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Langmuir and Langmuir–Blodgett films of octadecylaminodihydroxysalicylaldehyde

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Abstract

Octadecylaminodihydroxysalicylaldehyde, an amphiphilic schiff base has been prepared and the behaviour of both the stable Langmuir films at air/water interface as well as the Langmuir–Blodgett (LB) films have been studied using photoelastic-modulated Fourier transform infrared (PEM–FTIR), ellipsometry at Brewster angle and transmission electron microscopy (TEM). The results indicate that to accommodate the cross-sectional mismatch between the tail and the head group regions, the chains tilt allowing the film to organise in a stable arrangement. It is also seen that the competition between the packing of the head groups and the long alkyl chains has important consequences for the microscopic structure of the LB films and the size of the ordered domains. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Monolayers at the air/water interface are an appropriate system to study the influence of chemical variations on the microscopic quasi two-dimensional order. One of the most important influences on the packing of the monolayer is certainly the head group as a result of steric hindrance as well as of its specific interactions with the monolayer environment. Such ordered monolayers when transferred onto solid substrates using the Langmuir–Blodgett (LB) technique provide a means of organising complex molecules and have many potential applications, especially in the areas of molecular electronics, non-linear optics and conducting thin films [1]. Molecules with relatively large head groups compared to alkyl chains are often used as functionalised LB films. The design of such functional organic molecules require an understanding of the packing properties of the molecules with a cross-sectional mismatch between head and tail group. As an example of such a molecule, we present here the monolayer properties at air/water interface and the LB film forming capability of an amphiphile containing a rigid schiff base segment- octadecylaminodihydroxysalicylaldehyde (ODADS) (Fig. 1). Freyer et al. have shown that aromatic hydrocarbons with hydrophilic substituents

form stable layers provided there is a balance between hydrophobic and hydrophilic ends of the molecule [2]. LB films of such functionalised molecules with cross-sectional mismatch between head and tail are well characterised by synchrotron and electron microscopy (EM) [3]. X-ray diffraction (XRD), atomic force microscopy (AFM) and high resolution electron microscopy of fatty acids and related molecules in LB films have been reported earlier [4–8]. The schiff base containing amphiphiles reported in the literature as models of bilayer forming materials [9–11], in polymeric LB films [12] and in metal complexes of macrocyclic schiff bases and long alkyl chain schiff bases [13,14] are typical examples of such compounds with the cross-sectional mismatch between the hydrophilic and the hydrophobic parts. In this study ODADS has been synthesised and its monolayer properties at air/water interface using PEM (FTIR) [15] and ellipsometry [16] have been studied. The packing behaviour of this compound in LB films have been analysed using transmission electron microscopy (TEM).

2. Experimental details

The compound ODADS was obtained by reacting octadecylamine with 2,4-dihydroxy salicylaldehyde (Sigma Chemicals, USA) in methanol (HPLC grade) in equimolar amounts. The product obtained was recrystallised several

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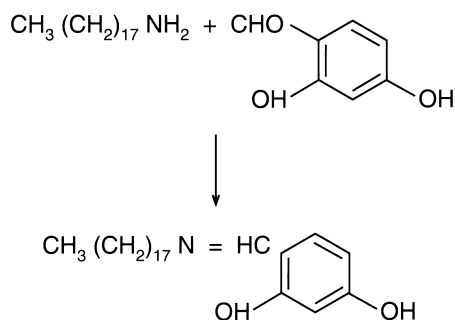


Fig. 1. octadecylaminodihydroxysalicylaldehyde (ODADS).

times in chloroform:methanol (3:1 v/v) mixture and characterised by gas chromatography that showed 99.5% purity and by elemental analysis confirming the expected amounts of C and H within 0.2%. The substance was dissolved in HPLC grade chloroform to a millimolar concentration and typically 100 μl of the solution was spread on an aqueous subphase (deionised double distilled water pH 6.5). The π -A isotherms, variation of π with time at constant area and compression-expansion isotherms were recorded using a NIMA 611 model trough with a thermostat ($T = 293\text{ K}$). The trough with a Wilhelmy balance setup registered surface pressure with an accuracy of 0.1 mN/m. The teflon trough has analytical area of 600 cm^2 , enabling a very accurate determination of the area/molecule. The measurements of PEM-FTIR and ellipsometry were carried out with a Bruker IF S48 spectrometer using ZnSe photoelastic modulator (Hinds type II) and two ZnSe plates at Brewster incidence. The ellipsometry measurements were carried out with a set-up at Brewster angle using a HeNe laser operating at 632.8 nm. Since the absorbance is negligible at this wavelength, the variation of the ellipsometric angle Δ is a relevant parameter which changes at the interface. In practice, the difference $\delta\Delta = \Delta_f - \Delta_r$ (Δ_f being the angle measured for the film on water and Δ_r that of pure water) which is related to the thickness and index of refraction of the interfacial films, were recorded simultaneously with π and A (Fig. 2). during compression of the monolayer. Spatial resolution of this technique is defined by the cross-section of the laser beam at the interface is about 1 mm^2 . The LB films were transferred onto carbon coated copper grids (mesh size 400) at $\pi = 5\text{ mN/m}$ and selected area diffraction ($1 - 5\text{ }\mu\text{m}^2$) from ordered domains were obtained by the small area method using a Philips STEM instrument.

3. Results and discussion

3.1. π -A isotherms

A solution of ODADS was used for spreading the molecules onto the surface of ultrapure water. Fig. 2 shows the isotherm measured at a compression speed of 0.05

$\text{nm}^2/\text{molecule min}$. The isotherm was independent of both the initial volume of the expanded solution and the concentration of the spread solution and was reproducible. The curve shows a smooth transition from the gaseous to a liquid expanded (LE) state with a slight kink at about 24 mN/m leading to a steep portion of the isotherm. The area/molecule at 30 mN/m is 0.25 $\text{nm}^2/\text{molecule}$. This value is in agreement with the head group area calculated from chem 3D which gave 0.27 nm^2 . The film collapses at about 60 mN/m with its compressibility reaching infinity and the surface pressure falling off. The stability of the isotherms (not shown in the text) was studied by analysing the change in the molecular area at constant pressure of 20, 25, 30 and 40 mN/m and showed maximum stability at 30 mN/m. It was observed that even after 6 h the molecular area loss was only about 1% of this pressure. The liquid expanded isotherm with a steep increase in surface pressure after about 25 mN/m is indicative of a solid–solid transformation.

3.2. PEM-FTIR studies

Fig. 3 shows the PEM-FTIR signals obtained for ODADS at $\pi = 2$ and 30 mN/m, respectively, in the region 3050–2750 cm^{-1} corresponding to $\nu_{\text{as}}\text{CH}_2$ and $\nu_{\text{s}}\text{CH}_2$ bands. The frequencies of the methylene stretching vibration modes have been previously used as an indication of the ordered states of the packing of the monolayer in the condensed state. The frequencies, shapes and intensities of the infrared C–H stretching bands provide information on the orientation, conformation and packing of the hydrocarbon chain in the monolayer. The $\nu_{\text{as}}\text{CH}_2$ and $\nu_{\text{s}}\text{CH}_2$ bands appearing in the spectrum correspond to a preferential in-plane orientation of transition moments which is consistent with the alkyl chains quasi perpendicular to the interface. The appearance of the symmetric and asymmetric stretching vibrations in the present experiment at 2918 and 2850 cm^{-1} indicate that the alkyl chain is highly ordered (trans zig-zag conformation) at $\pi = 2\text{ mN/m}$ as well as at 30 mN/m. the ratio of the

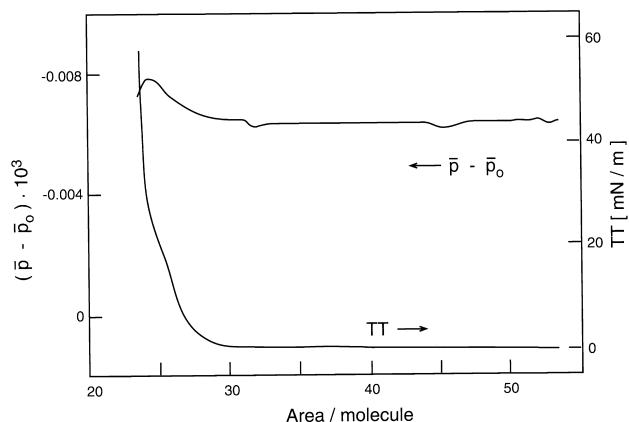


Fig. 2. π -A isotherm of ODADS. Y-axis title has to be changed as $\delta\Delta = (\Delta_f - \Delta_r) \times 10^3$.

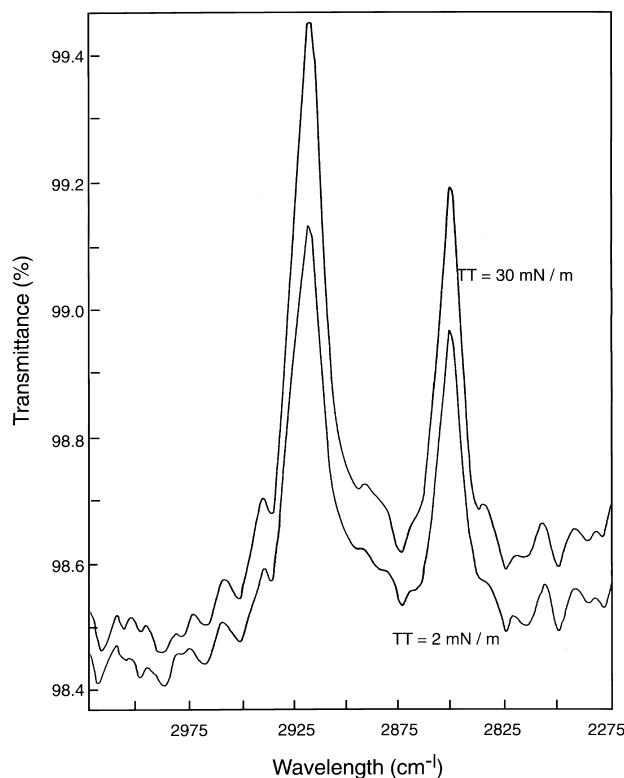


Fig. 3. PEM-FTIR signals for ODADS at $\pi = 2$ mN/m and 30 mN/m.

integrated intensities corresponding to I_{as}/I_s at both the surface pressures show a value of about 25 (Table 1).

This indicates that the monolayers are isostructural and that their constituent chains are preferentially oriented in a way that may be described as anisotropic. It is seen that as the surface density increases, the signal intensity increases indicating that the molecules spread at the air/water interface stretch further away from water. The signals from the hydrophilic groups immersed in water being weak cannot be observed directly in the spectrum. Hence only the bands corresponding to the long alkyl chains are indicated here.

3.3. Ellipsometry data

The ellipsometric data were recorded simultaneously

with the π -A isotherm (Fig. 2). The experiment was carried out to characterise the Langmuir films and also to get an estimate of the thickness of the interfacial layers. In the regions of very low surface pressure $\Delta\delta$ was equal to 8° . As the film was compressed $\Delta\delta$ was found to increase with the compression with a maximum $\delta\Delta_m = 11^\circ$. In principle, the thickness e_f of the interfacial film can be evaluated from $\delta\Delta$ if the refractive index n_f of the film is known [17]. We therefore take the representative values from n-alkanes ($n^{20}_D = 1.398$), this estimate assumes that there is no remaining solvent in the spread film (and hence the increase in the n_f value). A value of $n_f = 1.50$ is normally adopted for organic amphiphiles [1]. Using these values the thickness was estimated to be 1.95 nm. The good order seen in the Langmuir films points to refractive index anisotropy assuming that the film should have an isotropic refractive index.

3.4. TEM micrographs

Fig. 4 shows the transmission electron micrographs of ODADS at $\pi = 5$ and 30 mN/m, respectively. The selected area diffraction ($1 \mu\text{m}^2$) and electron diffraction obtained for the single ordered domains by the small area method confirm the phase transition to the liquid condensed state. Fig. 4a shows the electron diffraction patterns obtained for a single ordered domain obtained for the film transferred at 5 mN/m while Fig. 4b shows that of the film at 30 mN/m. It is seen that the electron diffraction pattern of the low and high pressure regions are distinct. The ring pattern seen at $\pi = 5$ mN/m is most probably tilted phase while in the condensed phase at $\pi = 30$ mN/m hexagonal patterns are obtained and the orientation does not change when the electron beam is moved across a single platelet. Moreover, it was observed that the crystal planes of different platelets exhibit the same orientation if they are merged whereas they are oriented differently when the 2D crystallites are separated. This is possibly due to a repulsive force between platelets arising from the different orientation of the crystal planes in the regions of contact. Also it was observed that the dark platelets exhibited a long range orientational order at all pressures above $\pi = 24$ mN/m. It is seen from the electron micrographs between the head and tail regions. Further the films clearly undergo a packing change in going from the larger molecular area to a close packed structure. The

Table 1

Values of integrated intensities for ν_{as} and ν_s CH_2 vibrations at $\pi = 2$ mN/m and 30 mN/m for ODADS from PEM-FTIR

Surface pressure (mN/m)	Peak position (cm^{-1})	Intensity	Width	Integral
2	2850	0.0045	10.44	0.075
	2889	0.0005	13.9	0.013
	2918	0.0065	18.21	0.019
	2941	0.0002	3.86	0.012
30	2850	0.0059	10.68	0.099
	2887	0.0007	9.66	0.011
	2917	0.0091	17.62	0.254
	2941	0.0005	3.86	0.004

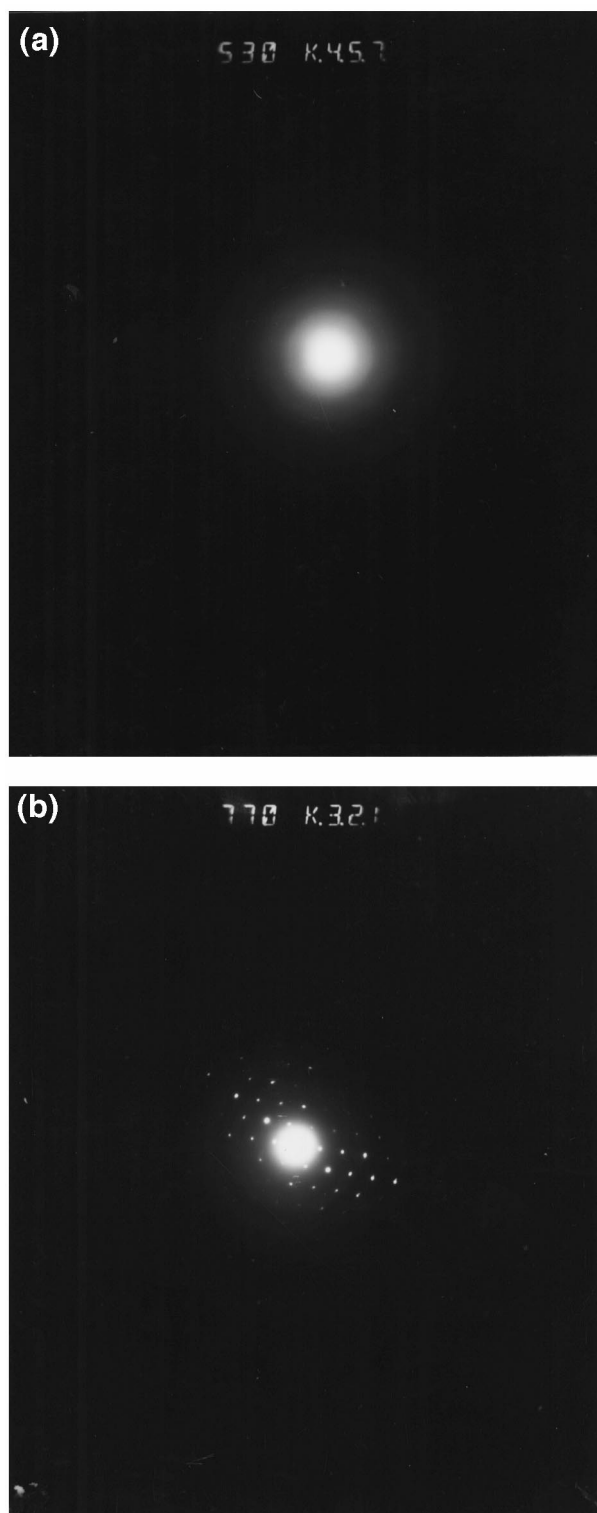


Fig. 4. Electron diffraction patterns for the films transferred at (a) 5mN/m and (b) 30mN/m.

observed discrepancy between the FTIR measurements indicating isostructural films as against the TEM results may be explained as follows: TEM measurements involve

resolution in the nanometer range. Also what appears in the 'liquid expanded' (LE) phase at 5 mN/m in the TEM as rings may be due to condensed microdomains consisting of similar tilt at higher surface pressures.

We have reported a study of a novel molecule with a shape that cannot be approximated with a simple cylindrical model and has a cross-sectional mismatch between the head group and the long alkyl chain that is capable of forming both stable monolayers at air/water interface as well as LB films. The introduction of head groups with large inplane dipoles seems to have very little effect on molecular conformation within the monolayer and the molecules are in trans conformation.

In contrast, these in-plane dipoles have a profound effect on the molecular tilt. This molecule is especially interesting due to the schiff base linkage and has potential applications in the field of organic/inorganic composites and in non-linear optics. Further from the results it can be concluded that the alkyl chains form a largely separate layer next to air and containing no water. Also the alkyl chain thickness does not vary with surface coverage due mainly to the 'trans' conformation of the chains.

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