



DPPC–DOPC Langmuir monolayers modified by hydrophilic silica nanoparticles: Phase behaviour, structure and rheology

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ABSTRACT

Langmuir monolayers of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and mixtures of DOPC with 1,2-dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC), at a ratio of 37:63 in weight, spread on pure water and on silica nanoparticle dispersions, have been investigated using a combination of thermodynamic, surface rheology, BAM and AFM diagnostics. The compression surface pressure isotherms were determined in a Langmuir trough as well as the surface pressure response to harmonic area variation of the monolayer. Composite layers were obtained at selected thermodynamic states by transfer from the fluid interface to solid substrates and then analysed by AFM diagnostics. Aim of this study was to evaluate the effect of the incorporation of silica nanoparticles on the phase behaviour and structural properties of these monolayers. In fact, as shown in previous works on similar lipid systems, the hydrophilic silica nanoparticles dispersed in the sub-phase are transferred into the monolayer due to the interaction with lipid molecules which makes them partially hydrophobic. The results here obtained indicate that the appreciable influence of silica nanoparticles, previously observed for DPPC alone, is also important for DOPC and DOPC–DPPC mixture. Moreover, as confirmed by the AFM results on the deposited layers, these effects are mainly due to the disruption of the molecular packing and to the modification of the miscibility between the two lipid components.

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1. Introduction

The effect of additional components, such as solid nanoparticles, on the properties of Langmuir monolayers of fatty amphiphiles is a topic of increasing interest because of its application as model in several fields involving biological systems, biomembranes response [1] or respiratory physiology [2,3]. Lipid monolayers have been widely investigated by the analysis of the surface pressure–area (Π – A) isotherms [1,4–6] which allows structural features to be identified through essentially thermodynamic information. The phase behaviour of these systems is in fact related to the structural changes induced by the molecular lateral packing in the monolayer [7,8], which is modified by the increasing of the lipid surface concentration. The structure of these monolayers has been investigated in many works using in situ diagnostic techniques, such as X-ray diffraction [9], infrared reflection absorption spectroscopy (IRRAS) [10], fluorescence microscopy [11], laser light scattering [12], and Brewster Angle Microscopy (BAM) [13,14].

The interaction and/or incorporation of external components modifies the phase behaviour and the structure of these monolayers essentially because of the effects on the lateral packing. This is

of particular importance for biologically relevant structures which are mostly composed by complex mixtures of surface active components [15], among them, the lung surfactant (LS) [2].

The study of the impact of nanoparticles on the respiratory functionality is a topic of extreme interest in relation to environmental particulate and to the increasing utilisation of nanomaterials [16–19]. Considering that, as show in previous works [20–24], the segregation of nanoparticles at the liquid surface influences the interfacial tension and the dilational rheology of surfactant systems, it is clear the importance to investigate the effects on the surface properties and dilational rheology of lipid Langmuir monolayers, to understand the potential negative effect on the respiratory functionality. LS is in fact a complex mixture of lipids and proteins whose surface tension changes during the respiratory cycle [2,25] ensuring suitable mechanical properties to the lungs.

In a previous work [26] the effect of nanoparticles on the properties of lipid monolayers has been investigated spreading 1,2-dipalmitoyl-sn-glycerol-3-phosphocholine (DPPC) and palmitic acid on silica nanoparticle dispersions. These systems were studied from the thermodynamic and structural point of view, using a Langmuir trough technique coupled with Brewster Angle Microscopy diagnostics. The above lipids are relevant in the field of LS.

In the present work, the effect of silica nanoparticles has been similarly analysed for Langmuir monolayers of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and a mixture, 63:37 in weight,

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of DOPC and DPPC. These lipids are in fact two of the essential components of the LS [2,3] and, in the above proportion, constitute about the 65% in weight of the total composition of the LS in mammals [2].

Besides the thermodynamic study of the lipid monolayers in the Langmuir trough coupled with BAM, we report here a deeper structural investigation based on AFM analysis of Langmuir–Blodgett films obtained by a controlled transfer of the mixed monolayers on solid substrates.

The last aspect investigated in this work is the effect of nanoparticles on the surface pressure response to oscillatory variation of the surface area. As already observed in previous works on similar systems [27], nanoparticles may have appreciable effects on the linearity of such surface pressure response when the amplitude of the perturbation increases and becomes comparable with that proper of the respiratory cycles [2,25].

2. Materials

DOPC and DPPC were purchased from Sigma (Germany) with a purity higher than 99% and used without further purification. The molecular weights of these lipids are 786.1 and 734.1 for DOPC and DPPC, respectively. Solutions of lipids for the spreading were prepared using chloroform for HPLC from Sigma (Germany).

Dispersions of silica nanoparticles at 1 wt% were obtained by diluting a commercial colloidal dispersion of spherical silica particles, presenting a narrow size distribution around an average diameter of 30 nm and high stability without the addition of any stabilizing components. These characteristics were checked by Dynamic Light Scattering and ζ -potential measurements which provided an hydrodynamic radius of 15 ± 2 nm and $\zeta = -42 \pm 1$ mV for the colloidal dispersion [28].

Water was deionised and purified by a multi-cartridge, Elix plus Milli-Q (Millipore), system, providing a resistivity greater than 18 M Ω cm. Its purity was checked by surface tension measurements, which provided a value of 72.5 ± 0.2 mN/m, at 20 °C, without any appreciable kinetics over several hours. The same constant value is found for the silica dispersions [21], proving the absence of surfactant impurity in the bare dispersion and that nanoparticles, being highly hydrophilic, do not segregate at the clean water/air interface.

3. Methods

The Langmuir trough used for all the reported experiments was a KSV minitrough (Finland), equipped with two hydrophilic Delrin® barriers allowing symmetric compression/expansion of the free liquid surface. The surface tension, γ , was measured by a paper Willhelmy plate (Whatman CHR1 chromatography paper, effective perimeter 20.6 mm, supplied by KSV), ensuring a zero-angle contact angle. Surface pressure is then obtained as $\Pi = \gamma_w - \gamma$, where γ_w is the surface tension of pure water.

A Brewster Angle Microscope, BAM (Multiskop, Optrel, Germany) is also implemented coupled with the Langmuir trough in order to obtain morphological information on the spread layers [13,14].

The spreading of lipids as Langmuir monolayer was made using a Hamilton syringe to drop a controlled volume of lipid solution on the aqueous sub-phase, pure water or nanoparticle dispersion. From this volume and the solution concentration (typically 1 g/L), it is then possible to control the number of molecules present on the surface after evaporation of the solvent. After the deposition, and before starting any experiments, the monolayer was left to equilibrate for 1 h. This time was checked to be sufficient for the complete evaporation of the solvent and the equilibration of the nanoparticle–lipid layers.

The surface pressure–area (Π – A) isotherms were determined by measuring the surface pressure during a controlled compression of the monolayer free area, at a rate of 2 cm²/min, equivalent to an area deformation rate, $d(\Delta A/A_0)/dt$, of about 3×10^{-5} s⁻¹.

The Langmuir trough was also used to measure the surface pressure response to harmonic variations of the surface area, A , at controlled amplitude, ΔA , and frequency, ν ,

$$A(t) = A_0 + \Delta A \sin(2\pi\nu t) \quad (1)$$

where A_0 is the initial area. This dilational rheology study was performed at increasing deformation amplitude in order to investigate the linearity of the monolayer behaviour. Under viscoelastic linear regime, usually obtained at small amplitude sinusoidal variation of the surface area, the surface pressure response presents a sinusoidal profile as well as the same frequency,

$$\Pi(t) = \Pi^0 + \Delta\Pi \sin(2\pi\nu t + \varphi), \quad (2)$$

where $\Delta\Pi$ is the amplitude of the response and φ a phase shift accounting for a possible viscous character of the layer. Increasing the deformation amplitude, distortions in the response signal may appear which means that the response is no longer linear [29]. The appearance of harmonics of higher order than the fundamental frequency, indicating the non-linearity of the response, are effectively evaluated by analysing the Fourier transform (FFT) of the surface pressure response [30]. A quantitative evaluation of the response non-linearity is provided then by the total harmonic distortion (THD) [31,32], defined as

$$\text{THD} = \frac{\sqrt{\sum_{k>1} \Delta\sigma_k^2}}{\Delta\sigma_1} \quad (3)$$

$\Delta\sigma_k$ are the k -Fourier coefficients, that is the amplitude of the k -order harmonics in the representation of the signal as a Fourier sum, $\Delta\sigma_1$ being, in particular, the amplitude of the fundamental harmonic. Linear systems present responses with vanishing THD, while larger values are associated to an increasingly non-linear behaviour.

The Langmuir trough is equipped with an automatic dipper for Langmuir–Blodgett (LB) films deposition onto solid substrates. This device allows the controlled transfer of the monolayer on solid substrates while keeping constant the surface pressure by the movement of the barriers. The dipper was utilised to transfer the LB film on a hydrophilic glass plate of dimensions 20 mm \times 20 mm, by a vertical pulling, at a constant velocity of 1 mm/min.

AFM images of the LB films were obtained using a Veeco Nanoscope III (Digital Instrument, Santa Barbara, CA). This allows a sample up to about 1 cm² to be fitted in the operational stage with a maximum scanning area of about 12 μ m and a Z resolution of about 4 μ m for imaging. It has been used in air Contact Mode with minimum force and when it was necessary in Tapping Mode.

For all the reported experiments the temperature was at a controlled value of 22.0 ± 0.1 °C.

4. Results and discussion

4.1. Equilibrium properties and structure of lipid monolayers

Fig. 1 reports the Π – A isotherms obtained for DOPC monolayer and for the DOPC–DPPC, 37:63 in weight, mixed monolayer. The Π – A isotherm found in Ref. [27] for pure DPPC is also reported for sake of comparison. The phase behaviour of DPPC monolayer has been widely investigated [33–37]. The typical characteristics of the DPPC isotherm are evident. These are the compression of the liquid expanded (LE) phase at high area per molecules, the surface pressure plateau corresponding to the coexistence of the disordered LE phase with the highly ordered liquid-condensed (LC) phase and the

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