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Scanning Force Microscopy and Wetting Study of the Surface Modification of a Polypropylene Membrane by Means of Langmuir-Blodgett Film Deposition

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Polypropylene membranes with deposited ultrathin "skin" layers are attractive for separation and cleaning of gaseous mixtures. In the present study, the surface morphology and wetting hysteresis of composite membranes, consisting of a microporous polypropylene support and Langmuir-Blodgett ("skin") films, are investigated. The effect of the interlayer molecular interactions and the substrate features on the integrity and homogeneity of the "skin" layers is examined. Langmuir-Blodgett films of arachidic acid and cadmium and calcium arachidate are characterized both on smooth silicon and on porous polypropylene supports. Contact angle measurements and scanning force microscopy (SFM) are applied for investigations of the membrane surface modification upon transfer of a different number of monolayers. It was found that the contact angle hysteresis of the bare membrane decreases after the LB-deposition of close-packed monolayers. Smoothing of the membrane surface is also evidenced by the SFM images, on different length scales, confirming a good coverage of the membrane pores.

Introduction

Semipermeable membranes have been widely utilized in a number of separation, concentration, and purification methodologies in industry and medicine.¹⁻³ Several types of membrane separation processes have been known to depend on the membrane structure and the mechanism and driving forces of the mass transport:³⁻⁵ micro- and ultrafiltration, reverse osmosis, gas separation, pervaporation, dialysis, etc.

Two types of synthetic membranes have been used for gas separation and gas cleaning under an applied pressure difference:^{5,6} (i) *asymmetric microporous membranes*, consisting of a very thin "skin" layer on a porous support (with pore diameter varying along the membrane cross section), and (ii) *homogeneous membranes* composed of densely packed (solid) films. Generally, the microporous membranes exhibit a high flux rate and selectivity. In contrast, the homogeneous membranes are characterized by low permeability and high selectivity.

The significance of the membranes' structure and morphology for their permeation and separation efficiency has long been recognized.⁵ In order to obtain selective gas flow through a membrane, the pore size has to be such

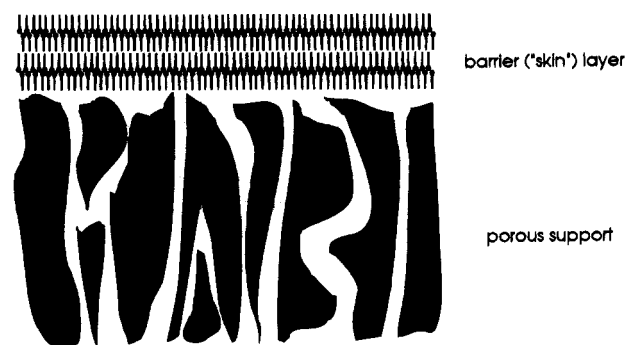


Figure 1. Schematic diagram of a composite membrane consisting of a microporous polymer support and a thin homogeneous barrier ("skin") layer.

that molecular collisions with the pore walls exceed any collisions between the permeate molecules. Membranes with homogeneous pore-free surface are required for this purpose.⁷ Attempts to improve the membranes parameters have led to the design of synthetic *composite membranes*, combining structural features and functional advantages of both the microporous and the homogeneous membranes (Figure 1). In this case, the materials of the fragile "skin" layer and the underlying support are different. Their proper selection provides enhanced permeability and mechanical stability of the membrane units.

Crucial parameters for the membrane selectivity are the thickness and the homogeneity of the "skin" layers. The gas transport is facilitated at very low thickness of the barrier layers. Such layers have been prepared by casting, dip-coating, vapor-phase deposition, or interfacial polymerization of thin films on microporous polymer supports. More recently, the Langmuir-Blodgett (LB) technique^{8,9} has been used for composite membranes

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preparation.^{10–20} Its advantage of producing very thin (a few molecular layers thick) ordered films has been employed.

Asymmetric membranes containing ultrathin "skin" films of both polymeric lipids and classical fatty acid derivatives have been investigated recently.^{10–15} LB-films allow a high permeation rate to be combined with a highly selective transport.^{5,12,15} The LB-layers deposited under optimum conditions have been robust enough to bridge the pores of the membrane supports, yielding pore-free films on a relatively small scale of examination.^{13,14} The established dependence of the gas permeability on the number of deposited monolayers has revealed the need of detailed characterization of the microporous morphology of the composite membranes. In general, the degree of substrate surface coverage improves upon increasing the number of transferred monolayers.^{21,22} However, this does not necessarily imply that the LB-films consisting of a larger number of monolayers are free of holes and defects approaching molecular dimensions (of relevance for gas permeation). The structure of the porous polymer supports has been predominantly characterized by means of scanning electron microscopy with a resolution limited to about 50 nm. Recently, scanning force and scanning tunnelling microscopies have been introduced and intensively explored for a precise characterization of the LB-films surface structure with a very high spatial resolution.^{22–35}

In the present work, the surface modification of a hydrophobic microporous polypropylene membrane by deposition of very thin arachidate LB-films is characterized by means of scanning force microscopy (SFM) and contact angle measurements. While the contact angle hysteresis measured reflects the alteration of the membrane surface roughness and porosity upon LB-film deposition, the SFM yields detailed information on the composite membranes surface topography from a molecular up to a micron scale. The combination of both techniques proved to be very sensitive and fruitful for ultrathin surface coverage characterization.^{22,32,33,36} The influence of counterions (Ca^{2+} , Cd^{2+}) and of the number of the deposited layers on the integrity and homogeneity of the membrane thin film coating is also reported. The gas transport through the composite membranes will be described in a separate publication.

Methods and Materials

Langmuir–Blodgett Deposition. A KSV-5000 Langmuir–Blodgett trough, operated under clean room conditions, was employed for the preparation of the LB-films of arachidic acid and its cadmium and calcium salts. The surface pressure was controlled by means of the Wilhelmy plate method.³⁷ The monolayers were transferred at a constant surface pressure of 30 mN/m. The deposition speed of 50 mm/min resulted in transfer ratios of nearly unity. The subphase temperature was held constant at $19 \pm 1^\circ\text{C}$.

All chemicals used for the preparation of the spreading solutions (1×10^{-3} M) and the subphases (2×10^{-4} M) were of highly pure grade (Merck). The water used for the preparation of the salt subsolutions was doubly filtered by means of the MilliQ system (Millipore Co.). Arachidic acid LB-films were deposited at pH 3.0, cadmium arachidate at pH 5.6, and calcium arachidate at pH 6.0.

The substrates for LB-deposition were polished silicon wafers or a commercial polypropylene membrane, Celgard 2400 (Celanese Corp., New York, NY). The silicon substrates were hydrophobized in hexamethyldisilazane (HMDS) vapors in a closed chamber for 1 h, rinsed with organic solvents and water, and dried at 110°C . The microporous structure of the membrane Celgard 2400 is formed by extrusion, annealing, and stretching of isotactic polypropylene.⁷ For LB-transfer, the porous polypropylene foils were fixed on mica stripes. This allowed deposition of arachidate layers on only one of the sides of the polymer substrates, yielding asymmetric composite membranes.

Contact Angle Determination. Static advancing, Θ_a , and receding, Θ_r , contact angles were measured for the bare substrates and for the deposited LB-films. Contact angle hysteresis, $\Delta\Theta = \Theta_a - \Theta_r$, was also determined. The experimental setup used for wetting hysteresis investigation has been described in detail previously.^{38,39} Contact angles were measured with a goniometer microscope (Carl Zeiss, Jena) by means of the sessile drop technique. The samples were placed in a sealed chamber at room temperature (about 25°C). Sessile drops of about 3–4 mm in diameter were formed on the samples by application of fluid through the horizontally cut tip of a microsyringe. The angles were measured on both sides of, at least, three drops without removing the syringe tip. The reported values were mean quantities of about 16 readings. The experimental error was $\pm 1.5^\circ$. Pure water (MilliQ) was used as probe liquid. The water surface tension was determined by means of a digital tensiometer (type KC 12, original glass beaker, platinum plate, and software provided by Krüss, Hamburg).

Scanning Force Microscopy. All samples were investigated by means of a Nanoscope III scanning force microscope (Digital Instruments, Santa Barbara). This instrument allowed a detailed study of the molecular order of the "skin" LB-layers, as well as of the micromorphology of both bare and composite membranes.

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Table 1. Static Advancing, Θ_a , and Receding, Θ_r , Contact Angles of Water on a Polypropylene Membrane, Celgard 2400

membrane side	$\langle\Theta_a\rangle$, deg	$\langle\Theta_r\rangle$, deg	$\langle\Delta\Theta\rangle$, ^a deg
A	118	80	38
B	124	86	38

^a $\Delta\Theta = \Theta_a - \Theta_r$ is the contact angle hysteresis (in degrees).

Table 2. Static Advancing, Θ_a , and Receding, Θ_r , Contact Angles and Their Hysteresis, $\Delta\Theta$ (in degrees), for LB-Films of Arachidic Acid Deposited on a Hydrophobized Silicon Substrate^a

number of layers	$\langle\Theta_a\rangle$, deg	$\langle\Theta_r\rangle$, deg	$\langle\Delta\Theta\rangle$, deg
0	97	92	5
2	109	93	16
6	110	90	20
12	110	92	18
20	110	86	24

^a The probe liquid was pure water.

The surfaces were scanned with a silicon tip at room temperature in the constant force mode with two different scanners (head A, maximum scan size of 1 μm ; head J, maximum scan size of 130 μm) and at a scan rate of 3.21 Hz.

Results

Wetting Hysteresis. The results of the contact angle measurements with water sessile drops on a bare polypropylene membrane are presented in Table 1. The wettability of both sides of the Celgard 2400 membrane, denoted respectively as side A and side B, was determined. The difference of the static contact angle values on the sides A and B demonstrates the asymmetry of the membrane surface characteristics. In addition, the advancing contact angles measured are larger than those for nonporous hydrophobic polypropylene materials.²² Side B of the investigated porous polypropylene support was selected for LB-film deposition because of its higher pores concentration as compared to side A.

To distinguish the effects on the wetting hysteresis due to the substrate surface roughness and porosity from those due to the LB-film coverage for a different number of deposited layers, contact angle hysteresis was compared for LB-films deposited on a nonporous smooth silicon substrate and on a membrane support. The results are presented in Table 2 and 3, respectively.

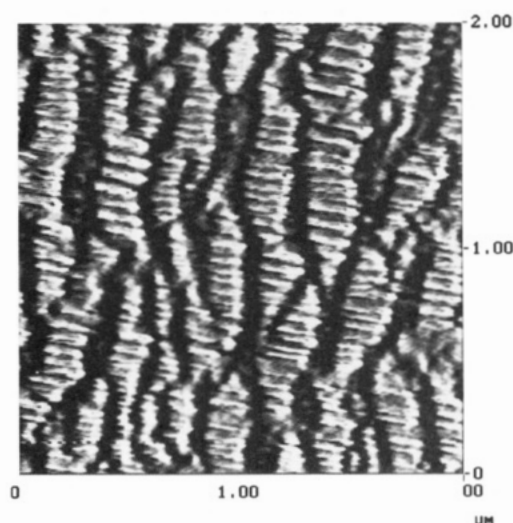
The small hysteresis determined for the hydrophobized silicon wafers (Table 2) indicated that these substrates can be really considered as very flat and homogeneous reference supports for LB-film deposition. The established increase in the wetting hysteresis upon LB-transfer of arachidic acid films seems to be related to the intrinsic structural features of these multilayers. Although the contact angle hysteresis on the LB-samples is larger than that for the hydrophobic silicon substrate, a systematic correlation with the number of deposited arachidic acid monolayers cannot be established from the obtained data. The contact angle hysteresis is a maximum for LB-film consisting of 20 monolayers.

Static contact angles of water on LB-films deposited on a polypropylene membrane are shown in Table 3. The effect of the LB-film is more pronounced on the advancing angles as compared to the receding ones. The effect of the number of deposited monolayers is negligible. In this case, the wetting hysteresis on arachidic acid films does not differ substantially from that of the bare polypropylene membrane. Its magnitude is considerably larger than

Table 3. Static Advancing, Θ_a , and Receding, Θ_r , Contact Angles and Their Hysteresis, $\Delta\Theta$ (in degrees), for LB-Films of Arachidic Acid (HA), Calcium Arachidate (CaA), and Cadmium Arachidate (CdA), Deposited on Polypropylene Membrane^a

LB films	number of monolayers	$\langle\Theta_a\rangle$, deg	$\langle\Theta_r\rangle$, deg	$\langle\Delta\Theta\rangle$, deg	R_a
	0	124	86	38	3.82
HA	2	118	80	38	1.43
	6	115	79	36	
	12	115	79	36	
	20	115	79	36	
CaA	2	111	82	29	1.29
	6	111	83	29	
	12	112	83	29	
	20	112	83	29	
CdA	2	111	86	25	1.24
	6	111	86	25	
	12	111	86	25	
	20	111	86	25	

^a The probe liquid was pure water. The film roughness R_a (in nm) was determined over 4 $\mu\text{m} \times 4 \mu\text{m}$ areas of the SFM images.

**Figure 2.** Microporous structure of the side B of the polypropylene membrane Celgard 2400. The pores are seen as numerous light thin horizontal stripes. SFM image size, 2 $\mu\text{m} \times 2 \mu\text{m}$.

that for the films deposited on silicon substrates. Table 3 illustrates that the contact angle hysteresis decreases in the order arachidic acid > calcium arachidate > cadmium arachidate.

Scanning Force Microscopy Images. A representative SFM image of the microporous structure of the bare polypropylene membrane is presented in Figure 2. The membrane surface is characterized by two kinds of regions: unstretched pore-free areas (seen as dark areas) and stretched regions (light areas). The lighter regions exhibit a typical size of about 250 nm \times 1000 μm . The average pore size, determined from the SFM images, is 250 nm \times 50 nm.

Surface morphology of the composite membranes was analyzed by means of SFM at two different scales of imaging. Figure 3 shows top views of the images of different LB-multilayers.

Surface roughness, estimated from the SFM images of LB-films consisting of a different number of monolayers, is presented in Table 3. The roughness, R_a , was calculated with the SFM surface analysis software (version 2.5) using the expression

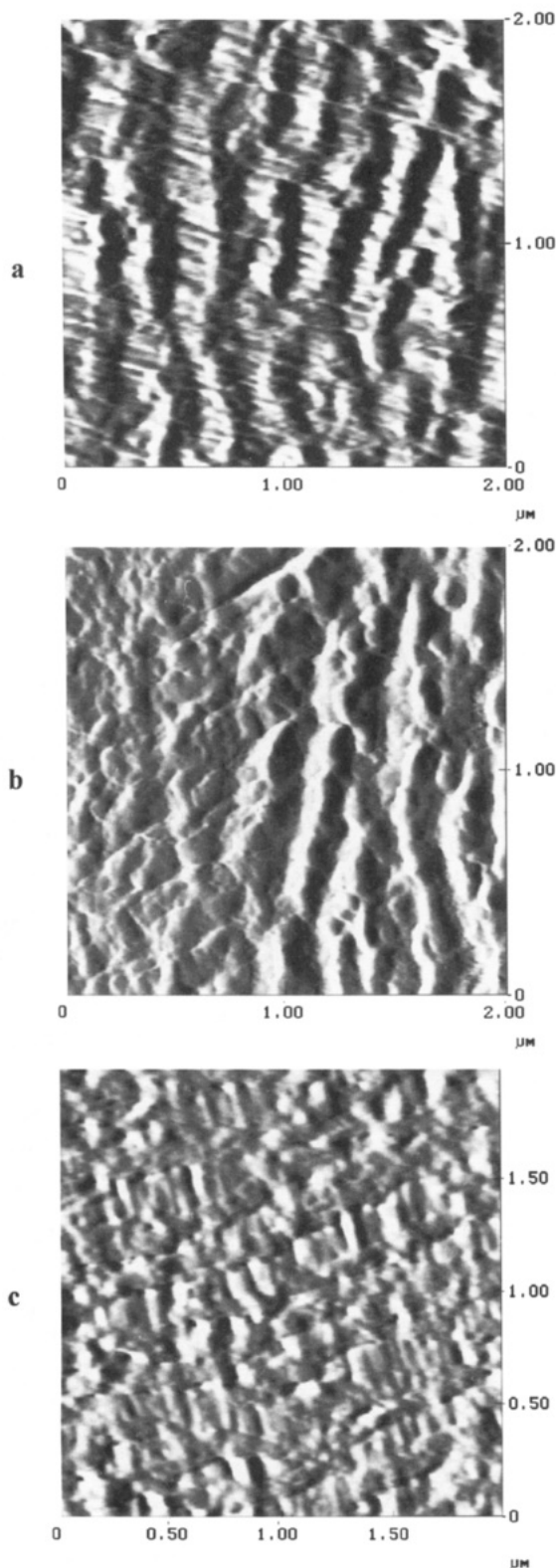


Figure 3. SFM images of the polypropylene membrane surface modified by deposition of six layer LB films of arachidic acid (a), calcium arachidate (b), and cadmium arachidate (c). Scan size (2×2) μm^2 .

$$R_a = L_x^{-1} L_y^{-1} \int_0^{L_y} \int_0^{L_x} |f(x,y)| dx dy$$

where $f(x,y)$ is the surface relative to the center plane, and L_x and L_y are the dimensions of the surface. Images of $4 \mu\text{m} \times 4 \mu\text{m}$ areas are used in all cases for the roughness calculation.

The comparison of R_a values for the investigated materials illustrates that the roughness of the porous

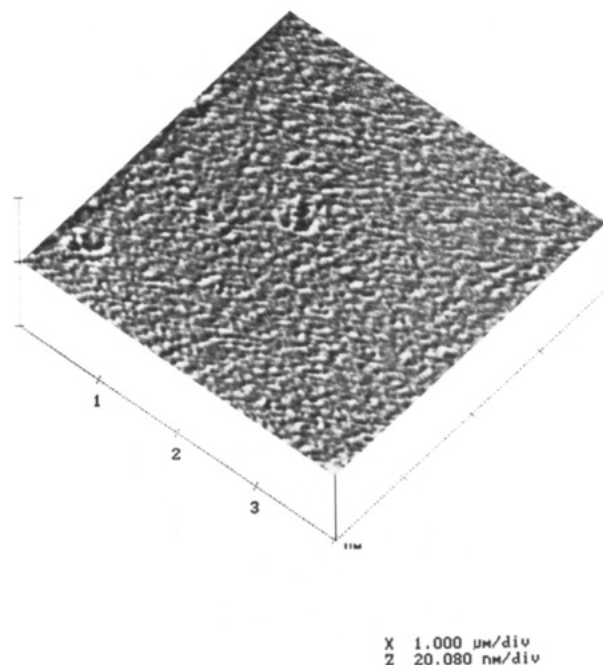


Figure 4. SFM image of a six-layer arachidic acid LB-film deposited on a hydrophobized silicon substrate. Image size, $4 \mu\text{m} \times 4 \mu\text{m}$.

membrane support is substantially reduced by the LB-film transfer. It decreases in the same direction as the wetting hysteresis (arachidic acid > calcium arachidate > cadmium arachidate). This result agrees with the topographic information obtained from Figure 3. It shows that the deposition of arachidic acid layers has a very little effect on the surface morphology of the polypropylene membrane. The same stretched and unstretched regions are seen both in Figures 2 and 3a. It seems that the film follows the substrate surface topology. Thus, porous and pore-free surface areas of the underlying membrane can be distinguished through the LB-film.

The comparison of the images in Figures 2 and 3b,c illustrates that in the cases of the arachidate salt films the pore structure of the polypropylene is masked. These LB-films prove to be more efficient in covering and bridging the membranes pores.

The morphological features observed for the composite membranes (Figure 3) are very different from those of the LB-films transferred to a silicon support (Figure 4). The latter exhibit a much smoother surface with absence of a long-range order on a large scale of imaging. The roughness ($R_a = 0.29$ nm) of the two-layer arachidic acid LB-films on a hydrophobized silicon substrate (Figure 3) is essentially higher than that of the bare hydrophobic support ($R_a = 0.017$ nm). However, it is much smaller than that of the bare Celgard 2400 membrane ($R_a = 3.82$ nm) as well as of the composite membranes (R_a values in Table 3).

Molecular resolution images of the LB "skin" layers of the composite membranes are presented on Figure 5. The high roughness of the supporting polypropylene membrane did not prevent the observation of molecular resolved areas in the images of the arachidic acid and calcium and cadmium arachidate layers. All LB-films studied showed a rather ordered structure. Individual terminal groups are clearly visible, and lateral distances along the scan line of about 6.8 \AA (arachidic acid), 5.5 \AA (cadmium arachidate), and 6.0 \AA (calcium arachidate).

Discussion

It is generally understood that the structural arrangement and quality of the transferred LB-films are deter-

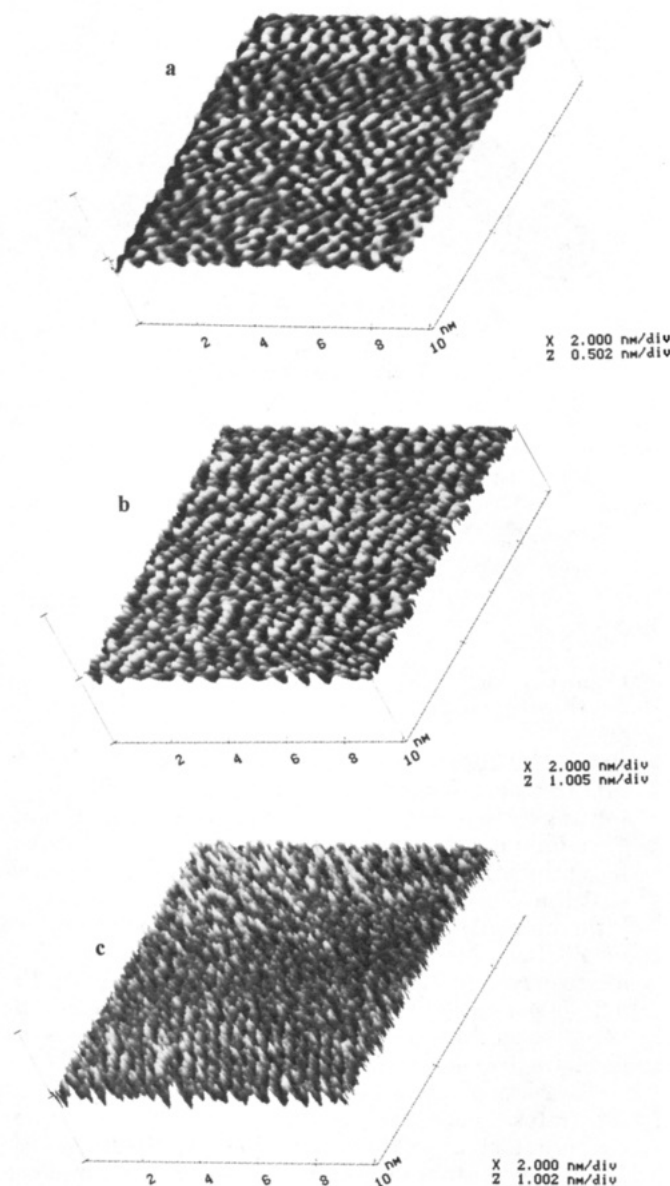


Figure 5. Molecular resolution SFM images of two-layers LB-films of arachidic acid (a), calcium arachidate (b), and cadmium arachidate (c) deposited on a porous polypropylene support. Scan size, $10 \times 10 \text{ nm}^2$.

mined by the organization of the corresponding floating monolayers, the deposition conditions, the inter- and intralayer interactions in the multilayers, and their adhesion to the substrate. Studies by means of scanning electron and scanning force microscopies^{10,40} have addressed the question about the role of the surface properties of the solid supports on the order and homogeneity of the transferred multilayers. Systematic investigations of the effect of the substrate wettability and surface roughness on the monolayer deposition and stacking order of the transferred LB-films have been performed only in a few studies.^{41–44}

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The polypropylene membrane investigated here was characterized by a very high hydrophobicity and the lack of swelling in water. This facilitated the film transfer. The membrane pores were found to be fine enough to have a weakly disturbing influence on the integrity of the deposited LB "skin" layers. It was surprising, at first sight, that molecular periodicity could be observed in films on such irregular surface substrates. However, the observation of the molecularly resolved areas is in agreement with the recent SFM finding⁴⁰ that the periodicity of the cadmium arachidate LB-layers is predominantly determined by the intermolecular forces, driving the film self-assembly, rather than by the surface features (disorder or periodicity) of the underlying substrate. The importance of the interactions of the head groups in the determination of the molecular order of the LB films has been proven in several SFM investigations^{24,32–34} as well.

It follows from the present study that the substrate surface features and its roughness do not have a considerable effect on the film morphology for those LB-layers with strong intermolecular interactions (e.g. cadmium arachidate). The morphological organization of the films characterized by weaker interlayer (hydrogen) bonds (e.g. arachidic acid) is determined by the underlying solid support. Homogeneous coverage of the membrane pores, essential for the performance of the composite membranes, was possible only by deposition of films with strong (ionic and coordination) interlayer bonds. In this case, the periodic arrangement of the molecules, stabilized by intermolecular interactions, is not prevented by the disorder of the membrane support. The SFM results for films deposited on a microporous substrate confirm the well-established sequence in the strength of the interlayer interactions and stability⁹ of the LB multilayers: cadmium arachidate > calcium arachidate > arachidic acid.

The two surface-sensitive techniques, presently employed, provided complementary information about the quality of the membrane porous surface coating by LB-film deposition. On the basis of the obtained micromorphological results, the wetting hysteresis can be better understood. Common reasons for the observation of contact angle hysteresis are the physical roughness and chemical heterogeneity of the solid substrate^{45–50} and the intermolecular interactions in the three-phase contact zone.⁵¹ Recently, several factors, other than surface imperfections, have been shown to cause contact angle hysteresis:^{22,52–54} molecular rearrangement occurring at the interfaces, relaxation phenomena, instability of the deposited films, and their desorption or displacement at the three-phase contact line.

There is an agreement between the conclusions which can be drawn from the present contact angle and SFM results regarding the surface roughness of the investigated surfaces. Since the investigated porous polypropylene

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support did not swell in water, the reasons for the observed large contact angle hysteresis for the bare membrane are predominantly related to the roughness and the heterogeneously distributed porosity of its surface. "Contact line corrosion"^{22,54} was not observed with the investigated LB films. This is an indication of good adhesion of the deposited organic "skin" layers on the polymer support.

Contact angles hysteresis of the bare polypropylene membrane ($\Delta\theta = 38^\circ$) was reduced after LB-deposition of the arachidic acid salts films containing bivalent counterions (Table 3). The difference in the wetting hysteresis values for the cadmium arachidate and calcium arachidate films ($\Delta\theta = 25^\circ$ or 29° , respectively) correlates with the different degree of the pores coverage which is achieved by the deposition of these "skin" layers. The magnitude of the hysteresis remains constant on increasing the number of transferred monolayers, though this magnitude is different for each surfactant salt. The inherent packing and in plane surface morphology of the different arachidate LB-films seem to account for the observed different wetting hysteresis values. The cadmium arachidate films are obviously more homogeneous than those of calcium arachidate. They mask completely the surface topography of the underlying porous substrate (Figure 4c).

The larger hysteresis found for the arachidic acid films, as compared to those for the metal salts films (Table 3), can be explained by the instability of the arachidic acid multilayer structure on aging and its disorder on a macroscopic scale. These films do not alter visibly either the surface morphology of the porous membrane support (Figure 4a) nor its wetting hysteresis. The increase of the contact angle hysteresis with the number of deposited arachidic acid layers on a smooth silicon substrate might be due either to an accumulation of defects during the deposition process or to a rearrangement of the multilayer structure after the deposition. Both processes will result in an increase of the roughness of the films, as it was established.

It is remarkable that regardless of the initial wettability of the substrate, LB-deposition of close-packed monolayers

leads to the same values of the advancing static contact angles of about 110° – 112° . Such values are characteristic for smooth surfaces exposing methyl terminal groups.^{48–50} Values of the static contact angles higher than these are indicative of the roughness of the CH_3 -group-terminated surfaces. Therefore, all results suggest that, irrespectively of their roughness, finely porous polymer supports can be homogeneously covered by densely packed ordered LB-multilayers stabilized by strong intermolecular interactions.

Conclusions

The presented results of contact angle hysteresis measurements and scanning force microscopy are in good qualitative agreement. Both surface-sensitive techniques illustrate that the polypropylene membrane surface becomes much smoother and more homogeneous upon transfer of cadmium or calcium arachidate "skin" LB-films. These LB-films show in-plane surface periodicity on a molecular scale which is essentially undisturbed by the irregularity of the porous support.

Surface roughness analysis of SFM images of micrometer scale reveals that LB-deposition of cadmium and calcium arachidate is more effective in membrane surface modification than the transfer of arachidic acid layers. The stronger interlayer interactions in these films facilitate the bridging of the membrane micropores, resulting in a decreased surface roughness and a reduced wetting hysteresis. The increase of the number of deposited monolayers does not change the surface homogeneity and order of the arachidate "skin" layers. The wetting hysteresis shows constant values after transfer of, 6–10 monolayers. The relation between the established composite membranes' micromorphology and the gas transport through them with addressed in a forthcoming publication.

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