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SHORT COMMUNICATION

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Surface viscoelasticity of phospholipid monolayers at the air/water interface

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Abstract The surface viscoelastic properties of monolayers of two phospholipids DPPC (L-α-dipalmitoylphosphatidylcholine) and DMPE (L-α-dimyristoylphosphatidylethanolamin), at the air–water interface have been investigated. Two techniques were used for the investigation. One involved use of an interfacial shear rheometer (torsion pendulum apparatus ISR1), to provide measurements of the shear viscosity η_s as a function of surface pressure, and the second, a modified LB trough with an oscillating barrier to generate periodic dilation and compression so as to measure the dilational elastic modulus E as a function of surface area.

Results indicate a strong dependence of η_s and E upon monolayer phases. This suggests that the viscoelastic relaxation of monolayers can be understood as molecular rearrangements, domain exchange and molecular reorientations between different monolayer states.

Key words Phospholipid – Langmuir monolayers – surface rheology – surface dilational elasticity – surface shear viscosity

Introduction

Phospholipid monolayers are well recognised as model systems of biomembranes anchored perfectly at fluid interfaces [1–5], and in technology as precursors of multilayer structures (LB films) [6]. Hence much attention has been paid to the measurements of the physico–chemical properties of the various phases of these monolayers and also their surface mechanical properties. These mechanical properties can be characterised by surface shear and dilational viscoelasticity and provide direct information on the stability of these films [7, 8]. Unfortunately, mechanical properties are rather difficult to measure as most mechanical devices used for measurement of these properties are based on the excitation of small amplitude surface waves with typical frequencies of about 100 Hz and cause a serious disturbance of the monolayer state. The technique of Surface Light Scattering is established as an ideal probe for studying surface viscoelasticity without direct mechanical contact. However the difficulty of the technique itself and the strict requirements on the film preparation and manipulation still bring about some restrictions on experiments.

In the present paper results of the surface mechanical properties of phospholipid monolayers at the air/water interface are given. Recently developed apparatuses are used in this study: the surface shear rheometer ISR1 and a modified Langmuir–Blodgett trough equipped with an oscillating barrier [9, 10]. Both instruments have an operational frequency of less than 0.1 Hz. The former instrument allows the determination of the shear viscosity, η_s, and the latter determines the dilational elasticity, E, of the monolayers [11] both parameters measured at varying surface pressures.

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Experimental details

Materials

The phospholipids, DPPC and DMPE (99% + purity) purchased from Sigma, were used without further purification. Chloroform with 99% purity was purchased from MERCK. The water used in all experiments was prepared in a Millipore apparatus.

Monolayer preparation

All measurements were performed at 20 ± 0.5 °C. The monolayers for the two troughs were prepared in the usual way by spreading a definite amount of phospholipid solved in chloroform onto the pure water surface. After evaporation of the solvent the monolayer was compressed to a definite film pressure π by moving the barrier.

Surface shear rheometer

The surface shear rheological experiments involve the use of a surface shear rheometer, ISR1 (LAUDA, Germany). The measuring principle has been described in detail elsewhere [10]. Basically a small deformation of the surface of the liquid under study is produced by a freely oscillating sharp-edged titanium ring which is touching the surface. The oscillation of the ring as a function of time $y(t)$, is recorded automatically by the instrument. From the mathematical representation of the oscillatory behaviour (Eq. (1)) important quantities such as the damping coefficient α and the circular frequency β of the torsion oscillation, can be calculated

$$y(t) = y_0 \exp\left(-\frac{t}{a}\right)\sin\left[\frac{2\pi}{T}(t - t_0)\right] + c\,. \qquad (1)$$

Here, a is the decay time $a = 1/\alpha$, T is the period of oscillation $T = 2\pi/\beta$, t_0 is the phase shift $t_0 = \varphi/\beta$ and c is the offset. The coefficients α and β as represented mathematically by Eqs. (2) and (3), are functions of the system parameters determined from calibration measurements, and the surface shear rheological quantities of the liquid surface (cf. Tschoegl [12]),

$$\alpha = \frac{F_r + (\eta_s H_s)}{2I_r}, \qquad \beta = \left[\frac{E_r + (G_s/H_s)}{I_r} - \alpha^2\right]^{1/2}, \qquad (2)$$

$$\eta_s = H_s(2I_r\alpha - F_r), \qquad G_s = H_s I_r(\alpha^2 + \beta^2) - H_s E_r\,. \qquad (3)$$

H_s is a geometric factor, and I_r, E_r and F_r are the system parameters.

Values of α and β are obtained from fitting Eq. (1) to experimental data, and hence the rheological parameters η_s and G_s of the adsorption layer can be calculated from Eqs. (2) and (3).

For the actual shear experiments a Langmuir trough divided into two compartments, rectangular and circular, was used. The rectangular part is used for measuring film pressure as detected by a Wilhelmy plate (TD1 from LAUDA, Germany) while the surface shear rheological measurement were made in the circular part. This part is formed by a Teflon ring. Inside this ring is another ring which is the measuring body of the surface shear rheometer. The shear stress acts in the gap between these two rings. The fixed outer Teflon ring has two gaps to allow the compressed monolayer flowing into the circular part of the trough. In this way the same film pressure is established in the rectangular and circular part of the apparatus. The surface shear viscosity was measured as a function of the film pressure. The experiments were carried out with a deflection angle of 2°, which corresponded to an initial relative shear deformation of the surface of 8.7%. The frequency of the deformation was of the order of 0.1 Hz.

Modified Langmuir through with oscillating barrier

The dilational rheological experiments involve the use of another Langmuir trough with a second barrier which allows periodic dilations and compressions of the monolayer. The schematic set-up has been described in detail elsewhere [9, 11].

This oscillating barrier method permits a direct measurement of the amplitude of surface pressure oscillation. It also provides the phase angle between generated area oscillation and the resulting pressure oscillations. The elastic modulus E can be calculated by using an approximation

$$E = \frac{-\,d\pi A}{dA} = \frac{-\,d\pi L}{dL} \approx \frac{\Delta\pi L}{\Delta L}\,, \qquad (4)$$

where L is the maximum distance between the oscillating barrier and the pressure sensor, ΔL is the amplitude of the sinusoidally varied distance.

Here the dilational elasticity E was also measured as a function of film pressure π. The measured pressure was then used to calculate the area/molecule from the π/A isotherm. The periodical movement of the oscillating barrier had an amplitude of $\Delta L = 7.5$ mm at a length of $L = 100$ mm and an oscillation frequency of 0.05 Hz.

Results and discussion

The surface shear viscosity data are obtained by fitting the relaxation function Eq. (1) to the experimental curves. An example is given in Fig. 1 for a DMPE monolayer at three different surface pressures. The fitted curves accurately agree with the experimental points which proves the applicability of the chosen rheological model for the present systems.

The results from surface shear experiments are summarised in Fig. 2 in form of surface shear viscosity η_s as a function of surface pressure π for both DPPC and DMPE monolayers. The insert at the upper left corner shows the π/A isotherms of DPPC and DMPE, respectively. In both isotherms the known coexistence region is well established. As we can see, the determined shear viscosities were almost zero below the coexistence region and independent of the surface pressure. With a further increase in π the shear viscosity increases sharply beyond 15 mN/m for DMPE and reaches the order of 2500 μNs/m at a surface pressure of 40 mN/m. For DPPC η_s steadily increases beyond a surface pressure of 32 mN/m to reach a final value of about 500 μNs/m.

The large difference between the two final viscosities reflects the difference in the construction of the compressed films. In principle, the contribution of surface shear viscosity results from the strain of the monolayer per unit area. In the liquid expanded/gas region and in the

Fig. 1 Relaxation functions of DMPE at air/water interface under three different surface pressures at 20 °C

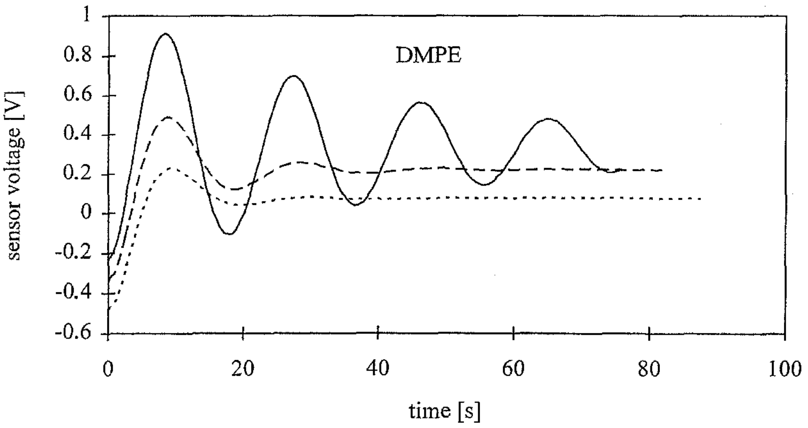


Fig. 2 Surface shear viscosity of DPPC and DMPE as a function of surface pressure

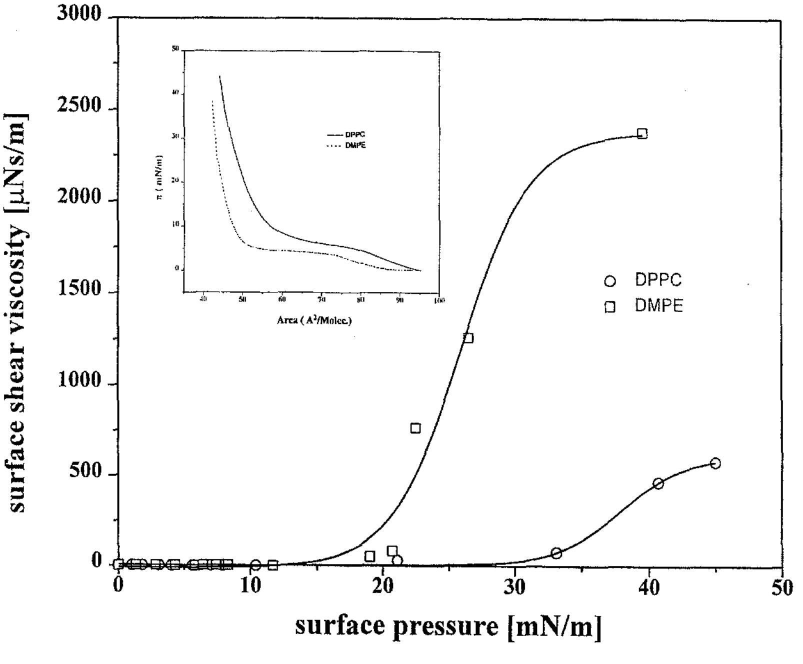


Fig. 3 Dilational elasticity modulus E as a function of surface area for DPPC and DMPE; $\Delta L = 7.5$ mm, $L = 100$ mm, $f = 0.1$ Hz

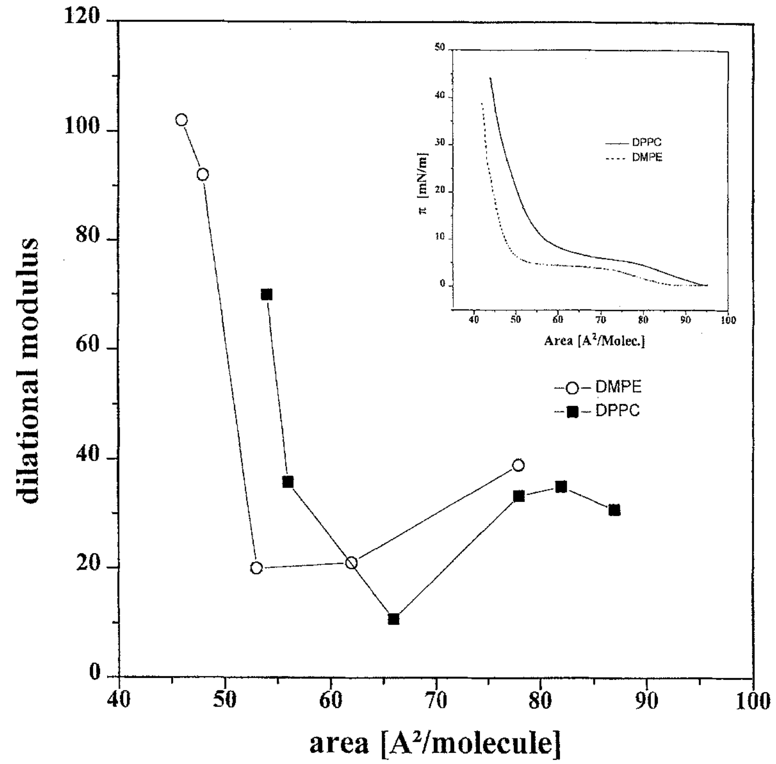
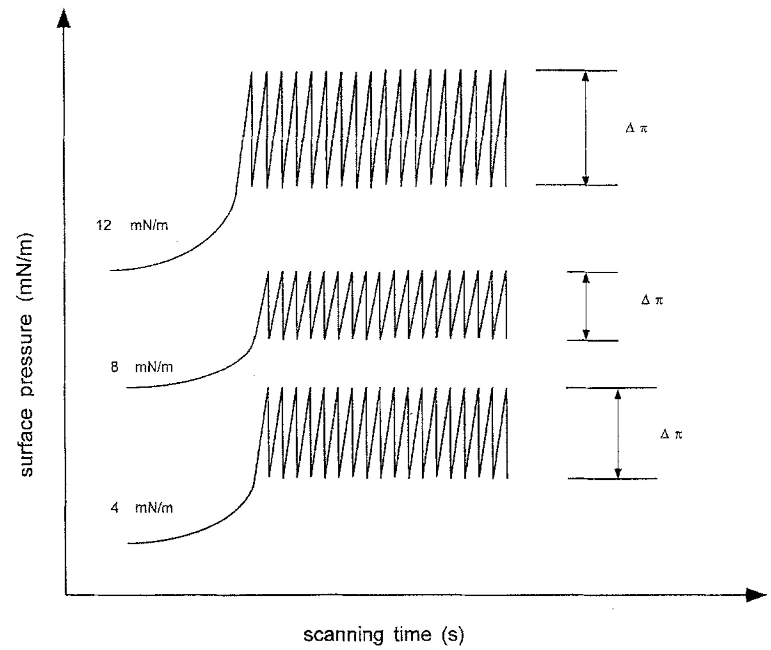


Fig. 4 Experimental plot of $\pi(t)$ of DPPC under periodic compression and dilation of the monolayer area



pure liquid expanded phase the monolayer undergoes molecular rearrangements, or diffusion processes between domains take place which allow the shear component to relax. Here the relaxation time must be substantially less than the period of strain. Therefore, we can emphasise that the composite properties of the monolayer control the shear parameters. The condensed film of DMPE was indeed more still and stable than that of DPPC because of the small head group. At very high surface pressure it can build up a triangular lattice with vertically oriented chains [13]. X-ray diffraction experiments provided data on the tilt angle of the aliphatic chains of DPPC close to the collapse point [14]. On the another hand, if a single-phase behaviour would affect the shear viscosity, viscous domains in an ambient fluid monolayer lead to a second relaxation process which corresponds to a significant value of η_s, that is, in the LE/LC two-phase region there is at least a slow relaxation affecting η_s. In fact, the experiments gave no evidence of such a process. As shown in Fig. 2, below a surface pressure of 15 and 32 mN/m for DMPE and DPPC, respectively, shear relaxation is negligible.

Figure 3 displays the surface dilation elastic moduli E of DPPC and DMPE monolayers as a function of surface area. In the LE phase the values of E for DPPC and DMPE were around 30 mN/m. On entering the coexistence region, by further compression, a decrease in E occurs, leading to values of 10 mN/m for both substances. When the condensed phase is reached E rises rapidly and reached values of 100 mN/m for DMPE and 70 mN/m for DPPC. In this region the dilational relaxations are extremely fast.

The dilational elasticity moduli of both monolayers display a strong dependence on the monolayer phase. The correlation of a rapid rise of E with the onset of the LE/LC transition reflects the fact that the relaxation process occurs within the monolayer. In the coexistence region the minimum values of E are ascribed to exchange between the LE and the LC phase. This means that a harmonic area change can only cause a small change of surface pressure. As shown in Fig. 4 at a fixed oscillation the amplitude of surface pressure oscillation $\Delta\pi$ has the smallest value in the coexistence region. Below and above the coexistence region surface area variation significantly changes the surface pressure and hence the dilational elasticity moduli of both substances.

The change of the measured dilational elasticity definitely consists with the variation of Gibbs elasticity which can be easily estimated via the slope of the π/A isotherm by Eq. (4). But the measured values are dramatically larger than the Gibbs' calculation. In particular, in the coexistence region, the Gibbs elasticities approach zero due to the nearly horizontal slope of the π/A isotherm for both substances. This difference can be interpreted by considering the results derived under nonequilibrium and equilibrium status. The measured elasticities are dynamic results with a frequency domain. If measurements are done with different oscillating frequencies, the measured E will be close to the Gibbs elasticities expected.

With that in mind, we performed extended measurements of our own with a frequency dependence and with different distances between the oscillating barrier and the pressure balance for a better understanding of the relaxation mechanisms.

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