Langmuir–Blodgett films from dioctadecylamine picrate

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Langmuir–Blodgett (LB) films prepared from picrate of dioctadecylamine(PDODA) and dioctadecylamine (DODA) were studied for the high picrate dipole moment, potentially effective in pyroelectricity. Stable condensed monolayers were obtained on pure water at pH from 5 to 8. About 90% of the PDODA in the films was hydrolysed to DODA. Moderate repulsion between ionized polar heads in the films promoted the desirable X- or Z-type deposition on solid supports, but it prevented a successive deposition of more than five monolayers. At pH below 5 the content of $CdCl_2$ or picric acid in the subphase decreased the PDODA hydrolysis. Strong repulsion under these conditions caused an expansion of the films and prevented the deposition of more than a single monolayer.

1. Introduction

Ordered molecular assemblies containing oriented dipole moments are studied for potentially useful pyroelectric, piezoelectric and second-order non-linear optical effects [1, 2]. One of the effective ways to make dipolar organic molecules form highly ordered assemblies is the Langmuir-Blodgett (LB) technique [3].

The deposition of uniform LB films onto various supports including metals and semiconductors is possible, thus rendering LB films applicable in electronic devices [4]. Owing to a very low thermal mass in superthin pyroelectric LB films, a short response time is expected. In conventional Y-type LB films the dipole moments of adjacent layers cancel each other, and therefore the neat polarization is zero. Spontaneous polarization is observed if the Y-type film is fabricated from alternate layers of complementary dipole character [5, 6] and/or if monolayers of dipolar molecules are arranged in X- or Z-type films [7, 8].

Although free picric acid has a dipole moment $\mu = 1.75\,D$ [9], picrates of amines have a high dipole moment (e.g. picrate of octadecylamine has $\mu = 12.3\,D$ in dioxan at 303 K [10]) mainly localized on the intimate ion pair $O^-...HN^+R_3$ and virtually independent of the amine nature [10]. Therefore, they seem to be adequate candidates for the construction of pyro- and piezoelectric devices. Unfortunately, these substances undergo hydrolysis to free acid and amine in contact with water and water solutions. It can be supposed, however, that in LB layers the hydrolysis of the picrates could be suppressed by a local increase in the picric acid concentration near the interface caused by the electrical field of a charged monolayer [11].

This paper deals with the LB films of picrate of

dioctadecylamine (PDODA)
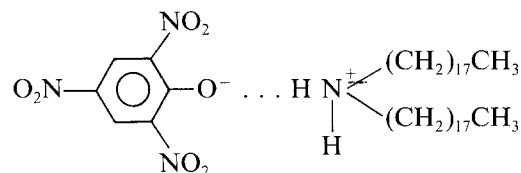
Technological conditions were investigated, under which monolayers containing unhydrolysed PDODA could be prepared and transferred on solid substrates as X- or Z-type LB films.

2. Experimental details

2.1. Materials

Dioctadecylamine (DODA, Fluka) was recrystallized from methanol. Picrate of dioctadecylamine (PDODA) was prepared by boiling DODA for 30 min with a small excess of picric acid in ethanol. The product was recrystallized from methanol three times, the melting point is 63 to 64° C.

2.2. LB films

PDODA and DODA were spread from rectified chloroform, usually at a 3.5×10^{-3} M concentration. Aqueous subphases were prepared by dissolving NaCl, KCl, $CdCl_2$, $(NH_4)_2SO_4$ and picric acid (PA) in quartz-bidistilled water (original resistivity 1 MΩ cm). The pH was adjusted with HCl or NaOH and checked again in a LB trough after the film experiments were finished. Microscope glass supports were rinsed in a solution of $K_2Cr_2O_7$ in H_2SO_4 for 1 min, washed with water, cleaned ultrasonically in water and then in isopropanol, cleaned in the isopropanol vapour and dried in a dust-free laminar air flow box (class 100). Glass, glass hydrophobized by reaction with a 10% solution of $ClSi(CH_3)_3$ in xylene at 50° C for 4 h, glass coated with two monolayers of arachidic acid

transferred from 2.5×10^{-4} M CdCl$_2$ subphase at pH 6.2, glass coated with vacuum deposited aluminium, and teflon were used as substrates for PDODA films deposition.

Monomolecular films were formed on aqueous subphases in teflon trough thermostated at 20°C. The films were compressed with a movable teflon barrier, usually at a rate of 1.5 mm min^{-1}, while measuring the surface pressure as a force on the floating polyethylene barrier. The films were transferred on the substrate by its vertical dipping at a rate 3.3 mm min^{-1}, while maintaining a constant surface pressure (usually 20 mN m^{-1}). The transfer ratio R ($R = \Delta A/P$, where ΔA is the decrease of the monolayer area on water and P is the area of the substrate on which the monolayer was transferred) was measured continuously.

2.3. Investigation of PDODA hydrolysis in contact with water

The transfer of PA from PDODA benzene solutions into water: 1 ml of a 1.7×10^{-4} M PDODA solution and 3 ml of an aqueous solution were mixed and shaken for 1 h. The solutions were separated, and the concentration of unhydrolysed PDODA in benzene and the concentration of free PA in the water phase were determined from UV–visible spectra (from 348 and 416 nm bands for PDODA and 356 nm band for PA).

PDODA hydrolysis at water–air interface. A large sessile drop (surface area about 550 cm^2) was formed by pouring 300 ml of the aqueous solution on the polyethylene foil. PDODA in chloroform was spread on the spot surface. After 2 h at 23°C a syringe needle was dipped under the water surface and the subphase was slowly drawn off. On reducing the water–air interface area, the PDODA film was transferred on the polyethylene surface at the receding air–water–polyethylene boundary. After all the subphase was removed the film was washed off the polyethylene surface with chloroform. The amount of unhydrolysed PDODA in chloroform was determined with UV–visible spectroscopy and compared with the amount of PDODA originally spread on the subphase. The spectral bands of free PA were observed in the aqueous subphase.

The content of unhydrolysed PDODA in three

monolayers deposited on two layers of arachidic acid on a hydrophobized glass plate was estimated from the transmission UV–visible spectra, assuming similar specific extinction coefficients for PDODA in the LB films and in chloroform solutions used for calibration.

3. Results and discussion

Free PA is easily soluble in water at low concentrations and only slightly soluble in benzene. For example no transfer of PA was observed from a 10^{-3} M PA aqueous solution into benzene. Therefore, the transfer of PA from PDODA in benzene into the aqueous solution during shaking could be qualitatively related to the hydrolysis of PDODA. The effect of the aqueous solution composition on the PDODA hydrolysis is shown in Table I. The decrease of the PDODA concentration in the organic phase corresponded to the increase of free PA in the aqueous solution. The transfer was most effective above pH 9 and ineffective under pH 4 (Table Ia). The addition of a neutral salt, CdCl$_2$, at pH 6.2 decreased the transfer (Table Ib); the addition of PA to the aqueous phase decreased the transfer only at the highest concentration used 10^{-3} mol l^{-1} (Table Ic).

Surface pressure–area (π–A) curves of PDODA and DODA at the air–water interface are presented in Figs 1 and 2, respectively. On water at pH 5 to 8 (PDODA) and at pH 6 to 8 (DODA) a slow increase of π with compression of the films was followed by a steep increase after the limiting area was reached. Such π–A curves are characteristic of condensed monomolecular films similar to that of straight-chain fatty acids, in which the interaction between hydrocarbon chains is dominant. At pH below 5.5 the films expanded, giving π–A curves typical of charged monolayers in which the long distance electrostatic repulsion increased the surface pressure considerably even at large areas per molecule. Here the ionization of amine groups was probably responsible for the repulsion. The expansion of the film at pH above 9 remains questionable. The ionization of the amine group in the films should be small at high pH. The expansion did not change if the pH in the subphase was adjusted by NaOH, KOH or NH$_4$OH. The adsorption and ionization of CO$_2$ from atmosphere and subphase at the interface may have been responsible for the expansion [12].

TABLE I Transfer of PA from 1.7×10^{-4} M PDODA benzene solution into various aqueous solutions (c = the concentration of unhydrolysed PDODA in benzene after shaking for 1 h, c_0 = the original concentration of PDODA in benzene)

(a) Water pH	3.67	5.2	6.5	7.9	9.12
c/c_0	0.94 ± 0.03	0.48 ± 0.05	0.5 ± 0.05	0.48 ± 0.07	0.4 ± 0.05

(b) CdCl$_2$, pH 6.2 CdCl$_2$ [mol.l^{-1}]	0	10^{-4}	10^{-3}	10^{-2}
c/c_0	0.5 ± 0.05	0.57 ± 0.02	0.66 ± 0.05	0.66 ± 0.07

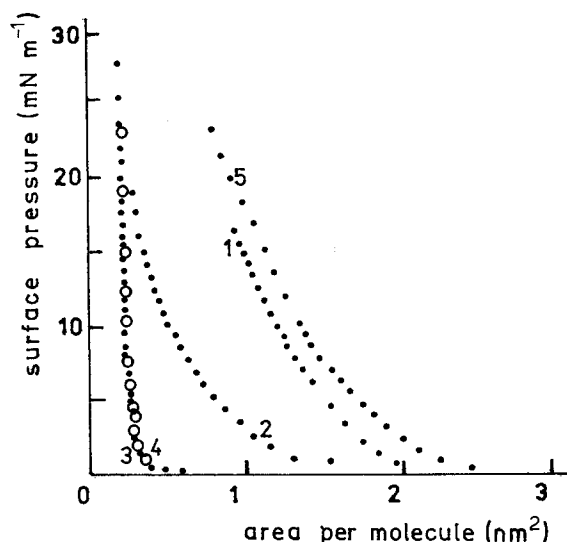| (c) Picric acid, pH 6.4 PA [mol.l^{-1}]	0	10^{-5}	10^{-4}	10^{-3}
c/c_0	0.54 ± 0.01	0.48 ± 0.04	0.50 ± 0.007	0.59 ± 0.002

Figure 1 Surface pressure–area curves of PDODA films on water at various pH: (1) pH 4.05, (2) pH 5.44, (3) pH 6.05 (. . .), (4) pH 7.7 (○○○), (5) pH 9.01.

Figure 3 Surface pressure–area curves of PDODA films on water containing various salts at pH 6.3; (1) H_2O (○○○), (2) 5×10^{-4} M $CdCl_2$ (. . .), (3) 5×10^{-4} M $(NH_4)_2SO_4$ (△△△), (4) 5×10^{-4} M PA (. . .), (5) 10^{-3} M KCl (□□□).

There were no qualitative differences between π–A curves measured on the PDODA or DODA films. The limiting area A_0 per one molecule in condensed films on water at neutral pH was $A_0 = (0.267 \pm 0.002)\,nm^2$ in PDODA films and $A_0 = (0.252 \pm 0.002)\,nm^2$ in DODA films. These small limiting areas (about 0.36 nm² was expected for two octadecyl chains) indicated that some three-dimensional structures were present in the condensed films.

PDODA films on the aqueous subphase containing different types of ions (KCl, $CdCl_2$, $(NH_4)_2SO_4$ and PA) were also formed (Fig. 3). All the films were expanded at pH 6.3. A similar expansion of DODA monolayers was observed if the ions were present in the subphase. There was no condensation of the films due to divalent counterions (SO_4^{2-}), such as that observed on fatty acid films on divalent cation solutions. Any expansion of films decreased the stability of the layer against the collapse. Small differences between PDODA and DODA films indicated that a great part of the PA was hydrolysed from the PDODA
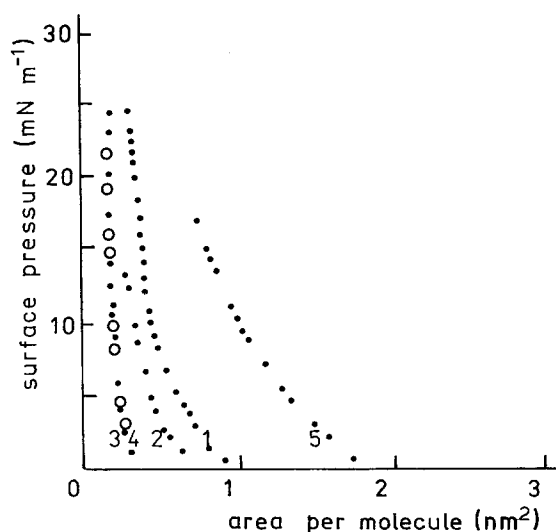
films into water. The expansion of the films can be explained using a theoretical approach suggested for lipid monolayers by Helm *et al.* [13]. Some amine groups of DODA in the film are ionized with protons from the subphase. The coulombic repulsion tends to expand the film. Simultaneously, the surface potential due to this positive surface charge decreases the effective proton concentration near the film. Thus, at a low ionic strength in our experiments represented by pure water at pH from 5 to 8 only a few DODA molecules are ionized, although the pH is smaller than the intrinsic pK, and condensed films are obtained. The addition of ions to the subphase reduces the surface potential, the proton distribution becomes more uniform, the degree of ionization of polar heads increases, the films are more expanded. Table II shows the content of PA in monolayers collected from the water surface and dissolved in chloroform. PA was completely removed from the films at pH above 9; about 10% of PDODA remained unhydrolysed at neutral pH; the hydrolysis was lower at low pH. The addition of neutral salts decreased slightly the hydrolysis. The results qualitatively corresponded

Figure 2 Surface pressure–area curves of DODA films on water at various pH: (1) pH 4.0, (2) pH 4.31, (3) pH 5.12 (. . .), (4) pH 8.2 (○○○), (5) pH 9.05.
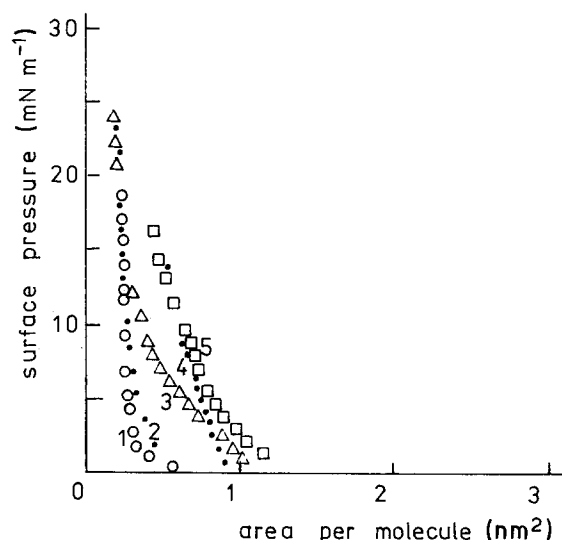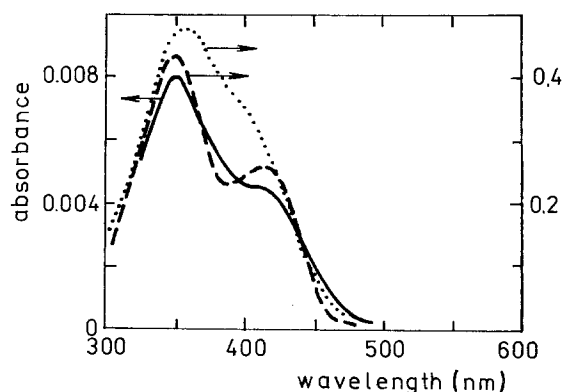

Figure 4 Absorption spectra of PDODA and PA; —— 6 LB monolayers of PDODA (three on each side of glass slide), — — — PDODA in chloroform (1.65×10^{-2} mg ml^{-1}), . . . PA in water (6.2×10^{-3} mg ml^{-1}).

TABLE II Content of unhydrolysed PDODA in monomolecular films collected from aqueous subphases and dissolved in chloroform (m = the amount of unhydrolysed PDODA determined in the dissolved monomolecular film: m_0 = the amount of PDODA originally spread at the air–water interface)

Subphase	Water pH 9.4	Water pH 6.01	Water pH 2.5	10^{-3} M NaCl pH 6.3	10^{-3} M CdCl$_2$ pH 6.3
m/m_0	0.0	0.11 ± 0.01	0.3 ± 0.08	0.13 ± 0.02	0.14 ± 0.02

with the effectiveness of PA transfer from benzene PDODA solutions into water (Table I).

The condensed PDODA films formed on pure water at neutral pH could be transferred on solid supports (glass, hydrophobized glass, aluminium on glass). If the support was placed in water before a monomolecular film was spread, the first monolayer and the successive layers were deposited while the plate moved upwards out of water, resulting in a Z-type tail-to-head deposition. If a hydrophobic plate was first immersed through the already existing mono-layer, the first monolayer and the successive layers were deposited only while the plate entered water, resulting in the X-type head-to-tail deposition. Usually, there was a good transfer of the first three layers with the transfer ratio $R \approx 1$.The transfer ratio of the successive three layers decreased and there was no further transfer in the following deposition steps. The expanded PDODA films could be deposited only as one monolayer. No further transfer occurred when the deposition was repeated. Uncompensed electric charges responsible for the expansion of the films obviously prevented their successive deposition. Even a small expansion of condensed films observed in some experiments on pure neutral water probably due to some impurities, restricted the multilayer deposition. The limited multilayer deposition of condensed films and only a monolayer deposition of expanded films occurred both with PDODA and DODA films. One could suppose that an increasing electrostatic repulsion between a multilayered film on the support and the film on the water surface decreased the transfer ratio of the successive layers and eventually stopped the transfer entirely. A small number of electric charges in the condensed films allowed only the X-type or Z-type deposition where the polar heads were separated with the hydrocarbon layer, while the Y-type deposition was prevented. After several deposition steps the neat effect of charges in the multiple layer was so strong, or some charged polar heads became so oriented toward film surface due to local defects of molecular arrangement, that further transfer was prevented.

The content of unhydrolysed PDODA about 10% in the multilayer film on glass was estimated from transmission spectra (Fig. 4). The value was in good agreement with that obtained for dissolved mono-molecular films in Table IV.

The content of unhydrolysed PDODA in the mono-layer on a teflon plate was estimated by ESCA from the nitrogen and oxygen atoms surface concentration. This content increased in the order: film transferred from water, film transferred from 5×10^{-4} M CdCl$_2$, and from 5×10^{-4} M PA (pH in all subphases was adjusted to 6.2 with NaOH). No chlorine, sodium, potassium or cadmium atoms were detected in the films.

4. Conclusion

PDODA in the form of the LB layer is partially hydrolysed during the contact with water. The LB films on various substrates consisting of several layers were obtained by transferring the monolayer from pure neutral water. The repulsion between electrical charges present in the films promoted the desirable formation of the X-type and Z-type structures. On the other hand, repulsion prevented the deposition of a greater number of condensed layers and the deposition of expanded films containing a higher amount of unhydrolysed PDODA. According to preliminary measurements, the multilayer PDODA system showed a pyroelectric effect.

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