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Phase separation in mixed monolayers of arachidic acid and a phthalocyanine of zinc

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ABSTRACT

Mixed Langmuir and Langmuir-Blodgett films of dissimilar components, arachidic acid and a phthalocyanine of zinc, have been investigated. These compounds form mixed films with phase separation, with domains at the sub-micro scale which are detected by AFM in LB films but not observed by BAM. These domains present different contrast in the surface potential images obtained with SP-AFM and in the friction images. The analysis of the isotherms and of the AFM images, at several compositions, reveals that the components are immiscible. The difference in height between the arachidic acid and the phthalocyanine of zinc phases is in accordance with the heights of the molecules, and points to the presence of a monolayer in the zinc phthalocyanine phase. AFM has revealed as a necessary technique to elucidate the miscibility in mixed films at the nanometric scale. UV–Vis spectroscopy shows changes in the spectra bands of LB films in respect to those in solution, due to the organization of the molecules in the LB film.

1. Introduction

The study of mixed films of dissimilar components [1–19] is of practical interest due to the fact that a great number of compounds of technological interest need a film former. Phthalocyanines (Pc), porphyrins (P), metallo-porphyrins (MP) and metallo-phthalocyanines (MPc) are an example. Fatty acids have been investigated as film formers in mixed films with macrocyclic compounds, and the transfer to a substrate by the Langmuir-Blodgett (LB) technique of a MPc or MP can be improved by the presence of a fatty acid which acts as a transfer promoter [5,6]. Usually a minimum percentage of fatty acid is required. Sheu et al. [6] used arachidic acid (AA) as fatty acid, and molar ratios for mixed CuPc:AA of 1:1, 2:1 and 4:1 where the MPc predominates, but Peng et al. [5] used molar ratios for CuP:Cd Arachidate with high molar fraction of Cd Arachidate ($\geq$0.8) in order to obtain quality films. High proportions of AA were also used by Lu et al. [3] in mixed films of $\mathrm{Ru(dpphen)_3}^{2+}$:AA, and found that the best mixture ratio for the stable mixed monolayer is 1:2. Del Caño et al. [7] have studied mixed films of titanyl(IV)Pc and AA using molar ratios of 1:1 and 1:4, thus also with a high proportion of AA.

The topographic mode of Atomic Force Microscopy (AFM) has become a general technique in the study of mixed Langmuir-Blodgett (LB) films, while a related technique such as surface potential-AFM (SP-AFM) has been scarcely used. These techniques provide useful information on the structure of the films, topographically or compositionally. Changes in the response of the different domains of the film can be attributed to differences in chemical composition, in structure or in molecular orientation. Phase separation is an important point to be considered in the film structure of mixed films, and these techniques can provide a powerful tool to investigate them, especially when domains present micrometric or nanometric size.

In mixed films of a macrocyclic compound, such as a phthalocyanine or a porphyrin, with a fatty acid, such as AA, an increase in the area per molecule has been observed [3,4,7] despite the small value of this parameter for fatty acids. Complemented with results of RAIRS, UV–Visible absorption and micro-Raman imaging, this phenomenon has been explained by a change in the molecular orientation of the macrocycle induced by the presence of the fatty acid. An increase in the area has also been observed in a mixed film of a thiomacrocyclic compound with AA [16,17], which has been attributed to a partial solubility of AA in the thiomacrocycle phase with a loss of compactness, and in a mixed film of a nitrostilbene derivative with behenic acid [10], which has been attributed to the ability of behenic acid to prevent aggregation of the nitrostilbene derivative. In other cases a decrease in the area per molecule has been observed [9,12], which has been attributed to the fact that fatty acid molecules can enter into the macrocyclic ring [12] or to the formation of a condensed phase [9]. Other authors [13] have found that the miscibility of an azacrown ether with palmitic acid depends on the surface pressure, and reported that miscibility

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occurs at intermediate pressures, at least on the macroscopic level based on the BAM observation of film homogeneity. As the behaviour of mixed films is not clear a priori, it must be investigated in each case.

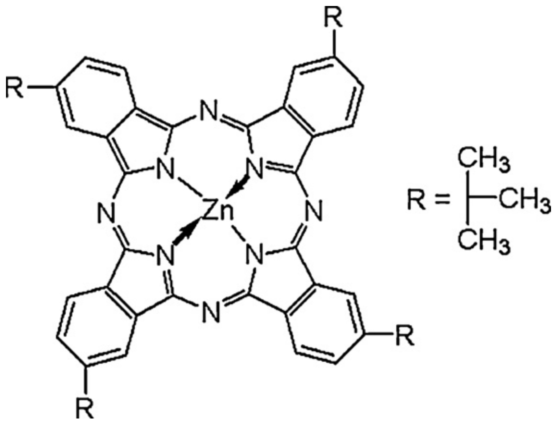
Pc and MPc have been used for many years as blue and green dyes, but recently they have also been investigated for their applications as catalysts and chemical sensors, as photosensitizers, in solar cells, and in electronic and photonic technologies [20–25]. In particular, zinc phthalocyanines (ZnPc) have received some attention [26] and recent investigations target applications in photodynamic therapy [27–29] or as promising materials for organic solar cells [25]. These applications usually require a thin film deposited on a solid substrate. Several studies have investigated these systems and their particular structure, and some of them have studied the characteristics of organized Langmuir and Langmuir-Blodgett (LB) films [1,20,30–35]. Studies in LB films of MPc are important in understanding of interfacial spectroscopic processes occurring in organic materials deposited on inorganic solid substrates, for further developing of photovoltaics and optoelectronic devices. One of the characteristics of these compounds is the strong aggregation they present and the difficulty with which they form homogeneous films. Low aggregation in ZnPc is important since aggregation causes drastic decay of optical properties [36]. Consequently, further investigation about the influence of fatty acids in the film formation of ZnPc is necessary, and to the author knowledge, no studies with this objective have been reported for PcZn.

The compound zinc tetra-tert-butylphthalocyanine (tbuPcZn) has a high value for the molar absorption coefficient, $\varepsilon = 19.73 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$ at $\lambda = 675$ nm (calculated by the author), and, on the other hand, is very soluble in chloroform, fact that facilitates the film formation at the air-water interface. These properties are of interest for investigating the applicability of this compound in photodynamic therapy or in thin films for solar cells.

This work studies the influence of arachidic acid in the film formation of the phthalocyanine tbuPcZn, and whether phase separation occurs. Several film compositions have been analyzed by using surface pressure-area isotherms, Brewster angle microscopy (BAM), UV-Vis spectroscopy, AFM and SP-AFM, in order to study the characteristics of the mixed films and conditions for a good film formation. In particular the scanning probe microscopy techniques provide the necessary information about the possibility of using AA as a transfer promoter, and the structure of the films at a nanometric scale. The UV-Vis spectroscopy has been used for observing the changes in the spectra of LB films in respect to those in solution.

2. Experimental

Langmuir films were obtained in a NIMA 1232D1D2 Langmuir-Blodgett trough and BAM images were obtained with a microBAM model (NIMA-Nanofilm), which has a lateral resolution of around 8 μm, both placed on an isolation platform. Pure water (Millipore MilliQ grade) was used as subphase, arachidic acid, AA ($M = 312.0$), and zinc 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine (Scheme 1), tbuPcZn ($M = 802.34$), were supplied by Sigma–Aldrich. A solution of pure component or mixed AA and tbuPcZn in chloroform was spread over the water subphase, and 15 min were allowed before compression in order to permit evaporation of the chloroform and stabilization. The compression speed was in between 1.3 and 1.8 Å^2/molec min. Basically, three compositions have been studied: $C_{\mathrm{tbuPcZn}} = 0.455$ mg/mL, $C_{\mathrm{AA}} = 0.50$ mg/mL ($C_{\mathrm{tbuPcZn}}/C_{\mathrm{AA}} \approx 1{:}1$), $X_{\mathrm{AA}} = 0.74$ ($X_{\mathrm{AA}}/X_{\mathrm{tbuPcZn}} = 2.8$), where X refers to the molar fraction; $C_{\mathrm{tbuPcZn}} = 0.303$ mg/mL, $C_{\mathrm{AA}} = 0.666$ mg/mL ($\approx 1{:}2$), $X_{\mathrm{AA}} = 0.833$ ($X_{\mathrm{AA}}/X_{\mathrm{tbuPcZn}} = 5.0$); $C_{\mathrm{tbuPcZn}} = 0.606$ mg/mL, $C_{\mathrm{AA}} = 0.333$ mg/mL ($\approx 2{:}1$), $X_{\mathrm{AA}} = 0.59$ ($X_{\mathrm{AA}}/X_{\mathrm{tbuPcZn}} = 1.4$). Mixed films with lower AA proportions have also been used but no good films were obtained. The LB films were transferred at constant pressure onto a freshly cleaved atomically flat mica surface. The transfer was done using a NIMA 1232 D1 dipper, at a surface pressure of 20 mN/m. The mica substrates were sheets of 1 cm × 1 cm cut from red mica. LB films were obtained following a Z deposition at a speed of 5 mm/min. For tbuPcZn the transfer ratio was slightly higher than 100%, and with the presence of AA the transfer ratio became closer to 100%. The experiments were done at a temperature of 23 °C.



Scheme 1. Molecular structure of the zinc 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine.

AFM images and friction images were performed with a Multimode atomic force microscope attached to a Nanoscope IV controller (Digital Instruments, Santa Barbara, CA). The microscope was placed on a N_2-operated vibration isolation table. Topographic images were acquired in tapping mode using Si tips with a nominal vertical spring constant of 40 N/m. Friction images, and the corresponding topographic images, were acquired in contact mode using silicon nitride tips of low spring constant [37]. Surface potential measurements were performed with a conducting Sb-doped Si tip with a nominal vertical spring constant of 1–5 N/m in non-contact mode. In that case, tapping topographic images and surface potential images were acquired using the LiftMode [38], which compensates for the height variations on the sample during SP imaging by using a two-pass technique. In SP imaging, sometimes referred to as Scanning Kelvin Probe Microscopy (SKPM),

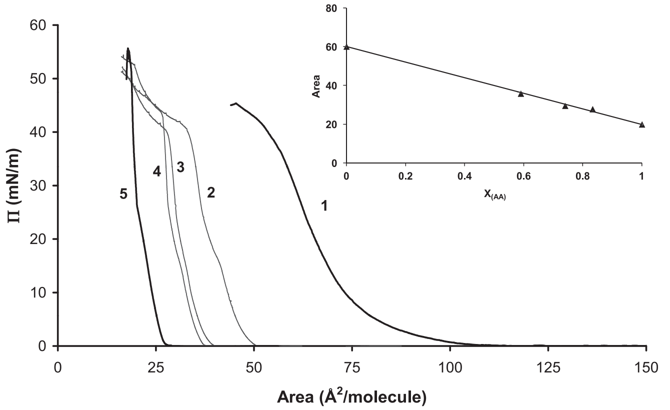


Fig. 1. Surface pressure–mean area per molecule isotherms for mixtures of arachidic acid (AA) and tetra-tert-butylphthalocyanine of zinc (tbuPcZn) at 23 °C: (1) pure tbuPcZn, (2) $X_{\mathrm{AA}} = 0.59$, (3) $X_{\mathrm{AA}} = 0.74$, (4) $X_{\mathrm{AA}} = 0.833$, and (5) pure AA. Inset: Mean area per molecule versus composition for mixtures of AA and tbuPcZn at $\Pi = 30$ mN/m (straight line corresponds to the additivity rule).