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# Combined surface pressure-interfacial shear rheology studies of the interaction of proteins with spread phospholipid monolayers at the air–water interface

Simon A. Roberts [a,*], Ian W. Kellaway [a], Kevin M.G. Taylor [b], Brian Warburton [c], Kevin Peters [c]

[a] *The School of Pharmacy, University of London, 29/39 Brunswick Square, London WC1N 1AX, UK*
[b] *University College London Hospitals, Camden and Islington Hospital Pharmaceutical Services and School of Pharmacy, University of London, London, UK*
[c] *Camtel Ltd., Brockley Road, Units 2-3 Avenue Business Park, Elsworth, Cambridgeshire CB3 8EY, UK*

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**Abstract**

The adsorption of two model proteins, catalase and lysozyme, to phospholipid monolayers spread at the air–water interface has been studied using a combined surface pressure-interfacial shear rheology technique. Monolayers of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), 1,2-dipalmitoyl-*sn*-glycero-3-[phospho-*rac*-(1-glycerol)] (DPPG) and DPPC:DPPG (7:3) were spread on a phosphate buffer air–water interface at pH 7.4. Protein solutions were introduced to the subphase and the resultant changes in surface pressure and interfacial storage and loss moduli were recorded with time. The results show that catalase readily adsorbs to all the phospholipid monolayers investigated, inducing a transition from liquid-like to gel-like rheological behaviour in the process. The changes in surface rheology as a result of the adsorption of catalase increase in the order DPPC < DPPC:DPPG < DPPG. Lysozyme behaves in a similar manner beneath a DPPG monolayer, but shows no measurable differences when injected beneath DPPC or the DPPC:DPPG (7:3) mixed monolayer. It is proposed that DPPG monolayers are more susceptible to penetration by adsorbing protein molecules. The interaction between DPPG and lysozyme is further enhanced due to electrostatic interactions between the negatively charged DPPG and the positively charged lysozyme.
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*Keywords:* Air–water interface; Interfacial shear rheology; Phospholipid monolayers; Protein adsorption; Surface pressure

## 1. Introduction

As a result of their amphiphilic nature, phospholipid molecules can be anchored at the air–water interface to form stable monolayers (Krägel et al., 1996). They are

* Corresponding author. Tel.: +44 20 7753 5800x4870; fax: +44 20 7753 5942.
*E-mail address:* simon.roberts@ulsop.ac.uk (S.A. Roberts).

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a major component of biological membranes and have a significant role in many biological processes. Phospholipid monolayers traditionally serve as simple, easy to study models of biological membranes (Phillips and Chapman, 1968; Möhwald, 1990). The understanding of interactions between insoluble phospholipid monolayers and proteins is of particular importance in many biotechnological and biomedical applications.

The kinetics and equilibrium properties of a variety of monolayer penetration systems have been investigated and were the subject of a recent review (Vollhardt and Fainerman, 2000). Despite the wealth of literature available on the dynamics of monolayer penetration, its effect upon the interfacial rheology of the monolayer has been ignored. Interfacial shear rheology is a powerful tool for investigating the structure of Langmuir-monolayers at the air–water interface. It can also provide valuable information about the formation and structure of adsorbed layers at that interface. This has led to the development of a number of techniques to measure the rheological properties of the interface (Krägel et al., 1994; Warburton, 1996; Miller et al., 1997; Bos and van Vliet, 2001; Jones and Middelberg, 2002; Murray, 2002). We have used a commercially available interfacial rheometer, which uses the principle of normalised resonance (Sherriff and Warburton, 1974) to derive the interfacial shear properties of the interface. Simultaneous measurement of the interfacial shear rheology and surface pressure was achieved by using the rheometer in combination with a Langmuir trough.

The current work investigated phospholipid monolayers composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), 1,2-dipalmitoyl-*sn*-glycero-3-[phospho-*rac*-(1-glycerol)] (DPPG) and a 7:3 DPPC:DPPG mixed monolayer. The monolayers are simple models of lung surfactant, the interfacial monolayer present within the lung, which reduces the surface tension of the air–water interface of the alveoli and prevents collapse of the lung. Two well characterised globular proteins, catalase and lysozyme, with different physicochemical properties (Deisseroth and Dounce, 1970; Blake et al., 1977), were chosen as model proteins to study the interaction of proteins with the spread monolayers. The effect of the model proteins on the measured interfacial properties of monolayers, in the condensed phase, is discussed in terms of the size and charge of the adsorbing protein and the charge of the monolayer spread at the interface. This information will be of value in the development of delivery systems for protein and peptide therapeutic agents administered by the pulmonary route.

## 2. Materials and methods

### 2.1. Materials

Catalase (bovine liver), lysozyme (chicken egg white) and 1,2-dipalmitoyl-*sn*-glycero-3-[phospho-*rac*-(1-glycerol)] sodium salt were purchased from Sigma-Aldrich Co. Ltd. (Poole, Dorset, UK). Chloroform, potassium dihydrogen orthophosphate and sodium hydroxide, all AnalaR grade, were purchased from BDH (VWR International Ltd., Lutterworth, Leics., UK). 1,2-Dipalmitoyl-*sn*-glycero-3-phosphocholine was purchased from Avanti Polar Lipids (Alabama, USA). The proteins, phospholipids and other reagents were used as supplied with no subsequent purification. Clean, purified water was prepared using an Elga Purelab Option Q purification system (Elga Labwater, High Wycombe, Bucks, UK) and had a resistivity of not less than 18 MΩ cm. The purified water was used in all cleaning procedures and in the preparation of all buffer solutions.

Solutions of DPPC, DPPG and DPPC:DPPG (7:3) were prepared in chloroform at a concentration of $1\,\mathrm{mg\,ml^{-1}}$ total phospholipid. These solutions were then used in the creation of phospholipid monolayers at the air–water interface. Phosphate buffer solutions were prepared at a concentration of 0.05 M and a pH 7.4. Solutions of catalase ($25\,\mathrm{mg\,ml^{-1}}$) and lysozyme ($100\,\mathrm{mg\,ml^{-1}}$) in phosphate buffer were freshly prepared for each experiment.

### 2.2. Combined surface pressure-interfacial shear rheology

Simultaneous measurements of surface pressure ($\pi$) and interfacial shear rheology were performed using a NIMA Langmuir trough (NIMA, Warwick, UK) in combination with a Camtel CIR-100 interfacial rheometer (Camtel Ltd., Elsworth, Cambridgeshire, UK). The Langmuir trough was used to present the air–water interface under investigation to the measuring geometry of the interfacial rheometer,

and also to provide temperature control. Temperature was controlled by a circulating waterbath, connected to the Langmuir trough. The pressure sensor on the Langmuir trough uses a Wilhelmy plate, cut from chromatography paper (Whatmans Chr1, 10.25 mm × 24 mm × 0.25 mm), to measure the surface pressure. The measuring geometry of the interfacial rheometer consists of an oscillating Pt/Ir Du Noüy ring, 13 mm in diameter. Rheological parameters were determined by oscillation of the Du Noüy ring at a given frequency ($\omega$) under an applied stress ($\sigma$). The ratio of applied stress to the resultant measured strain ($\gamma$) gives the total elastic modulus ($G^*$) of the interfacial layer.

$$G^* = \frac{\sigma}{\gamma} \quad (1)$$

The storage and loss moduli, $G'$ and $G''$, respectively, can then be derived using $G^*$ and the phase angle, $\theta$.

$$G' = G^* \cos\theta \quad (2)$$

$$G'' = G^* \sin\theta \quad (3)$$

Simultaneous measurement of the changes in $G'$, $G''$ and $\pi$, with respect to time, were performed using the apparatus described above, at a constant frequency of 5 Hz, an applied strain of 2500 μrad and a constant temperature of 25 °C. Rheological measurements were all made relative to a reference sweep of a clean air–water interface under identical conditions.

### 2.3. Experimental procedure

The Du Noüy ring was flame cleaned immediately before presentation to the air–water interface, and a fresh Wilhelmy plate was used in each experiment. The Langmuir trough was meticulously cleaned by wiping with chloroform, and subsequently rinsing with copious amounts of purified water. The air–water interface was created by introducing 0.05 M phosphate buffer (pH 7.4) to the Langmuir trough. The surface was then cleaned by compressing the trough surface area to a minimum followed by aspiration to remove any surface contaminants. The compression and aspiration steps were repeated until the $\Delta\pi$ upon compression was $\leq 0.1\,\mathrm{mN\,m^{-1}}$. At this point the air–water interface was deemed to be clean and was brought into contact with the Du Noüy ring and the reference measurement recorded. A 100 μl Hamilton syringe (Hamilton Bonaduz AG, Bonaduz, Switzerland) was used to spread phospholipid solutions onto the clean air–water interface until the required surface pressure was achieved. Approximately 30 μl of solution was deposited in the case of DPPC and the DPPC:DPPG mixed monolayer, and approximately 80 μl in the case of DPPG solution. The surface pressure was chosen to be in the liquid-condensed phase of the phospholipid under investigation, where the phospholipid molecules are aligned vertically at the interface. The spread monolayer was left for a period of 15 min to equilibrate and for the spreading solvent to evaporate. The interfacial rheology and surface pressure of the spread monolayer was recorded for a period of 60 min, after which a Hamilton syringe was used to inject 100 μl of protein solution into the subphase below the spread monolayer. The changes in interfacial rheology and surface pressure were then monitored for a further 120 min. Each experiment was carried out in triplicate, and the results presented herein are averages of those repeats.

## 3. Results

### 3.1. Protein adsorption to DPPC monolayers

The effect of the injection of catalase solution beneath a spread monolayer of DPPC, on the interfacial rheology and surface pressure is shown in Figs. 1 and 2, respectively. During the initial 60 min period, prior to the introduction of the catalase, the measured values of $G'$, $G''$ and $\pi$ remained relatively constant. The mono-

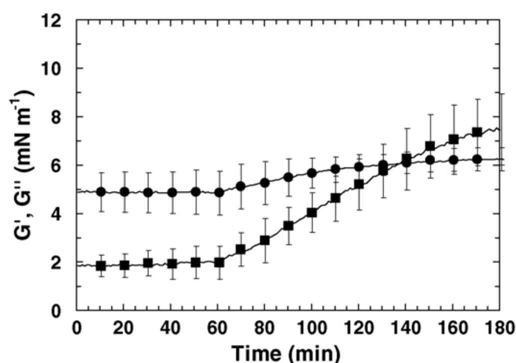


Fig. 1. Interfacial rheological measurements of a spread DPPC monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

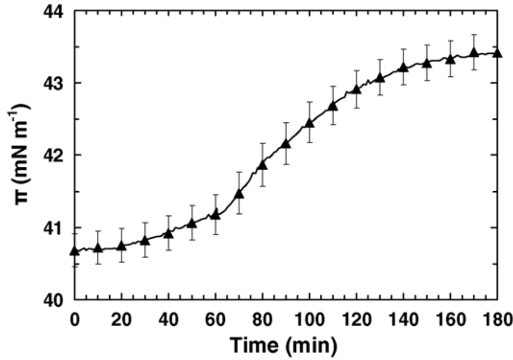


Fig. 2. Surface pressure measurements of a spread DPPC monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min.

layer was liquid-like in nature with values of $G'' > G'$. Injection of the catalase solution induced an immediate change in the observed surface phenomena, with the values of $G'$, $G''$ and $\pi$ all increasing as catalase was adsorbed from the subphase to the spread DPPC monolayer at the air–water interface. As catalase was adsorbed, the values of $G'$ increased at a faster rate than the values of $G''$ and $\pi$. This resulted in a change from a liquid-like monolayer to a gel-like monolayer when the value of $G'$ crossed that of $G''$ approximately 77 min after the injection of the catalase solution.

Figs. 3 and 4 show the effect on interfacial rheology and surface pressure, respectively, of a spread DPPC monolayer with injection of lysozyme solution after 60 min. The figures clearly show that following the injection of lysozyme beneath the spread DPPC monolayer the values of $G'$, $G''$ and $\pi$ remained constant with no observable influence due to the adsorption of lysozyme from the subphase to the interface.

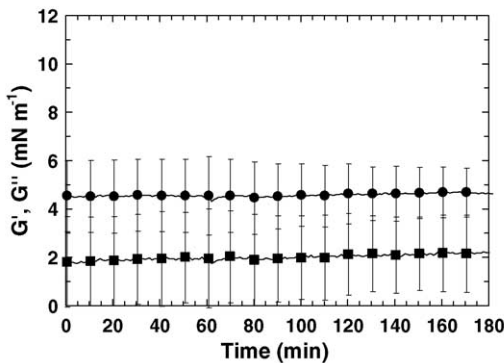


Fig. 3. Interfacial rheological measurements of a spread DPPC monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

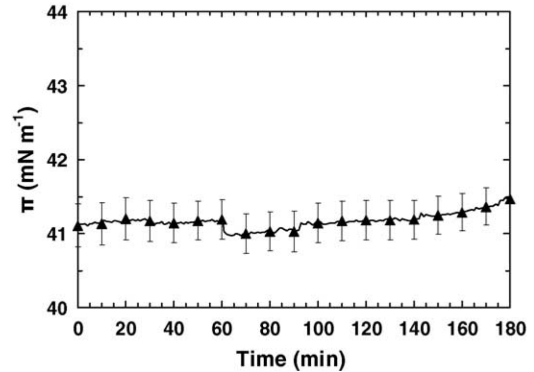


Fig. 4. Surface pressure measurements of a spread DPPC monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min.

### 3.2. Protein adsorption to DPPG monolayers

The measured interfacial rheological characteristics of a spread DPPG monolayer with injection of catalase after 60 min are shown in Fig. 5. Fig. 6 shows the simultaneous surface pressure measurements. The interfacial properties of the DPPG monolayer were similar to those observed in the previous section for DPPC. During the initial 60 min the values of $G'$, $G''$ and $\pi$ were constant and the monolayer was liquid-like in nature with $G'' > G'$. The injection of catalase solution beneath the DPPG monolayer resulted in increased

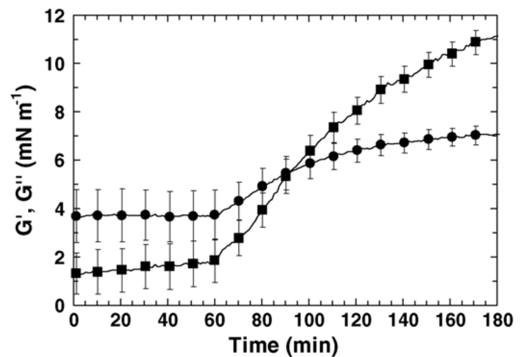


Fig. 5. Interfacial rheological measurements of a spread DPPG monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

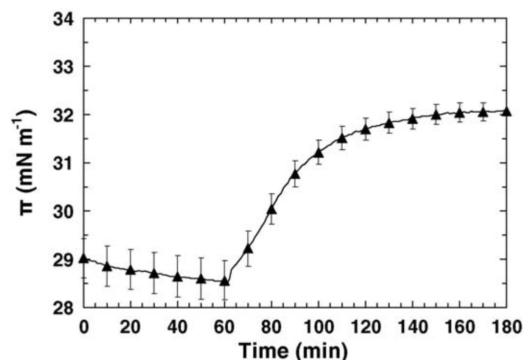


Fig. 6. Surface pressure measurements of a spread DPPG monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min.

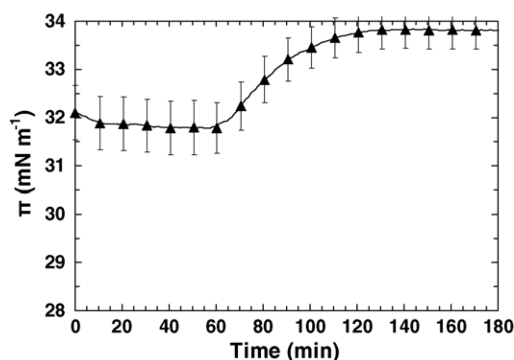


Fig. 8. Surface pressure measurements of a spread DPPG monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min.

values of $G'$, $G''$ and $\pi$. The rate of increase in the value of $G'$ was greater than that of $G''$, resulting in change from liquid like ($G' < G''$) to gel-like ($G' > G''$) behaviour approximately 34 min after the injection of the catalase solution.

The simultaneous interfacial rheology and surface pressure measurements for a DPPG monolayer with an injection of lysozyme solution after 60 min are plotted in Figs. 7 and 8, respectively. The interfacial properties were constant prior to the injection of the lysozyme solution. Injection of the lysozyme solution caused the measured surface phenomena to increase, in contrast to the behaviour observed previously for an injection beneath DPPC. The resultant increases in $G'$, $G''$ and $\pi$ were similar to those observed for the injection of catalase beneath DPPC and DPPG. The liquid-like monolayer became gel-like approximately 19 min after the injection of lysozyme into the subphase. The magnitudes of the increase in surface properties were smaller than the corresponding changes observed for the injection of catalase.

### 3.3. Protein adsorption to DPPC:DPPG (7:3) monolayers

Injecting catalase into the subphase below a DPPC:DPPG monolayer after a 60 min equilibration period resulted in the measured surface phenomena shown in Figs. 9 and 10. An immediate increase in the recorded values of $G'$, $G''$ and $\pi$ was again observed when catalase solution was introduced to the subphase. The mixed monolayer underwent a transition from

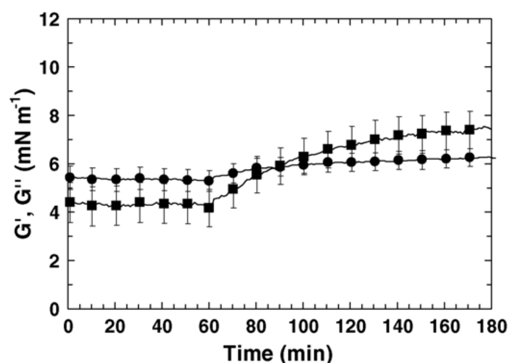


Fig. 7. Interfacial rheological measurements of a spread DPPG monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

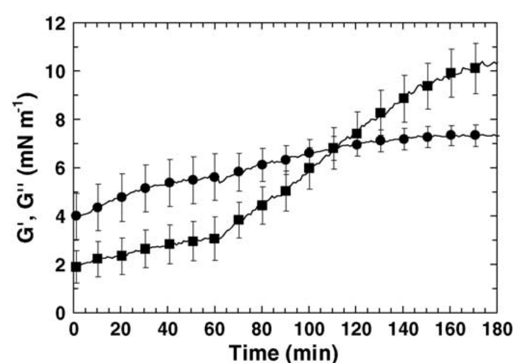


Fig. 9. Interfacial rheological measurements of a spread DPPC: DPPG (7:3) monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

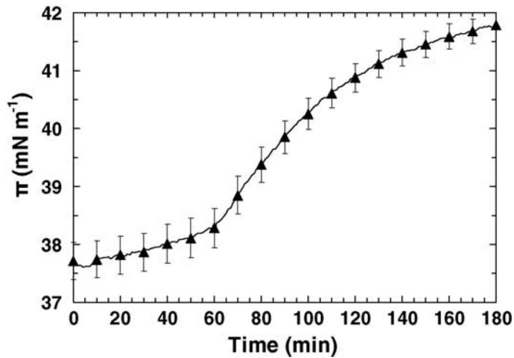


Fig. 10. Surface pressure measurements of a spread DPPC:DPPG (7:3) monolayer. Injection of 100 μl catalase solution (25 mg ml$^{-1}$) into subphase after 60 min.

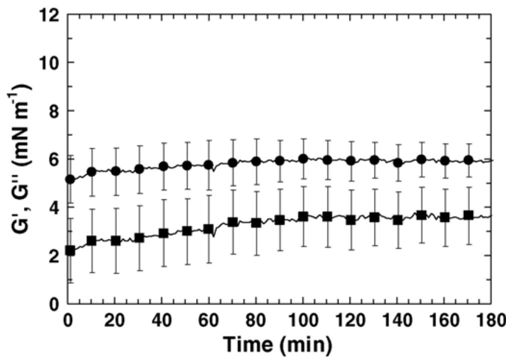


Fig. 11. Interfacial rheological measurements of a spread DPPC: DPPG (7:3) monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min ($G'$ (■), $G''$ (●)).

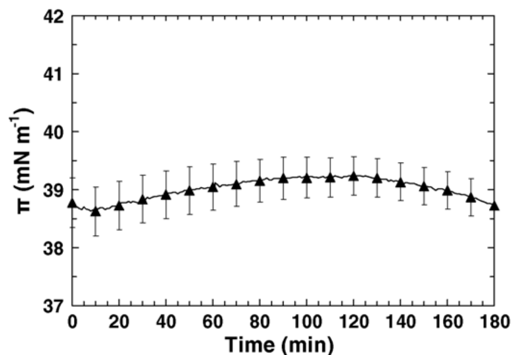


Fig. 12. Surface pressure measurements of a spread DPPC: DPPG (7:3) monolayer. Injection of 100 μl lysozyme solution (100 mg ml$^{-1}$) into subphase after 60 min.

liquid-like to gel-like approximately 52 min after the injection of the catalase solution.

When lysozyme was injected into the subphase beneath a DPPC:DPPG monolayer there was no effect on the measured surface properties. These results are shown in Figs. 11 and 12.

## 4. Discussion

The measured interfacial rheology and surface pressure of the monolayers studied were all increased by the adsorption of catalase from the subphase. However, only the pure DPPG monolayer was affected by the adsorption of lysozyme. The surface properties of monolayers containing DPPC were unaffected by the injection of lysozyme into the subphase. In all cases, the subphase consisted of phosphate buffer at pH 7.4. At this pH catalase is above its isoelectric point of ∼5.4 and therefore is negatively charged, whereas lysozyme is below its isoelectric point of ∼11 and carries a positive charge. DPPG is an ionic phospholipid which forms negatively charged monolayers when spread at the air–water interface (Vollhardt et al., 2000). The presence of an additional, positively charged, tertiary amine group ($N^+(CH_3)_3$) in the DPPC molecule makes it a neutral molecule, which forms a neutral monolayer when spread at the air–water interface. Therefore, it is reasonable to assume that the positively charged lysozyme molecules will be attracted to the negatively charged DPPG monolayer, where they can interact with the phospholipid molecules of opposite charge. This electrostatic attraction to the DPPG monolayer at the air–water interface will enhance the adsorption of lysozyme, producing the observed changes in $G'$, $G''$ and $\pi$ which are absent when lysozyme is injected beneath the neutral DPPC, and predominantly neutral DPPC:DPPG monolayer.

Despite this electrostatic drive towards adsorption, the influence of lysozyme upon the measured surface phenomena is small when compared to the results observed for the injection of catalase beneath DPPG. The injection of catalase resulted in increases in $G'$, $G''$ and $\pi$ in all three monolayers investigated. The increase in $\pi$ as a result of the adsorption of catalase to the phospholipid monolayers was ∼3 mN m$^{-1}$ for all monolayers studied. The magnitude of the changes in interfacial rheology, especially $G'$, of

the phospholipid monolayers decreased in the order DPPG > DPPC:DPPG > DPPC. Adsorption of catalase also induced a transition from a liquid-like interface ($G' < G''$) to gel-like interface ($G' > G''$). The time taken for this transition to occur increased in the order DPPG < DPPC:DPPG < DPPC. From these observations, it can be seen that despite there being a potential electrostatic repulsion between the negative charges on the catalase molecules and those of the DPPG monolayer, catalase readily adsorbs to the spread DPPG monolayer. In aqueous solution catalase is known to be unstable (Tanford and Lovrien, 1962) and undergoes "surface denaturation" at the air–water interface (MacRitchie, 1986). In an earlier study, the authors showed that catalase undergoes rapid adsorption to a clean air–water interface at pH values in excess of the isoelectric point (Roberts et al., submitted for publication). The partially unfolded, negatively charged catalase molecules can readily form cross-links with adjacent molecules at the surface, leading to the formation of a gel-like monolayer. The conformational changes associated with the formation of cross-links within the surface film are sufficient to overcome any electrostatic repulsion between the DPPG containing monolayers and the adsorbing catalase molecules. The larger, more rapid increases in $G'$ observed show that catalase penetration of the mixed DPPC:DPPG monolayer, and the pure DPPG monolayer occurs more readily than with lysozyme. This could be considered to be counterintuitive given the large differences in molecular mass and solution conformation between the two proteins. The extent of penetration of the phospholipid monolayers by catalase is controlled by the different head groups of the phospholipid molecules. The smaller phosphoglycerol (PG) head group on DPPG is readily penetrated by both catalase and lysozyme. Changing the head group to phosphocholine (PC) in the DPPC monolayers blocks the penetration of lysozyme, and reduces the rate and extent of penetration by catalase. In the mixed monolayer, where the interface is populated by regions of both PG and PC head groups, the penetration of lysozyme remains blocked, whereas the results for catalase are closer to those of the DPPG monolayer than the DPPC monolayer. Therefore, we can conclude that inclusion of DPPG within the DPPC monolayer opens up the interface to penetration by the partially unfolded catalase molecules.

Lysozyme, in contrast to catalase, retains its more compact, globular structure in solution and at the air–water interface (Lu et al., 1998; Lechevalier et al., 2003). These more compact protein molecules adsorb individually to the air–water interface, initially forming small isolated regions of protein network, which eventually combine to form a continuous gel-like interfacial gel (Erickson et al., 2000). During the adsorption of lysozyme to a clean air–water interface this results in an induction period prior to the onset of the development of surface properties. The magnitude of the increases in $G'$, $G''$ and $\pi$ accompanying the formation of the interfacial protein gel were smaller for lysozyme than for catalase (Roberts et al., submitted for publication). The current work has shown that increases in $G'$, $G''$ and $\pi$ were only observed during the adsorption of lysozyme to a DPPG monolayer. No changes were observed in the surface properties of DPPC or DPPC:DPPG (7:3) monolayers upon the injection of lysozyme to the subphase. The results observed for catalase have shown that DPPG monolayers are more susceptible to penetration by an adsorbing protein network than DPPC monolayers. Therefore, when lysozyme is injected beneath a DPPG monolayer the electrostatic attraction, in combination with the more penetratable monolayer, results in an immediate increase in $G'$, $G''$ and $\pi$, with an accompanying change from a liquid-like to gel-like interfacial film. The monolayers containing DPPC are less susceptible to penetration by the lysozyme molecules, and offer no electrostatic attraction, and as a result over the time course of our experiments no changes in $G'$, $G''$ and $\pi$ were observed upon injection of lysozyme to the subphase.

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