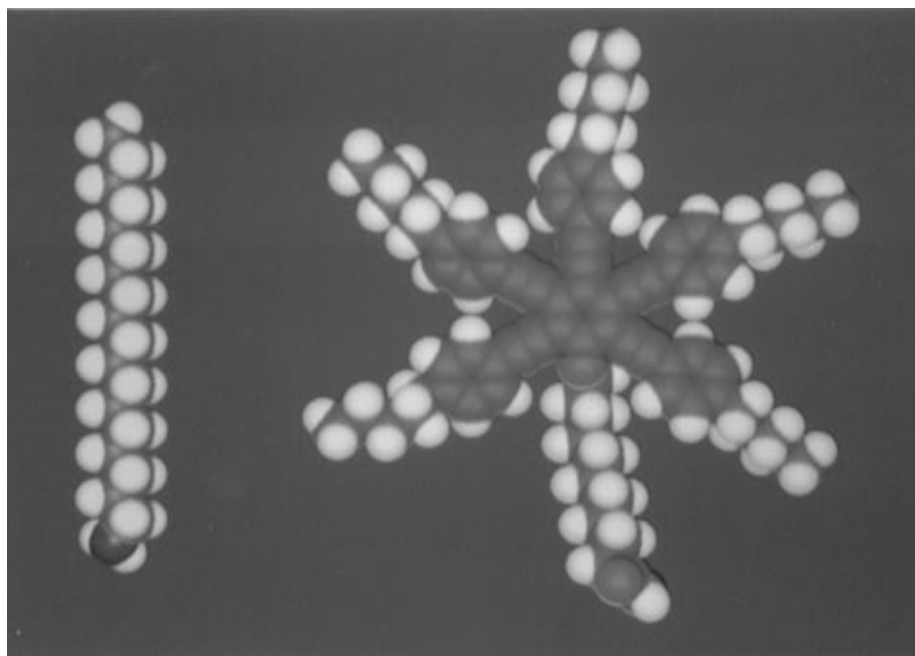
Figure 2. Space-filling molecular presentation of the investigated rodlike octadecylamine (left) and disklike 11-(pentakis((4-pentylphenyl)ethynyl)phenoxy) undecanoic acid (right). The nitrogen atom is presented in blue and the oxygen ones in red.

such amphiphiles, steric effects[67] and intermolecular (e.g. $\pi-\pi$ and dipole−dipole)[52,67] interactions play an essential role in determination of their structural arrangement in thin films. Generally, for a given amphiphile, the deposition pressure and velocity,[14−21,68−70] the subphase composition and temperature,[1,10,11,21] the substrate hydrophilicity,[15−17] and coarseness[71] could be varied in wide regions in order to establish optimum LB deposition conditions.

In the present study, a comparison is made of the structure and morphology of LB films prepared by partial (asymmetrical and "mixed" types) and complete ("Y"-type) monolayer transfer. Two amphiphiles of a rodlike and a disklike geometrical shape are investigated (Figure 2). Both the octadecylamine (ODA) and the 11-(pentakis((4-

Table 1. General Hypothetical Relationship between the Type of LB Deposition and the Magnitudes of the Apparent Dynamic Contact Angles Established upon Dipping and Withdrawal Strokes (See the Three-Phase Systems in Figure 1)

LB deposition	dynamic contact angles (deg)		transfer ratios	
	dipping θ_d	withdrawal θ_w	dipping α_d	withdrawal α_w
X-type	>90	>90	1	0
Y-type	>90	<90	1	1
Z-type	<90	<90	0	1

pentylphenyl)ethynyl)phenoxy)undecanoic acid (PUA) possess ionogenic head groups, which allow the LB deposition to be influenced through interactions of the monolayers with counterions from the aqueous subphase. Common and specific features of the LB transfer of monolayers of the rodlike and the disklike amphiphiles are considered.

General Principals of the Langmuir−Blodgett Deposition Process

The transfer ratio values, i.e., the type of monolayer transfer, could be influenced[7−23,68−72] through changes of the surface pressure, deposition velocity, substrate wettability and roughness, pH and temperature of the aqueous subphase, interactions with counterions. Although experimentally well established, the fundamental reasons for these effects have often been somewhat hidden behind the empirical facts. It has been suggested since by Langmuir[8] and Bikermann[31] that the mechanism of the LB deposition process is related to the magnitudes of the dynamic contact angles (Table 1), formed in the three-phase systems on dipping and withdrawal strokes (Figure 1). This hypothesis has been explored in the thermodynamic studies of Egusa et al.[15] and Aveyard et al.,[14] who have demonstrated that representative for the type of monolayer transfer is the dynamic force applied to the moving three-phase contact line in the LB system. Generally, this force is determined by the dynamic contact angle, $\theta_{d(w)}$, the interfacial tensions of the three-phase

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boundaries, the interactions in the three-phase contact zone, the interfacial viscosity, and the deposition velocity, $V_{d(w)}$. (The subscripts d and w denote the dipping and the withdrawal direction, respectively.)

As a dynamic process, the LB deposition occurs, at an appropriate constant surface pressure π_{const}, upon forced movement of a monolayer-covered fluid/vapor interface along a solid substrate (Figure 1). The successful monolayer transfer onto a solid support appears to be a thermodynamically irreversible process. Under steady-state conditions, the interfacial force acting on the three-phase contact line, F, can be expressed, for a perfect solid surface, as

$$F = \gamma_{SV} - \gamma_{SM} + \gamma_{MV} \cos \theta_{d(w)}$$

where γ_{SV}, γ_{MV}, and γ_{SM} are the interfacial tensions of the solid/vapor and the monolayer-covered liquid/vapor and solid/liquid interfaces, respectively. The surface pressure of the monolayer, π, is determined as the difference of the interfacial tension of the pure liquid/vapor interface, γ_{LV}, and that covered by a monolayer, γ_{MV}

$$\pi = \gamma_{LV} - \gamma_{MV}$$

For displacement of the contact line and effective monolayer transfer, the energy barriers for molecular advancement (on dipping) or recession (on withdrawal) have to be overcome. The work, W, done by the applied interfacial shearing force for unit displacement of unit length of the three-phase contact line is given by[73]

$$W = \gamma_{MV}(\cos \theta° - \cos \theta^d)$$

where $\theta°$ and θ^d are the static and dynamic values of the contact angles. The assumption that the interfacial driving force for contact line movement in the direction of the applied shear is determined by the out-of-balance surface tension forces[73] implies that dissipation in the three-phase zone does not occur through other mechanisms.

Effect of the Deposition Velocity on the Type of the Monolayer Transfer. The relationship between the dynamic contact angle during LB transfer, $\theta_{d(w)}$ (the driving force for contact line movement), and the deposition velocity, $V_{d(w)}$, is not simple and may vary within different velocity regions. It is generally expected that the dynamic angle θ_d will increase and θ_w will decrease with the deposition speed. However, measurements of dynamic contact angles in model three-phase systems with pure liquids[73,74] have established diverse empirical correlations between $\cos \theta^d$ and V: from a velocity independence, at very low velocities ($< \sim 1.10^{-3}$ cm/s), to logarithmic and linear dependences (at medium speeds), or inverse square and cubic at higher ones ($> 1-10$ cm/s) (for summary, see, e.g., Table 1 of ref 74a). In addition, it has been found that the dependences θ^d *vs* V may not always be symmetrical (with respect to velocity) for the immersion (dipping) and emmersion (withdrawal) strokes. The diverse dynamic contact angle/velocity relationships have been interpreted[73,74] as owing to different mechanisms of forced contact line motion.

Best results in description of the kinetics of a three-phase contact line movement in the steady-state regime have been obtained[74] on the basis of the molecular-kinetic
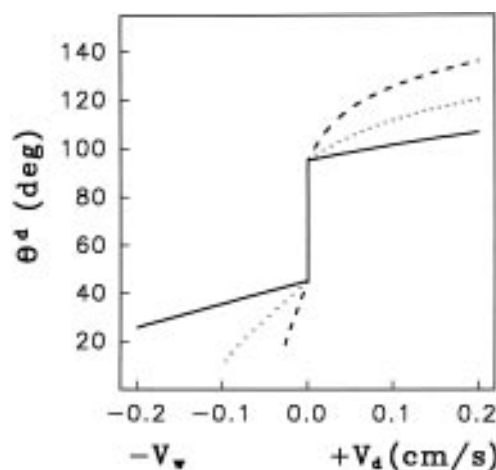

Figure 3. Dependence of the dynamic contact angle, θ^d, on the three-phase contact line velocity, $V_{d(w)}$, estimated according to the molecular-kinetic theory (eq 1).[73] Parameters used for the dipping and withdrawal LB deposition strokes: static contact angles $\theta_d° = 95°$ and $\theta_w° = 45°$; $\gamma_{MV} = 47.5$ mN/m; $\lambda = 9.1 \times 10^{-8}$ cm; $K° = 1 \times 10^6$ s^{-1} (solid line), 3×10^5 s^{-1} (dotted line), and 1×10^5 s^{-1} (dashed line).

theory of Blake and Haynes.[73,74] This theory treats the contact line motion as an activated molecular rate process, proceeding through a sequence of elementary (adsorption/desorption) displacement events. The magnitude of the dynamic contact angle, θ^d, is predicted at different velocities, $V = V_{d(w)}$, from the static value, $\theta°$ (at $V = 0$), by the equation

$$\cos \theta^d = \cos \theta° \pm (2nkT/\gamma_{MV}) \text{arcsinh}(V_{d(w)}/2K°\lambda) \quad (1)$$

where $K°$ is the rate constant of the molecular displacement (adsorption/desorption) processes at the solid surface, n is the density of adsorption sites on the solid surface, λ is the in-plane distance between these sites ($\lambda \approx n^{-1/2}$), T is the absolute temperature, and k is the Boltzmann constant. The signs plus and minus refer to the cases of substrate withdrawal and dipping, respectively. This equation indicates that the dynamic contact angels could be influenced both by the velocity of the contact line motion, $V_{d(w)}$, and by the interfacial (material) characteristics of the three-phase system (i.e., average distance between surface adsorption sites, λ, and interfacial tension of the fluid interface, $\gamma_{MV} = \gamma_{LV} - \pi_{const}$).

The molecular-kinetic theory[73,74] is applied here for a quantitative evaluation of the conditions leading to a symmetrical or an asymmetrical type of LB transfer. The significance of the changes of γ_{MV}, $\theta°$, $K°$, and $V_{d(w)}$ in influencing the values of θ^d, with respect to the deposition type (Table 1), is examined by means of simulations performed on the basis of eq 1. Figures 3−5 present exemplary plots θ^d *vs* $V_{d(w)}$ for selected molecular-kinetics parameters, physically feasible for the LB deposition processes. The application of eq 1 reveals that for typical regions of LB deposition velocities (−0.2 to +0.2 cm/s) and constant λ and γ_{MV} (determined by the deposition conditions), dependences of θ^d on $V_{d(w)}$ can be established for values of $K°$ of about 1×10^5 to 1×10^7 s^{-1}.

It has been experimentally shown[12−14,23,68,72,75,76] that Y-type LB deposition correlates with a large difference between the dipping and withdrawal static and dynamic contact angles. This case is simulated in Figure 3 with the condition of $\theta_d° > 90°$ and $\theta_w° < 90°$, using the parameters γ_{MV} and λ for the PUA LB deposition (see the

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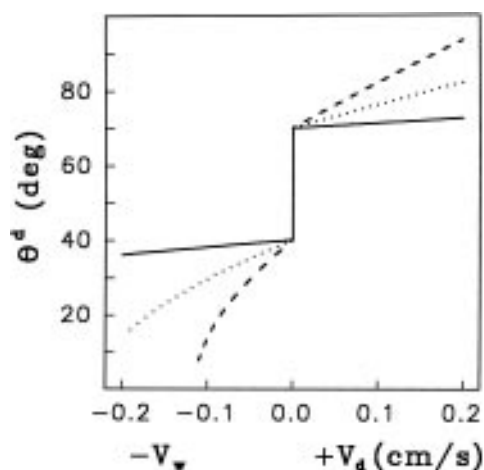(76) Petrov, J. G.; Angelova, A.; Möbius, D. *Langmuir* **1992**, *8*, 206−212.

Figure 4. Dependence of the dynamic contact angle, θ^d, on the three-phase contact line velocity, $V_{d(w)}$, estimated according to eq 1. Parameters used for the dipping and withdrawal LB deposition strokes: static contact angles $\theta_d° = 70°$ and $\theta_w° = 40°$; $\gamma_{MV} = 42.5$ mN/m; $\lambda = 4.5 \times 10^{-8}$ cm; $K° = 5 \times 10^7$ s^{-1} (solid line), 1×10^7 s^{-1} (dotted line), and 5×10^6 s^{-1} (dashed line).
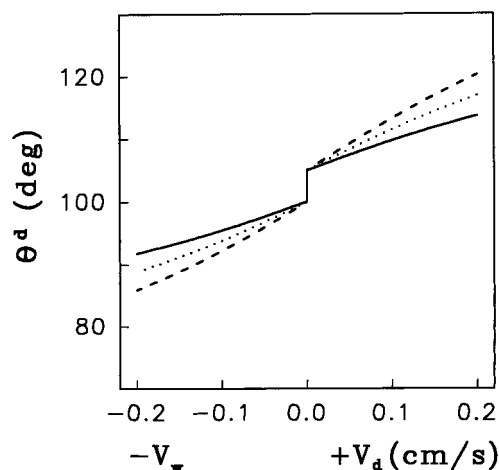

Figure 5. Dependence of the dynamic contact angle, θ^d, on the three-phase contact line velocity, $V_{d(w)}$, estimated according to eq 1. Parameters used for the dipping and withdrawal LB deposition strokes: static contact angles $\theta_d° = 105°$ and $\theta_w° = 100°$; $\lambda = 9.1 \times 10^{-8}$ cm; $K° = 1 \times 10^6$ s^{-1}; $\gamma_{MV} = 64.5$ mN/m (solid line); 47.5 mN/m (dotted line), and 37.5 mN/m (dashed line).

experimental part below). The obtained plots demonstrate that larger differences between the dipping and withdrawal dynamic contact angles are observed, at constant λ and π, upon decreasing the value of $K°$, which causes steeper variation of θ^d with V. However, a lowering of $K°$ below $\sim 1 \times 10^5$ s^{-1} results in a quick drop of θ_w to 0° (with a respective increase of θ_d to 180°) corresponding to a monolayer transfer accompanied by aqueous (or air) film entrainment. The transfer onto a microscopically thin aqueous layer has been regarded as "nonreactive" LB deposition.[77] It has a reversible character upon subsequent dipping stroke and, hence, is ineffective for LB multilayer preparation. These estimates show that there is an optimum region of deposition velocities, within which monolayer transfer could be controlled through changes of the dynamic angles θ_d and θ_w. Under usual (Y-type) LB deposition conditions, the dynamic contact angle values have been found to differ by about 10−15° from the static ones.[15,16,77]

The tendency toward asymmetrical and partial LB deposition is favored upon decreasing the difference

(77) Gaines, G. L., Jr. *J. Colloid Interface Sci.* **1977**, *59*, 438−446.

between θ_d and θ_w (Figures 4 and 5). Figure 4 presents θ^d *vs V* dependences for the case of both dipping and withdrawal static contact angles taking acute values ($\theta_{d(w)}° < 90°$). The calculations, performed with constants γ_{MV} and λ for the ODA LB deposition (see below), demonstrate that a transition from a Z-type transfer ($\theta_d < 90°$, $\theta_w < 90°$) to a Y-type one ($\theta_d > 90°$, $\theta_w < 90°$) (Table 1) can be simulated upon increasing V_d and decreasing the values of $K°$. This results in an enhancement of θ_d above 90° and bigger differences between θ_d and θ_w. Experimentally, the effect of $K°$ could be related to changes of the intermolecular interactions in the three-phase zone upon changing the ODA monolayer polarity and ionization with pH. Strong interactions between the adjacent monolayers in the three-phase zone, corresponding to lower $K°$ values, are characteristic of irreversible molecular adsorption upon contact line movement.[73]

Correlations between the transfer ratio values and the apparent static and dynamic contact angles during monolayer deposition have been experimentally established in a number of studies.[14−16,23,75] High transfer ratios have been achieved upon "dry" LB deposition[5] when $\theta_d°$ and $\theta_w°$ take large values.[12,14,72] Although the apparent static and dynamic contact angles are measured as macroscopic quantities at some distance away from the three-phase line, they reflect the changes in the microscopic interactions in the three-phase contact zone.[16,72,76] For alkanoic acid monolayers, Aveyard et al.[14,75] have reported that high (close to unity) transfer ratios α_d and α_w are provided at large θ_d, exceeding 90°, and nonzero θ_w, of values considerably less than 90°. Since the dynamic angles $\theta_{d(w)}$ could be influenced by $V_{d(w)}$ (Figure 3), this implies that the transfer ratios on dipping and withdrawal should increase with the velocity, with which the substrate moves. The observed asymmetry (with respect to V) of the velocity dependences of the dynamic angles θ_d and θ_w (Figures 3−5) corroborates the statement that the underlying mechanisms of contact line motion and LB deposition should be different on dipping and withdrawal strokes.[12,72]

Effect of the Surface Pressure on the Monolayer Deposition Type. The effect of the surface pressure of the LB deposition efficiency is realized on the basis of the molecular-kinetic theory as well. Figure 5 (solid line) shows an exemplary θ^d *vs* $V_{d(w)}$ plot, estimated according to eq 1 for close, obtuse values of $\theta_d°$ and $\theta_w°$ and parameters γ_{MV} and λ for the deposition of PUA monolayers. The effect of the deposition surface pressure, π_{const}, on the dynamic contact angles is demonstrated at a constant value of $K°$. Depending on π_{const}, the dynamic angle θ_w can be reduced from a value above 90° (at very slow withdrawal) to less than 90° (at higher deposition speeds). The dashed and dotted lines in Figure 5 indicate that the increase of π_{const} (with respective decrease of γ_{MV}) results in a transition from X-type deposition ($\theta_d > 90°$, $\theta_w > 90°$) to a Y-type one ($\theta_d > 90°$, $\theta_w < 90°$) (Table 1). Hence, in addition to the deposition velocity,[20,21] the enhancement of the surface pressure provides another (thermodynamic) means for changing the LB deposition type.

The surface pressure influences the integrity of the monolayer to be transferred. At low surface pressures, the applied interfacial force is insufficient to cause monolayer deposition onto the solid substrate. High surface pressures have been found to favor complete ($\alpha \approx 1$) monolayer transfer onto a solid support.[11,15,18] They provide appropriate in-plane cohesion and high 2D density of the amphiphilic molecules, requested for transferring monolayers in a close-packed state. It has been repeatedly shown[19−21] that Y-type LB transfer is favored by the

increase of the surface pressure, π_{const}. These experimental findings are supported by the theoretical estimates presented in Figure 5.

Thermodynamic studies[15,18] have supposed the existence of a *critical* magnitude (π_{crit}) of the applied constant deposition pressure (π_{const}) for occurrence of successful LB transfer. In the absence of specific electrostatic and polar dipole interactions in the three-phase contact zone, successful monolayer transfer onto a solid could be effected by proper selection of the deposition surface pressure (i.e., γ_{MV}). For example, transfer of lipid alcohol and phosphocholine monolayers, which normally do not form LB layers, has been achieved[15,18] at surface pressures, π_{const}, exceeding threshold values π_{crit}. Osborn et al.[18] have suggested that a bilayer formation is favored by deposition pressures of at least 20 mN/m, while Egusa et al.[15] have shown that π_{crit} depends on the hydrophobicity of the solid support.

The adhesion energies, ΔW, i.e., the free energy costs for separation of adjacent monolayer surfaces from adhesive contact in the bilayers (as repeat units of the LB multilayers), are expressed in terms of π as

$$\Delta W_d = \gamma_{MV}(1 + \cos\theta_d°) = (\gamma_{LV} - \pi_{const})(1 + \cos\theta_d°)$$

for the hydrophobic adhesion energy at dipping stroke and

$$\Delta W_w = \gamma_{MV}(1 - \cos\theta_w°) = (\gamma_{LV} - \pi_{const})(1 - \cos\theta_w°)$$

for the polar adhesion energy at withdrawal stroke. These thermodynamic expressions do not account for specific intermolecular interactions or molecular reorganization in the three-phase contact zone during deposition, but it is clear that the increase of the surface pressure facilitates the contact of the adjacent monolayers in forming bilayers.

The investigations of Zisman[78] and Fowkes[79] have established the existence of critical surface tensions of wetting, γ_{crit}, characteristic of three-phase (solid/liquid/vapor) systems. A linear relationship $\cos\theta°$ *vs* γ_{LV} has been experimentally found[78] for pure liquids forming nonzero contact angles on low-energy solids

$$\cos\theta° = 1 - C(\gamma_{LV} - \gamma_{crit})$$

where C is the constant of the Zisman plot. For $\gamma_{LV} = \gamma_{crit}$, $\cos\theta° = 1$, and one observes a transition from partial to complete wetting of the solid surface.

The equation of Fowkes[79] predicts an S-shaped dependence $\cos\theta°$ *vs* γ_{LV}. It has been derived for phase boundaries interacting through dispersion interactions

$$\cos\theta° = -1 + 2(\gamma_{SV}{}^d \gamma_{LV}{}^d)^{1/2}/\gamma_{LV} - \pi_{S,V}/\gamma_{LV}$$

where d denotes the dispersive contribution to the interfacial tensions, $\pi_{S,V}$ is the surface pressure of the vapors adsorbed at the solid/gas interface, and $\theta°$ is the equilibrium contact angle. Independent of the exact mathematical relationships, both the Fowkes and the Zisman's treatments indicate the existence of γ_{crit}. The plots[73b] $\cos\theta°$ *vs* γ_{LV} intersect the axis $\cos\theta° = 1$ at certain critical γ_{LV} values. Liquids of surface tension, γ_{LV}, lower than γ_{crit} will spread completely on the solid surface, while those of $\gamma_{LV} > \gamma_{crit}$ will form nonzero contact angles.

In analogy with the case of spreading of pure liquids on solids, it could be expected that a monolayer-covered liquid/vapor meniscus (Figure 1) will form a nonzero (or zero) dynamic contact angle with a low-energy solid surface

below (or above) a particular critical surface pressure value, $\pi_{crit} = \gamma_{LV} - \gamma_{MV,crit}$. According to the experimental results of Egusa et al.,[15] obtained in a steady-state regime of withdrawal, the two cases will correspond to nontransfer or transfer onto the solid substrate. Down-stroke deposition has been observed[15] at $\pi_{const} > \pi_{crit}$ for $\cos\theta_d \neq 0$.

Effect of the Interfacial Viscosity on the Monolayer Deposition Efficiency. The effect of the interfacial viscosity, η_s, on the LB deposition process is included, through the capillary number Ca = $(\eta_s V/\gamma_{MV})$, in the velocity dependence[73] of the dynamic contact angles. It is well-known that a certain fluidity of the monolayers is requested for successful LB deposition. Highly viscous monolayers can not be transferred onto a solid substrate by means of the LB technique.[20] The influence of η_s becomes essential at very high deposition velocities, when the viscous drag forces in the three-phase contact zone, opposing the contact line motion, adopt large magnitudes.

Methods and Materials

Monolayer characterization and LB film transfer were performed with an automated Langmuir film balance. Monolayers of octadecylamine (Sigma) and 11-(pentakis((4-pentylphenyl)-ethynyl)phenoxy)undecanoic acid (synthesized according to the method described in ref 80 were spread from chloroform (Merck, spectroscopic grade, stabilized with ethanol) solutions of concentration 1×10^{-3} M. The deposition of the ODA monolayers was performed at a surface pressure of 30 mN/m from 1×10^{-2} M Na_2HPO_4 (Merck, p.a.) aqueous subphase. Y-type film transfer was accomplished at subphase pH 7.0 and Z-type deposition at pH 10.0. The pH values were adjusted by adding HNO_3 or NaOH to the subsolutions. The PUA monolayers were successively transferred from 2×10^{-4} M $BaCl_2$ (Merck, p.a.) subphase. The magnitudes of the constant deposition surface pressures were selected from the monolayer π/A isotherms (see Figure 7 below). Values of 8 and 25 mN/m were applied for the PUA LB film deposition from acidic (pH 3.0) and alkaline (pH 10.0) aqueous subsolutions, respectively. They resulted in partial XY- and symmetrical Y-type film deposition, respectively. Hydrophobized, smooth silicon and Corning glass plates were used as solid substrates. Twenty deposition strokes were performed at deposition velocities of 0.14 cm/s, on dipping, and 0.02 cm/s, on withdrawal. The subphase temperature was kept constant (19.0 ± 0.2 °C) using a thermostat.

Structural characterization of the deposited ODA and PUA films was performed by means of a "Siemens D-500" X-ray diffractometer. The radiation wavelength was copper $K_{\alpha 1}$ (λ = 1.540 51 Å). X-ray patterns were recorded in the 2θ region from 0.6° to 10°. A symmetrical Bragg geometry was used. The diffraction intensities were measured by means of a scintillation counter, coupled with a graphite monochromator. On the basis of the X-ray diffraction patterns of bulk samples of the investigated amphiphiles, Bragg spacings of 52.0 and 15.5 Å were determined for the ODA and PUA materials, respectively. These values indicated a multibilayer periodicity of the bulk ODA lipid and a body-centered orthorhombic bulk structure of the diskotic amphiphile PUA at room temperature.

Optical microphotographic images of the surface morphology of the deposited LB layers were taken at magnification of about 3400×. Variations of the contrast of the images could be caused by inhomogeneities in the film thickness, phase state, or chemical composition (leading to local changes of the refractive index of the deposited film).

Experimental Results

The type of LB transfer of the investigated rodlike and disklike amphiphiles (Figure 2) was found to depend on the ionization state of their monolayers (influenced by the subphase pH). In this study, two representative cases are considered for each amphiphile, which correspond to conditions of partial and complete types of monolayer

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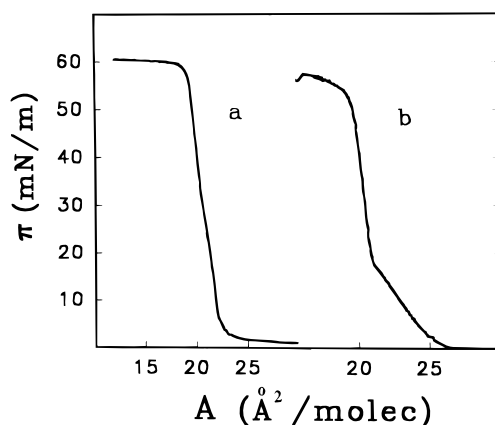
Figure 6. Surface pressure/area isotherms of octadecylamine (ODA) monolayers spread on 1×10^{-2} M Na$_2$HPO$_4$ aqueous subphases of pH 10.0 (a) and 7.0 (b), respectively. Subphase temperature was 19 °C.

Figure 7. Monolayer π/A isotherms of the disklike PUA amphiphile spread on 2×10^{-4} M BaCl$_2$ aqueous subphase of pH 3.0 (a) and 10.0 (b), respectively. Subphase temperature was 19 °C.

transfer. On phosphate buffer subphases,[22,72,81] long-chain alkylamine monolayers are in a fully ionized (R–NH$_3^+$) state at pH 7, while they exist in an unprotonated (R–NH$_2$) form at pH 10. Interaction with divalent anions facilitates the Y-type transfer of the charged ODA monolayers. A tendency toward Z-type deposition was established for strongly alkaline (pH 10) subphase. The carboxylic groups of the disklike derivative (PUA) are in a nondissociated (D–COOH) state on acidic (pH 3.0) aqueous subphase. Under these conditions, the transfer of the PUA monolayers was of a partial type. The ionization of the carboxylic groups (D–COO$^-$), and their interaction with divalent (Ba^{2+}) counterions from subsolution of pH 10, favored Y-type transfer of the PUA films.

Monolayers of ODA and PUA were characterized by surface pressure/area isotherms and area relaxations at constant deposition surface pressures. Parts a and b of Figure 6 show π/A curves of uncharged (at pH 10.0) and protonated (at pH 7.0) ODA monolayers, respectively. The established high maximum ("collapse") pressures, close to 60 mN/m, demonstrate the stability of the monolayers against compression and the possibility for LB deposition at enhanced surface pressures (e.g., $\pi_{const} = 30$ mN/m). The latter ensures in-plane close-packed molecular arrangement of the ODA films.

The π/A isotherms of the disklike amphiphile (Figure 7) indicate that these monolayers can be compressed to higher maximum surface pressures when they are in an ionized state (Figure 7b). It follows from Figure 7a that LB deposition of PUA from acidic subsolutions can be performed at constant deposition pressures of maximum 10 mN/m, while this value can be increased up to three times for alkaline, Ba^{2+}-containing subphases (Figure 7b).

Since the stability of the monolayers is crucial for the quality of the prepared LB films, monolayer area relaxation kinetics was followed at the selected constant deposition surface pressures. Figures 8 and 9 reveal that both ODA and PUA form stable monolayers, showing little area relaxations with time at a constant deposition pressure (π_{const}). The stability of the monolayers at a given π_{const} is represented by the ratio, $A(t)/A(0)$, of the monolayer area at time t, $A(t)$, to that at time $t = 0$, $A(0)$. In all cases, the contraction of the monolayer area at π_{const} was less than 5% during typical compression times for monolayer deposition. The reported transfer ratio values were corrected for relaxation effects. Microscopic examination of the monolayers indicated that the monolayer area
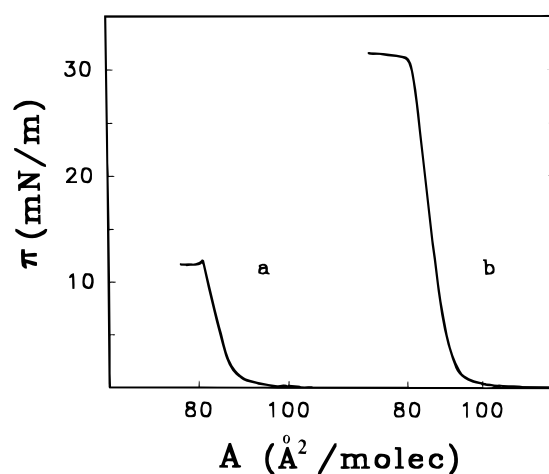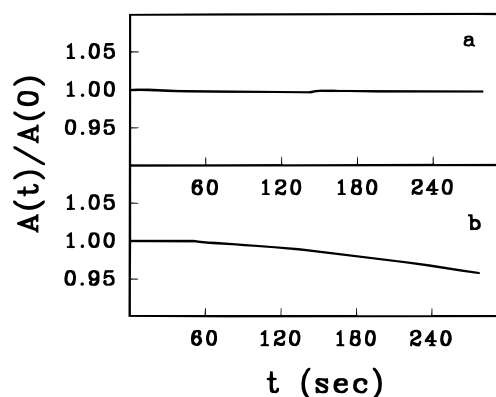

Figure 8. Stability *vs* time of ODA monolayers compressed at constant surface pressure $\pi_{const} = 30$ mN/m on 1×10^{-2} M Na$_2$HPO$_4$ subphases of pH 10.0 (a) and 7.0 (b).
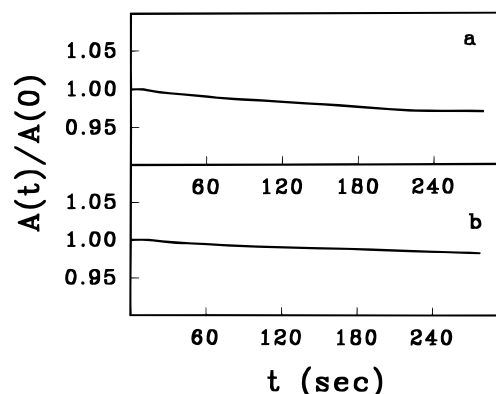

Figure 9. Stability *vs* time of PUA monolayers compressed on 2×10^{-4} M BaCl$_2$ subphase of (a) pH 3.0 and $\pi_{const} = 8$ mN/m and (b) pH 10.0 and $\pi_{const} = 25$ mN/m.

relaxation should be due to slight dissolution of amphiphilic material into the aqueous subphase, rather than to nucleation of three-dimensional structures at constant surface pressure.

Structural and morphological features of LB films of the rodlike and disklike amphiphiles were compared for two representative samples from each lipid, deposited under conditions of partial and complete monolayer transfer. Small-angle X-ray diffraction pattern of an octadecylamine LB film, prepared by asymmetrical "Z"-type deposition, is presented in Figure 10a. The observed Bragg peaks determine a periodic film structure of a repeat

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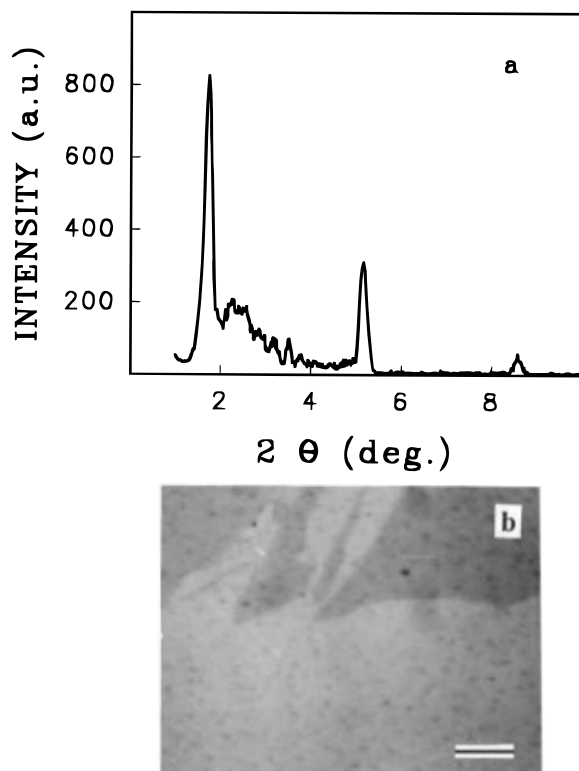
Figure 10. (a) Small angle X-ray diffraction pattern of an ODA LB film asymmetrically deposited from 1×10^{-2} M Na$_2$HPO$_4$ aqueous subphase of pH 10.0. The average transfer ratios $\alpha_d = 0.14$ and $\alpha_w = 0.97$ are indicative of "Z"-type LB deposition. (b) Optical microphotograph of a "Z"-type deposited ODA LB film, showing a patchy film morphology (darker areas in the upper part of the image). The bar corresponds to 10 μm.

Figure 11. (a) Small angle X-ray diffraction pattern of an ODA LB film symmetrically deposited from 1×10^{-2} M Na$_2$HPO$_4$ aqueous subphase of pH 7.0. The "Y"-type deposition is characterized by average transfer ratios $\alpha_d = 0.93$ and $\alpha_w = 0.98$. (b) Optical microphotograph of a "Y"-type deposited ODA LB film, showing plane surface morphology. Microholes are observed upon film storage under ambient conditions. The bar corresponds to 10 μm.

spacing $d = 52.0$ Å. This indicates that molecular overturning accompanies the ODA monolayer transfer at pH 10. Although deposited upon one-direction (up-stroke) mode of transfer, the films appear to be of a bilayer ("head-to-head"/"tail-to-tail") structure.

The optical microphotograph (Figure 10b) of the "Z"-type deposited ODA film shows that the partial ($\alpha_d < 1$) LB transfer, from 1×10^{-2} M Na$_2$HPO$_4$ subphase of pH 10, results in patchy film morphology. The molecular overturning to a bilayer structure causes formation of steps in the films, which are seen as areas of different darkness (Figure 10b, top). It was found by means of atomic force microscopy[82] that the height of such steps is divisible by the bilayer repeat unit of the ODA film (52.0 Å). These results indicate that the symmetrical "head-to-head"/"tail-to-tail" molecular arrangement is energetically more favorable for the transfer of the rodlike ODA amphiphile. A multibilayer structure is formed in the Z-type deposited films. This structure covers inhomogeneously the substrate surface, over which the transfer was attempted (Figure 10b). Effectively, patches of a bilayer periodicity and different heights are established in the asymmetrically (Z-type) transferred multilayers.

The ODA multilayer prepared by symmetrical Y-type LB deposition, from 1×10^{-2} M Na$_2$HPO$_4$ subphase of pH 7, exhibits a multibilayer "head-to-head"/"tail-to-tail" structure as well. A repeat spacing $d = 56.6$ Å was estimated from the small angle X-ray diffraction pattern of the LB sample (Figure 11a). This bilayer periodicity is larger than that of the film prepared at pH 10. The established difference should be due to the inclusion of divalent phosphate counterions in the multilayers trans-
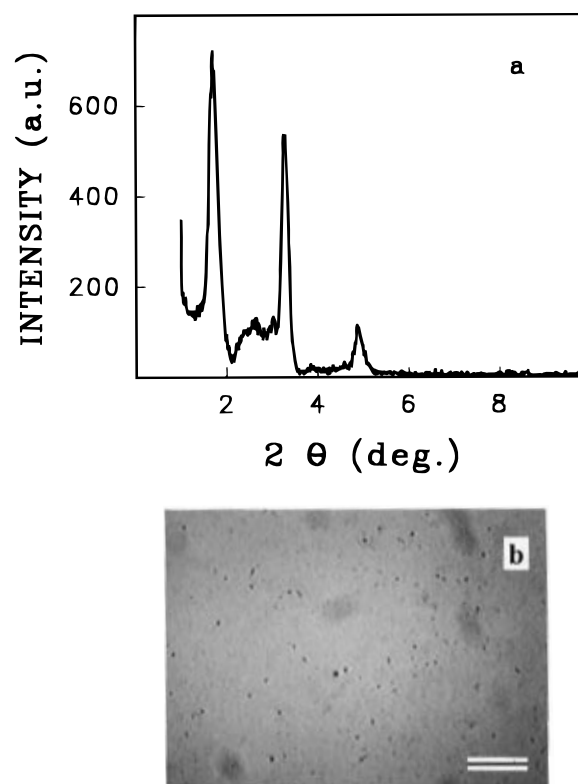
ferred at pH 7. The average transfer ratios of nearly unity, both on dipping and withdrawal, correspond to complete coverage of the solid substrate. The optical microphotograph of the multilayer (Figure 11b) demonstrates flat surface morphology of the film over large areas of examination.

LB samples of the disklike amphiphile were deposited from Ba^{2+}-subsolutions of pH 3.0 and 10.0. The transfer of PUA at $\pi_{const} = 8$ mN/m, from acidic aqueous subphase, yielded average $\alpha_d = 0.6$ and $\alpha_w = 0.3$. LB deposition of such α values could be regarded as "partial" (mixed) type. Usually, such poor transfer onto a solid substrate is considered as unsatisfactory for preparation of periodic film structures. Unexpectedly, the X-ray pattern of the film shows a Bragg peak (Figure 12a). It corresponds to a repeat unit $d = 15.5$ Å. The same periodicity was found to be characteristic of the bulk structure of the PUA amphiphile at room temperature. The constant of the corresponding body-centered orthorhombic unit cell (31.0 Å) fits to the dimension of the PUA molecule (30.2 Å), estimated from the molecular model (Figure 2).

The optical microphotograph (Figure 12b) of the PUA film, prepared by partial LB transfer, demonstrates that the amphiphilic film material is aggregated into dendritic islands. Dendritic morphologies are typical for crystalline thin films. This result is in agreement with the X-ray data, indicating a crystalline structural organization of the transferred layers. The applied constant deposition pressure of 8 mN/m appears to be insufficient to provide close packed arrangement of the disklike molecules and homogeneous surface coverage of the solid support. Under these conditions, the PUA molecules self-organize into crystalline, dendritic patches of structure, which is

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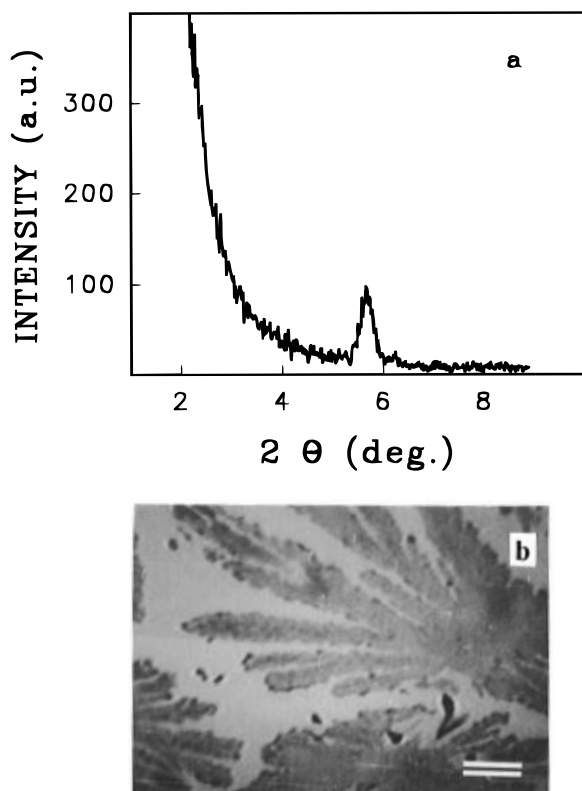(82) Angelova, A.; et al. Unpublished results.

Figure 12. (a) Small angle X-ray diffraction pattern of a PUA LB film deposited at π_{const} = 8 mN/m from 2×10^{-4} M BaCl$_2$ aqueous subphase of pH 3.0. The partial transfer is characterized by average transfer ratios $\alpha_d = 0.6$ and $\alpha_w = 0.3$. (b) Optical microphotograph of the same diskotic film, demonstrating its dendritic crystalline morphology. The bar corresponds to 10 μm.

Figure 13. (a) Small angle X-ray diffraction pattern of a diskotic LB film deposited at π_{const} = 25 mN/m from 2×10^{-4} M BaCl$_2$ subphase of pH 10.0. The average transfer ratio $\alpha = 0.9$ (i.e., $\alpha_d = 1.0$ and $\alpha_w = 0.8$) determines LB deposition of close to "Y"-type. (b) Optical microphotograph of a symmetrically deposited PUA multilayer, showing smooth and homogeneous surface morphology of the film. The bar corresponds to 10 μm.

characteristic of the bulk phase of the amphiphile at room temperature.

Another periodic structure was established with the diskotic films deposited from strongly alkaline subphase. Figure 13a shows the small angle X-ray pattern of the PUA multilayer, deposited by symmetrical "Y"-type of LB deposition in the presence of divalent cations in the subphase. The average transfer ratios, approaching unity at pH 10, are related to preparation of a periodic multilayer structure that is essentially different from the bulk diskotic one. The recorded two Bragg peaks determine a bilayer repeat spacing of the film $d = 44.5$ Å. The latter indicates that the disklike molecular planes are vertically ("edge-on") oriented (with respect to the solid substrate) within the bilayers. The established well-defined Kiessig fringes (Figure 13a), as well as the optical microphotograph of the film (Figure 13b), show that this diskotic multilayer is very smooth and homogeneous. It covers completely the substrate surface. This example of LB deposition, with $\alpha \approx 1$ at high π_{const}, demonstrates the ability of the LB technique to create ordered multilayer assemblies of molecular arrangement other than in the bulk amphiphilic phase ($d = 15.5$ Å).

Discussion

Common Features of Irreversible Monolayer Transfer. It follows from the general considerations presented above that the type of LB transfer can be altered in kinetic or thermodynamic ways through variations of the deposition speed and deposition surface pressure. These effects do not depend on the type of the monolayers used for LB film preparation. Independently on the steric nature of the amphiphiles, e.g. a rodlike (i.e., long-chain)
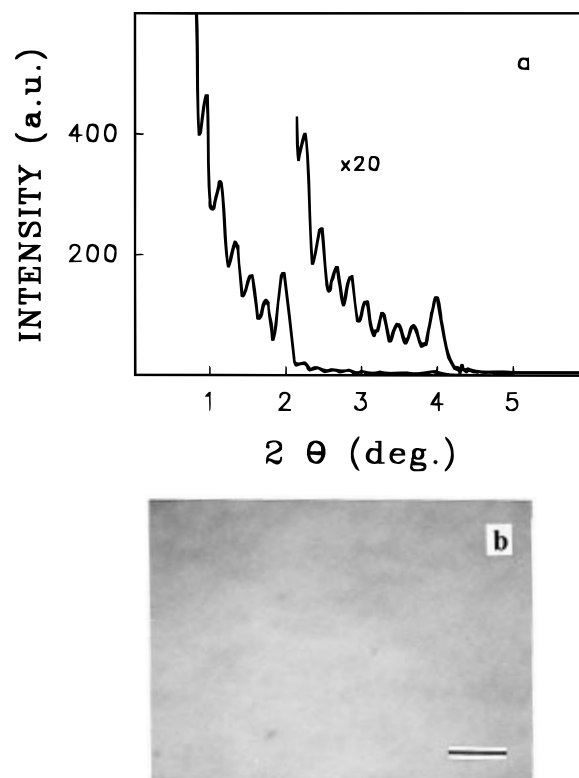
or a bulky one (like disk-shaped or sphere-shaped), adhesion should be achieved between the viscoelastic monolayer being transferred (considered as a complex fluid[70]) and the moving hydrophobic or hydrophilic substrate (Figure 1). On the basis of the established general correlations, the occurrence of *partial* LB deposition follows naturally, rather than seems to be a mystery.[23] The deposition conditions (π_{const} and $V_{d(w)}$), utilized in the present experiments, were selected as to allow a comparison of the effects of partial and complete monolayer transfer on the structural organization of the obtained LB layers.

Influence of Intermolecular Interactions in the Three-Phase Contact Zone on the Type of Monolayer Transfer. The type of monolayer transfer depends also on experimental parameters affecting the intermolecular interaction in the three-phase contact zone (e.g., subphase pH, concentration, and type of counterions).[11,21,44,76,83,84] In the cases, when strong attractive intermolecular interactions are present (between the two adjacent monolayers) in the three-phase contact zone (Figure 1, insets), irreversible LB transfer is easily performed.[22,72] Electrostatic mismatch of the approaching interfaces causes a reversibility of the monolayer transfer.[10,12,14] Z-type LB deposition seems to result from increased monolayer head group polarity and reduced ability for rapid expulsion of water from the three-phase contact zone.

The subphase pH influences the LB deposition efficiency by changing the ionization state of the monolayers and their interaction with species from the aqueous subphase.

(83) Engel, M.; Riegler, H. *Makromol. Chem. Macromol. Symp.* **1991**, *46*, 395−400.

(84) Angelova, A.; Petrov, J. G.; Kuleff, I. *Langmuir* **1992**, *8*, 213−216.

First, the ionization of the monolayer head groups with pH usually leads to enhancement of the monolayer stability (expressed in enhanced "collapse" pressures), which allows high deposition pressures to be applied for LB transfer (see, e.g., Figures 6 and 7). Second, the ionized head groups may interact (within specific pH regions) with dissolved polyvalent counterions. This favors the irreversibility of the LB transfer by creation of ionic and coordination bonds between the adjacent monolayers in the multilayer. Third, it has been established[14,23,75] that the up-stroke deposition of alkanoic acid monolayers may change its type (from transfer to nontransfer) at pH values corresponding to half degree of ionization of the monolayer carboxylic head groups.

Structural Peculiarities and Specific Effects with the LB Deposition Process. The specificity of the LB deposition process is determined by the chemical nature of the selected amphiphiles (ionic or uncharged) and their steric and bulk phase properties. Structural defects in LB films, prepared at high transfer ratios, could be caused by steric molecular mismatch in the three-phase contact zone (Figure 1, insets). Morphological and structural imperfections have been observed with LB multilayers prepared at surface pressures below[18] or above[17,19] the established optimum deposition surface pressure. It is natural to suppose that the partial LB transfer at low π_{const} will yield defect-rich layers, characterized by a domain (island) structure and gradients in the film thickness. Often, the effect of the low deposition pressure on the transfer efficiency could not be compensated by an increase of the deposition velocity.

The incomplete ($\alpha \sim 0.2-0.5$) down-stroke transfer of phospholipid monolayers on silicon substrates has resulted[18] in a striated morphology of the deposited bilayer films. The numerous line and point defects, observed in the micrographs of bilayers prepared at average transfer ratios of about 0.5, have indicated[18] that little lipid has adhered to the substrate at low deposition pressures. Contraction of the amphiphilic material on the high-energy solid surface has yielded elongated, pinstripe defects, which are energetically preferable (as compared to circular ones) in films of bilayer-forming lipids.[18]

In the present study, the partial transfer of the diskotic PUA monolayers resulted in incomplete film coverage of the solid substrate (Figure 12b). However, this amphiphilic material did not form disordered films even at little ($\alpha \sim 0.5$) transfer ratio values. The self-organizing properties of the disklike amphiphile appear to be an important factor in determination of the PUA film organization in the absence of counterion binding to the monolayers. The molecular aggregation and ordering into a crystalline phase are owing to the steric peculiarities of the molecule and $\pi-\pi$ interactions between the delocalized π-electrons of the disklike planes.[52] Despite of the partial LB deposition of very low α, the X-ray pattern presented in Figure 12a revealed a periodic film structure. This result, which was very reproducible, demonstrated the strong tendency of the disklike molecules toward self-organization into a crystalline structure, characteristic of the bulk phase of the amphiphile at room temperature.

It has been reported on the basis of X-ray data[46,54] that the LB film structures could be often identical to the bulk phase ones. Sometimes, X-ray periodicity has not been detected with films prepared by multiple deposition of definite monolayers, even at high transfer ratios. Bardosova et al.[48] have established that Z-type deposited amylose triacetate LB layers do not show Bragg X-ray peaks and have stressed the importance of the "drying" time in producing good quality films. The lack of a multilayer periodicity of such polymer LB films is indica-

tive of randomness of their organization (as in a bulk phase). Probably owing to tearing of the monolayers during Z-type deposition, no correlation between the individual transferred monolayers has been found in the *z*-direction to the solid substrate by means of X-ray diffraction. A patchy film morphology was established here with the Z-type transferred ODA LB film (Figure 10b), which, however, did not lose its multilayer periodicity after preparation.

The performed X-ray studies indicated that the case of asymmetrical, Z-type of ODA deposition is not completely reciprocal to that of the X-type (one-direction) transfer of fatty acid multilayers.[1,23,33] Fatty acid salt films, prepared by both X- (at pH > 8.5) and Y-type (at pH < 7.0) deposition, have shown multibilayer structural arrangement.[1,21,23] Owing to molecular overturning during the X-type of transfer, nearly equal X-ray repeat spacings have been found for both kinds of multilayer structures.

Overturning was established (Figure 10a) with the asymmetrical (one-direction) ODA monolayer transfer as well. Monolayer deposition at $\pi_{const} = 30$ mN/m ensures closed-packed arrangement of the ODA molecules. Therefore, the determined X-ray spacing ($d = 52.0$ Å) could be associated with a nearly vertical arrangement of the molecules in the multibilayer deposited at pH 10. The comparison of this bilayer spacing with the doubled extended-state length of the amphiphile (48.2 Å), estimated from the molecular model (Figure 2), indicates that the deposited multilayer (of presumably vertically oriented molecules) might have included one or two molecular sublayers of hydration water. Water may enter into the gaps (Figure 10b) formed upon the rearrangement of the film molecules into a multibilayer structure. The periodicity of the Z-type deposited alkylamine LB film was found to be equal to that of the bulk crystalline ODA ($d = 52.0$ Å). This confirms that the multilayer, deposited from strongly alkaline (pH 10) subphase, is composed of neutral RNH_2 species. The bilayer structural organization of the film is favored by formation of hydrogen bonds between the polar amine head groups of the adjacent monolayers.

The obtained results showed that the LB technique does not always change the structure existing in the bulk phase of the amphiphiles. Partial LB transfer is not sufficiently effective to induce new kinds of periodic structures in the deposited thin layers. In the present investigation, new structural organizations were induced by controlling the electrostatic intermolecular interactions in the three-phase contact zone (Figure 1), which favor formation of multibilayer molecular arrangements.

ODA multilayer structures, prepared by Z- and Y-types of LB deposition, showed an essential difference of more than 4 Å in their bilayer repeat units (Figures 10a and 11a). The established large period of the multilayer deposited at pH 7.0 could be again interpreted as owing to vertical orientation of the ODA molecules with respect to the solid support. The Y-type transfer of cationic RNH_3^+ monolayers is facilitated by their interaction with polyvalent anions from the subsolution.[22,84] The cationic monolayers are transferred onto the solid substrate together with their bounded counterions. The effective 2D projection of the HPO_4^{2-} counterions is sufficiently large (2.55 Å) and is easily detected as the increase of the repeat spacing of the ODA film prepared at pH 7.0. Although visibly "dry" LB transfer was performed, the obtained X-ray spacing (56.6 Å) indicates that the deposition under conditions of room humidity is probably accompanied by inclusion of a small amount of hydration water in the ODA multilayers. This problem will be addressed in a separate publication.

It was established that the structure of the diskotic layers may also be altered by changes of pH of the aqueous subphase and interaction with divalent counterions. Upon ionization of the diskotic films, an essential difference was found between the bulk (body-centered orthorhombic crystalline) structure of PUA (Figure 12a) and the thin film structure, induced by means of the LB technique upon Y-type multilayer transfer in the presence of Ba^{2+} counterions (Figure 13a). The periodicity of the LB films, established by means of the X-ray method, corresponded to a multilayer structure of a bilayer repeat unit and "edge-on" molecular arrangement. It was very stable with time and almost defect-free upon microscopic examination (Figure 13b).

Conclusion

The films deposited by means of the LB technique should be distinguished from ideal, regular multilayers. Their periodic structural arrangement should be evidenced by means of structural methods. Low-angle X-ray diffraction is the first good, but insufficient, evidence for the quality of the deposited multilayers, since it provides information about the film structure in *z*-direction to the solid substrate. Periodic, multilayer structures could be obtained also by means of vacuum deposition[37] or spreading of amphiphiles from organic solution.[39] These techniques, as well as the partial LB deposition, yield films of domain in-plane structure of usually irregular thickness.

Structural organization, distinct from that existing in the bulk phase of the amphiphiles, could be induced by means of the LB technique in the cases when the monolayer properties can be influenced by interaction with species from the aqueous subphase. Inclusion of counterions in the multilayers may essentially change their molecular arrangement. For the Y-type deposition of both the rodlike ODA and the disk-like PUA amphiphiles, multilayer structures of repeat spacing, very different from that in bulk, are established. In the case of partial transfer and in the absence of ionic interactions of the ODA and PUA monolayers with counterions from the subphase, the periodicity of the films was the same as that of the bulk lipid phase. The one-direction Z-type deposition of ODA is accompanied by molecular overturning to a multibilayer ("head-to-head"/"tail-to-tail") structure.

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