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ORIGINAL CONTRIBUTION

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Interfacial properties of mixtures of lecithin with a block copolymer surfactant at the water/air and water/oil interfaces

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Abstract Surface pressure-area isotherms have been determined for both a pure lecithin (L,α-dipalmitoyl phosphatidyl choline) and an impure lecithin (soya bean lecithin) at the water/air and water/oil interfaces. Equations of state have been applied and an equation of Gaines was found to be particularly successful in describing the isotherms. Mixed monolayers with an ABA nonionic block copolymer surfactant (A is poly(12-hydroxystearic) acid and B is poly(ethylene oxide)) were also investigated. The additivity rule was obeyed only at high surface pressures; inefficient packing was observed at low surface pressures. The polymer may promote a horizontal headgroup orientation in the lecithin, which gives rise to this effect. The presence of electrolyte up to very high concentrations in the aqueous phase (8.75 mol dm^{-3} NH_4NO_3) was shown to expand the lecithin monolayer.

Key words Lecithin – block copolymer surfactant – poly(12-hydroxystearic) acid – pressure-area – ammonium nitrate – monolayer

Introduction

Lecithin is a naturally occurring surfactant that is widely used in practice to prepare oil-in-water or water-in-oil emulsions. Various materials can be obtained depending on the source e.g. Egg Lecithin, Soya Bean Lecithin etc. There is ample literature on the properties of a spread monolayer at the air/water interface [1]. Results at the oil/water interface are scarce. In this paper we will report some results on the surface pressure-area isotherm for dipalmitoyl lecithin (a pure form of the material) and Soya Bean Lecithin both at the air/water and the oil/water interfaces. Results will also be shown for mixtures of lecithin with a block copolymer, namely B246, supplied by ICI Speciality Chemicals. This block copolymer is of the A-B-A type where A is poly(12-hydroxystearic) acid and B is polyethylene oxide. Surface pressure-area isotherms for B246 were obtained previously [2], and it was shown that a coherent film readily forms at the water/air and water/oil interfaces. B246 is a very effective stabilizer for water-in-oil emulsions. To investigate the effect of adding lecithin to the B246 monolayer we have obtained π-A isotherms for various mixtures of lecithin with B246 at the air/water and oil/water interfaces. The effect of adding electrolyte up to high concentrations, namely NH_4NO_3, is also investigated. As will be seen later, the film properties are characteristic of the block copolymer which tends to displace the more weakly adsorbed lecithin molecules.

Experimental

Materials

The water was deionised followed by a double distillation in an all glass still (surface tension 72.0 mN m^{-1} (25 °C), and conductance $< 10^{-6}$ S cm^{-1}). All electrolytes were

AR grade. Ammonium nitrate was purchased as the pure recrystallised material from Frederick Allen and Sons Ltd., London; a 70% W/V solution in water had a pH of 5.0 ± 0.1 and a surface tension of 81.8 $\mathrm{mN\,m^{-1}}$ at 25 °C. No surface active impurities from the solutions were detected using the Langmuir trough.

The spreading solvents were glass-distilled *n*-hexane from Rathburn Chemicals Ltd and AR ethanol; both were checked for surface active impurities using the Langmuir trough. The oil phase was an aliphatic hydrocarbon oil 'Isopar M' (Esso Chemicals). The material is a high quality distillation product comprising a mixture of aliphatic oils. It is characterised by a density, at 15 °C, of 0.784 $\mathrm{g\,cm^{-3}}$, and a refractive index and viscosity of 1.436 and 2.46×10^{-4} Pa s, respectively, at 20 °C. Total aromatics in the oil are less than 0.3%. The initial boiling point is 207 °C, and the dry point (complete distillation) is 254 °C. To ensure the absence of interfacially active impurities, the oil was purified using a pre-roasted Fullers earth column; the purified oil had an interfacial tension against water of 51 $\mathrm{mN\,m^{-1}}$ at 25 °C.

The polymeric surfactant B246 is an A-B-A block copolymer; the headgroup (B) is a polyethylene oxide chain (PEO) and the tails (A) are poly(12-hydroxystearic) acid (PHS); it was supplied by ICI speciality chemicals. Gel Permeation Chromatography gave a polydispersity of 1.94. The number average molar mass by vapour pressure measurements was 3543 $\mathrm{g\,mol^{-1}}$. X-ray data gave a lamellar bilayer structure with an average PHS chain length of five 12-hydroxystearic acid units [3].

Two types of lecithin were used. *L*,α-dipalmitoyl phosphatidyl choline (DPL) from Sigma Chemicals (purity by gas chromatography – 99.7%; molar mass 734.1 $\mathrm{g\,mol^{-1}}$). Soya bean lecithin (SBL) was BOCM – Silcock's 'Bolec C' grade, which is a standardised pale soya lecithin, the major ingredient is dipalmitoyl lecithin but distearoyl and dioleyl are also present (mass percentages 90, 7, and 3 respectively). It is acknowledged that the presence of impurities can markedly affect monolayer behaviour, and it is true that in recent times most monolayer studies with lecithins have used highly purified materials. However, the present study forms part of a broader investigation of the properties of a commercial water-in-oil emulsion system stabilized by three commercial amphiphiles – soya bean lecithin, the polymer B246 and sorbitan sesquioleate. The behaviour of the commercial system itself might well be affected by the presence of impurities in the amphiphiles, and it is for this reason that it was necessary to examine both the pure and the impure lecithin. A molar mass of 780 $\mathrm{g\,mol^{-1}}$ was used in all calculations based upon the quoted value of Shah and Schulman [4]. (Vapour pressure measurements gave a molar mass of 2044 $\mathrm{g\,mol^{-1}}$, suggesting that some association occurs and this is also reflected in the anomalously thick bilayers which have been found for SBL in thin film measurements [5].)

Techniques

A semi-automatic Langmuir trough was used, based on the design of Doroszkowski [6], enabling measurements to be carried out at both W/A and W/O interfaces [7]. The glass trough assembly was housed in a thermostatically controlled cabinet and the subphase temperature controlled by water circulating through a glass coil. The working area of the trough was 205.8 $\mathrm{cm^2}$. The surface pressure was determined by the Wilhelmy plate method, using a roughened platinum plate. The plate was prewetted with water for the W/O measurements to ensure a good contact angle; a silvery appearance indicated good wetting. A 9:1 v/v mixture of *n*-hexane and ethanol was used as the spreading solvent in all the W/A monolayer experiments. Stock solutions contained a total surfactant concentration of 300 $\mathrm{mg\,dm^{-3}}$. Monolayers were spread from an 'Agla' micrometer syringe in 10 or 20 μl dosages. Sufficient time was always allowed between surfactant additions for evaporation of the spreading solvent from the monolayer (W/A measurements), and for the surface pressure to reach a steady value. The low π region of the isotherm (0–15 $\mathrm{mN\,m^{-1}}$) was obtained by successive additions of aliquots of the surfactant stock solutions at constant trough area. The monolayer was then compressed using the moving barrier to obtain the higher π values (barrier speed 1.0 $\mathrm{cm^2\,s^{-1}}$). This procedure was found to minimise dissolution of surfactant into the oil phase in the water/oil measurements. For the W/O measurements the spreading solvent was a 9:1 v/v mixture of Isopar M and ethanol; the syringe needle was placed below the interface and the solution ejected onto a glass 'claw' with a tip in the interface; re-cleaning of the trough and fresh oil between each run was required as the oil phase became contaminated with surfactant.

Results and Discussion

Monolayers containing a single surfactant

Lecithin

L,α-dipalmitoyl lecithin (DPL) is zwitterionic so the experiments were carried out at a constant ionic strength of 0.02 $\mathrm{mol\,dm^{-3}}$ (NaCl) and pH 5. (The block copolymer is nonionic and the π-A isotherms are unaffected by electrolyte at this low ionic strength.) The π-A isotherms for DPL

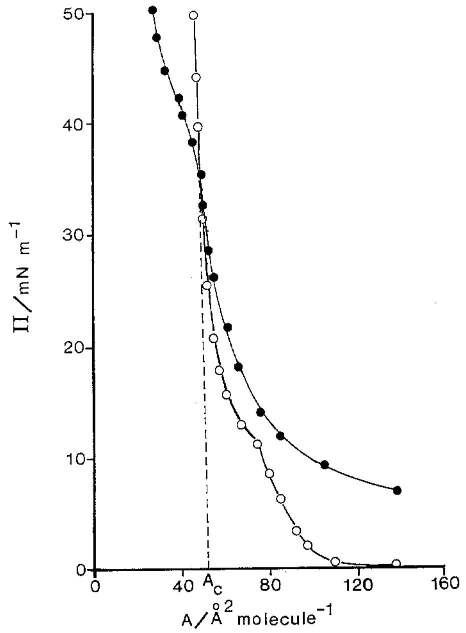

Fig. 1 *L*,α-dipalmitoyl lecithin (DPL) W/A and W/O isotherms at 25 °C. o W/A interface; ● W/O interface Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

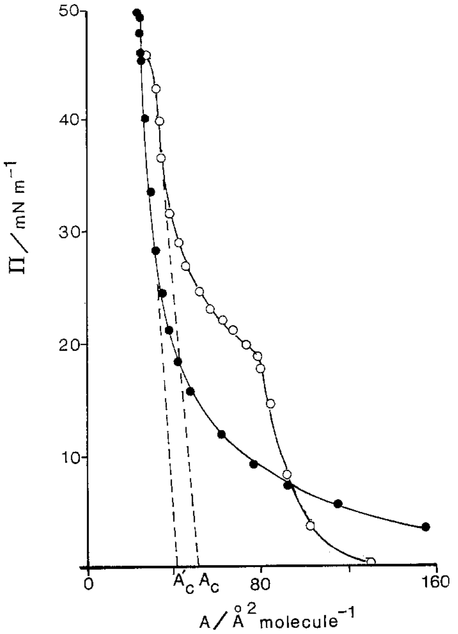

Fig. 2 Soya bean lecithin (SBL) W/A and W/O isotherms at 25 °C. o W/A interface; ● W/O interface Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

and Soya bean lecithin (SBL) are shown in Figs. 1 and 2 respectively. The W/A curves both show an incipient *L–C* transition around 12 and 20 mN m^{-1} respectively, which may correspond with the reorientation of the lecithin head group from a horizontal to a more vertical configuration. The SBL transition is more extended and involves a larger change in area; the fact that a transition is shown is perhaps surprising as it is not one homologue. Pallas and Pethica [1] obtained a first order transition for highly purified dipalmitoyl lecithin at the 0.01 mol dm^{-3} NaCl/air interface at a π value of 11.5 mN m^{-1}. Although the DPL transition commences at approximately the same surface pressure in the present work, the transition region is not horizontal: however, no impurities were detected by TLC in the DPL. Furthermore, Fig. 1 is in good agreement with the results of Albrecht et al. [8]. The close-packed area per molecule A_c value of 53.0 ± 2.5 Å^2 molecule^{-1} is in good agreement with the value of 52.0 Å^2 molecule^{-1} of Albrecht et al. [8]. Pallas and Pethica did, however, control the humidity of the system very carefully.

At the W/O interface the DPL isotherm shows a transition at 37 mN m^{-1} corresponding to a molecular area of 50 Å^2 molecule^{-1}. At this relatively small molecular area the transition possibly represents a gradual staggering of the headgroups with increasing pressure or dissolution into the oil phase; it probably does not correspond to the liquid condensed (*L–C*) transition observed by Yue and Sehgal [9, 10] in distearoyl lecithin monolayers at the W/O interface, which occurred at relatively large molecular areas. In the present work, the DPL and SBL W/O isotherms are condensed with respect to the respective W/A curves, above surface pressures of 35 mN m^{-1} and 8 mN m^{-1} respectively. The continued condensation of the DPL W/O curve at surface pressures above 43 mN m^{-1} is most probably explained by loss of film material from the interface. For SBL, possibly oil-soluble impurities in the SBL are lost from the interface on compression, but the effect is large and is more probably the effect of the oil phase in assisting a gradual but efficient packing of the variable alkyl chains; this is consistent with the transition found for DPL but not for SBL.

C.P.K. molecular models of DPL gave a minimum projected area of 51.6 ± 2.2 Å^2 with the headgroup vertical and 85.5 ± 5.4 Å^2 with the headgroup horizontal. The former agrees with the experimental A_c values at the W/A interface of 53.0 ± 2.5 and 51.7 ± 2.2 Å^2 molecule^{-1} for DPL and SBL respectively. The DPL W/O isotherm has an estimated A_c of 65 ± 15 Å^2 molecule^{-1} whereas that for SBL is rather low at 41.1 ± 3.6 Å^2 molecule^{-1} implying very efficient alkyl chain packing. The larger area/molecule (at zero pressure) for DPL at the W/O interface, as opposed to the W/A interface, must arise from oil penetration between the alkyl chains, especially at low pressures. Where the condensed regions of the two curves coincide (Fig. 1), the oil is probably compressed out; at

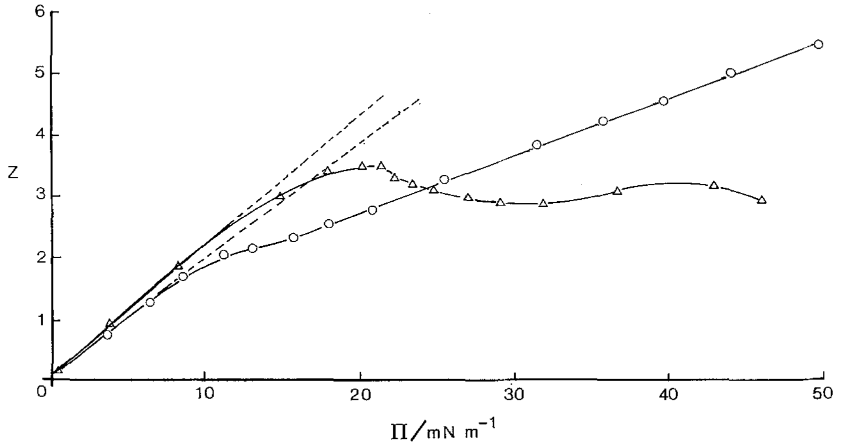

Fig. 3 *L*, α-dipalmitoyl lecithin (DPL) and soya bean lecithin (SBL) Z-π isotherms at 25 °C at the W/A interface ○ DPL; Δ SBL Ordinate: Z Abscissa: π/mN m^{-1}

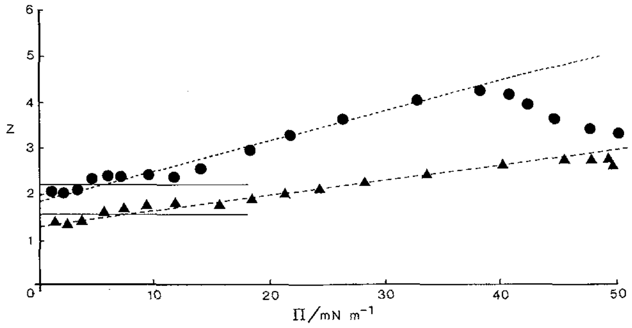

Fig. 4 *L*, α-dipalmitoyl lecithin (DPL) and soya bean lecithin (SBL) Z-π isotherms at 25 °C at the W/O interface ● DPL, ▲ SBL Ordinate: Z Abscissa: π/mN m^{-1}

higher pressures either head group staggering occurs (assisted by the oil phase?) or DPL is lost from the interface.

To observe deviations from the 'ideal' equation of state the compressibility factor, $Z(Z = \pi A/kT)$ is plotted against π; a monolayer obeying the equation $\pi(A - A_0) = ikT$, would give a straight line of slope A_0/kT and intercept i. Both lecithins give linear $Z - \pi$ graphs up to a surface pressure of 10 mN m^{-1} at the W/A interface (Fig. 3). A_0 is 77.1 ± 2.4 and 81.9 ± 1.3 Å^2 molecule^{-1} and i is 0.10 ± 0.02 and 0.16 ± 0.02 for DPL and SBL respectively. The A_0 values are consistent with a horizontal headgroup orientation prior to transition (< 10 mN m^{-1}). The low values of i perhaps indicate the formation of 'islands' at low pressures. For DPL the $Z - \pi$ plot is linear in the post-transition region, giving A_0 as 39.7 ± 1.1 Å^2 molecule^{-1} and i as 0.83 ± 0.05, implying a reduced headgroup area on compression and the absence of islands. However, an equation of the form $\pi(A - A_0) = ikT$ would not be expected to apply at high π values, where the van der Waals forces between the alkyl chains are acting.

The $Z - \pi$ graphs at the W/O interface for both lecithins are shown in Fig. 4. Lecithin behaves 'ideally' at low π values (horizontal black lines) giving i values of 2.2 ± 0.1 and 1.5 ± 0.1 for DPL and SBL respectively. Application of the equation $\pi(A - A_0) = ikT$ (dashed lines – Fig. 4) gives sensible i values of 1.85 ± 0.07 for DPL and 1.30 ± 0.03 for SBL, but the A_0 values of 26.7 ± 1.8 and 13.8 ± 0.9 Å^2 molecule^{-1} are too low for meaningful molecular areas.

Several workers have developed two-dimensional equations of state analogous to those used for gases; for example, de Boer [11] used an analogy of the van der Waals equation and Pethica et al. [12] tried a virial equation. However, all 2D analogues ignore the presence of the sub-phase. It must be remembered that fitting equations to isotherms is a necessary but not sufficient condition for the film to behave according to the model on which the equation is based. A rigorous thermodynamic method has been applied by Gaines [13], based on the previous ideas of Saraga and Prigogine [14], Fowkes [15] and Lucassen – Reynders [16], to derive the equation.

$$\pi = \frac{kT}{\omega_1}\left[\ln\left(1 + \frac{\omega_1}{(A - \omega_2)}\right) - \ln f_1^\sigma\right], \qquad (1)$$

where A is the area per molecule of the spread surfactant, ω_1 is the partial molar area of water (area per molecule for water $= 9.65$ A^2, 25 °C), ω_2 is the partial molar area of the surfactant (close-packed area per molecule of surfactant), f_1^σ is the activity coefficient of water in the surface region. By expressing the above equation in the form

$$\pi + \frac{kT}{\omega_1}\ln f_1^\sigma = \frac{kT}{\omega_1}\ln\left\{1 + \frac{\omega_1}{(A - \omega_2)}\right\} \qquad (2)$$

a master plot of $\pi + (kT/\omega_1)\ln f_1^\sigma$ against $(A - \omega_2)$ was prepared. By shifting the axes the master plot can be superimposed on the experimental curves. The required vertical displacement gives the value of $(kT/\omega_1)\ln f_1^\sigma$ and the horizontal displacement the value of ω_2.

The application of Gaines equation of state is shown in Fig. 5 for DPL and Fig. 6 for SBL. With appropriate values for ω_2 and f_1^σ, the equation describes the isotherms well, both in the pre-transition and post-transition regions. The values of ω_2 and f_1^σ, are summarised in Table 1. A reduction in ω_2 for the W/A films occurs during the transition, in keeping with a change from a horizontal to a vertical headgroup. For both lecithins, the ω_2 values for the W/O films are approximately equal to the W/A post-transition values. This might explain why an L–C transition was not observed at the W/O interface; the oil phase assists the vertical-orientation of the alkyl chains and hence of the head groups at low surface pressures. The low values of ω_2 for SBL in both cases again implies soluble impurities or improved packing. The values of f_1^σ for the W/A pre-transition region and the W/O interface seem reasonable for a liquid film. However, the lower values found for the W/A post-transition regions are surprising, since these are condensed films for which the water in the surface region would be expected to behave less ideally.

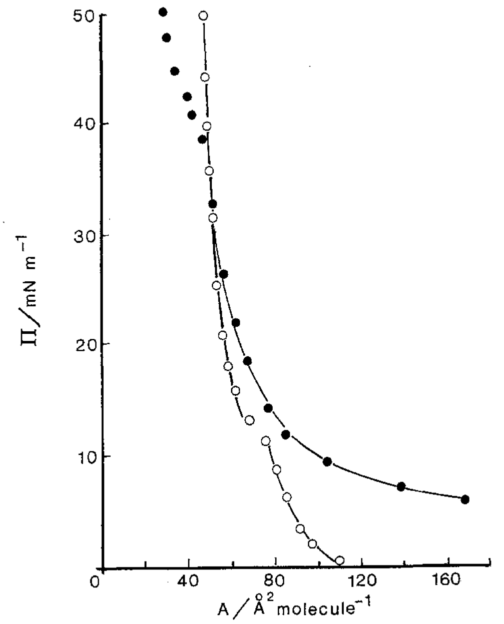

Fig. 5 Application of Gaines' equation to the π-A data of L,α-dipalmitoyl lecithin (DPL). ○ W/A interface; ● W/O interface Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

Table 1 Values for ω_2 and f_1^σ obtained by applying Gaines' equation to the lecithin experimental data

	ω_2 / Å^2 molecule^{-1}	f_1^σ
DPL, W/A interface		
(i) pre-transition	60.5 ± 0.5	1.20 ± 0.01
(ii) post-transition	42.5 ± 0.5	1.04 ± 0.01
DPL, W/O interface		
(pre-transition region)	44.0 ± 1.2	0.93 ± 0.01
SBL, W/A interface		
(i) pre-transition	70.0 ± 0.8	1.19 ± 0.01
(ii) post-transition	24.5 ± 0.5	0.75 ± 0.01
SBL, W/O interface	23.7 ± 2.0	0.98 ± 0.01

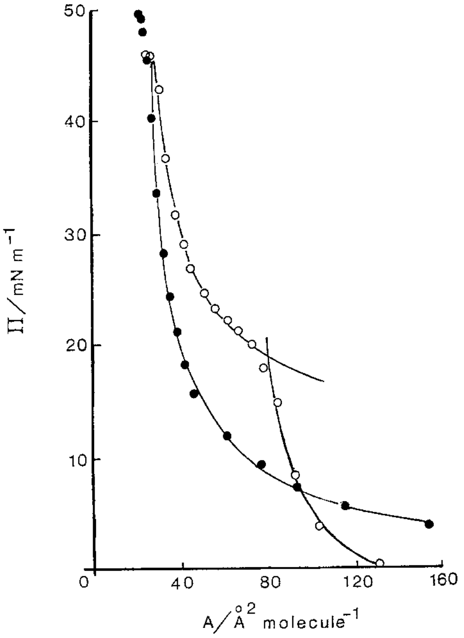

Fig. 6 Application of Gaines' equation to the π-A data of soya bean lecithin (SBL). ○ W/A interface; ● W/O interface Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

The block copolymer

The W/A and W/O π-A isotherms for the ABA block copolymer B246 are given in ref [2]. Both isotherms are essentially liquid-like, as expected for a high polymer.

Mixed surfactant monolayers

Block copolymer and lecithin

The π-A isotherms at the W/A interface are shown in Fig. 7. Except at low surface pressures, where slight negative deviations occur, the additivity rule is obeyed; that is

$$A_t = x_1 A_1 + x_2 A_2 + \cdots \quad \text{at constant } \pi ,$$

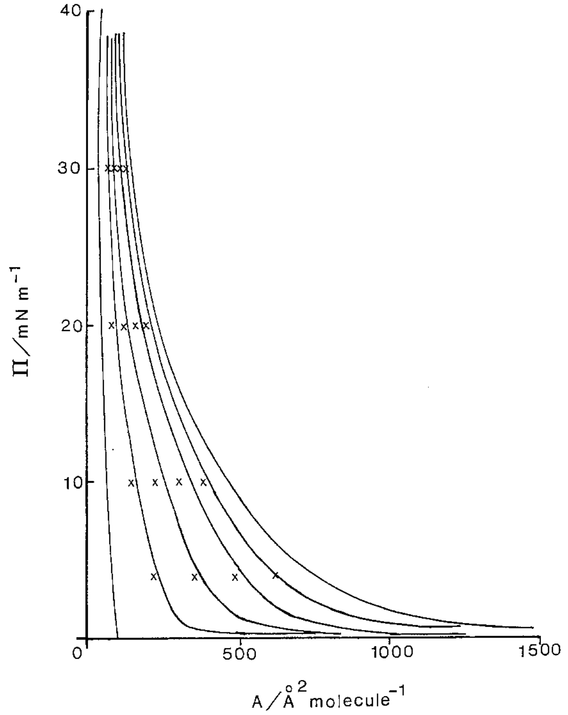

Fig. 7 B246 - L,α-dipalmitoyl lecithin (DPL) mixed monolayer isotherms at the W/A interface at 25 °C. From left to right $x_{B246} = 0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0. The theoretical positions for the isotherms are indicated (X). Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

where A_t is the theoretically-predicted average area per molecule for the mixed monolayer, $A_1, A_2, \ldots$ are the molecular areas of the single component monolayers, and $x_1, x_2 \ldots$ are the mol fractions of the components in the monolayer (based on molar mass of block copolymer). An excess area term, ΔA, is defined by

$$\Delta A = A_e - A_t \quad \text{at constant } \pi ,$$

where A_e is the experimentally-determined area per molecule. A positive value for ΔA implies inefficient surfactant packing, whereas a negative value implies improved packing. The packing efficiency is shown in Fig. 8. Except at high surface pressures, packing is inefficient, the maximum deviations occurring at 0.5 mol fraction. Results for this mol fraction at the W/O interface are shown in Fig. 9 and Table 2. Here, a higher surface pressure of 40 mN m^{-1} is required to achieve efficient packing. Measurements at the W/A interface using the impure lecithin (SBL) (Fig. 10) showed that it behaved in a similar manner to DPL, so that the impurities do not influence the packing.

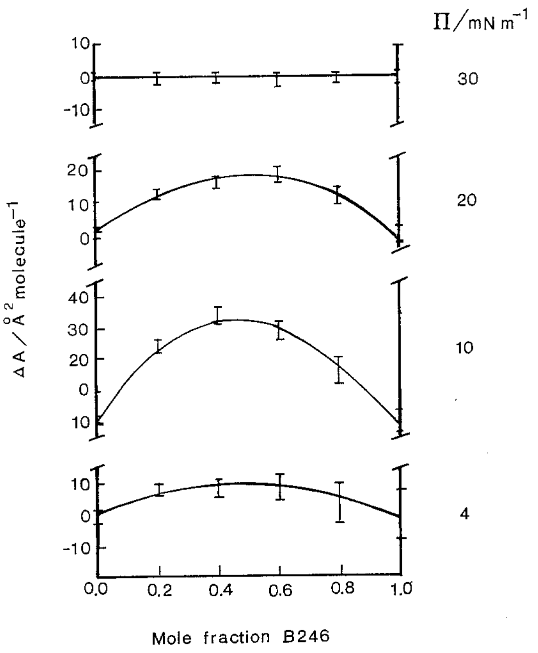

Fig. 8 Deviations from additivity for B246-L,α-dipalmitoyl lecithin (DPL) mixed monolayers at the W/A interface at 25 °C. Ordinate: ΔA/Å molecule^{-1} Abscissa: Mole fraction B246

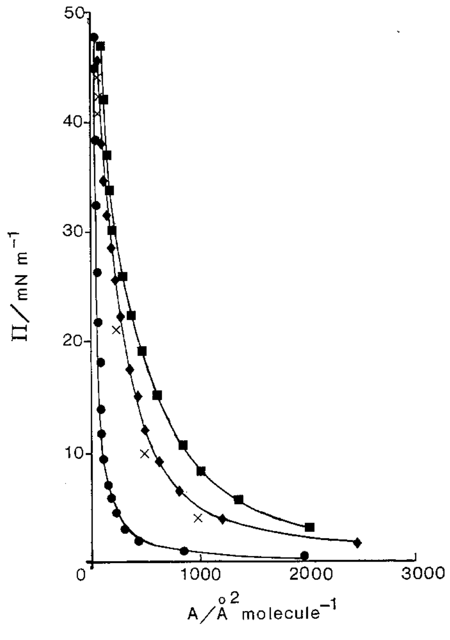

Fig. 9 B246 – L,α-dipalmitoyl lecithin (DPL) mixed monolayer isotherms at the W/O interface at 25 °C. From left to right $x_{B246} = 0.0$, 0.5 and 1.0. The theoretical positions for the isotherms are indicated (X). Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

The inefficient packing of these two amphiphiles is more likely to be associated with headgroup rather than with hydrocarbon tail interactions as the packing is inefficient even at the W/O interface where van der Waals interactions between the alkyl chains are reduced. At low surface pressures the horizontal headgroup orientation for lecithin would minimise ionic repulsions between the phosphatidyl choline groups; perhaps the cosurfactant

Table 2 Deviations from additivity for the composition $x_{B246} = x_{DPL} = 0.5$, at the W/O interface at 25°C

π/mN m^{-1}	ΔA/Å^2 molecule^{-1}
4	165 ± 12
10	94 ± 6
20	81 ± 3
30	45 ± 1.2
40	1.4 ± 0.8

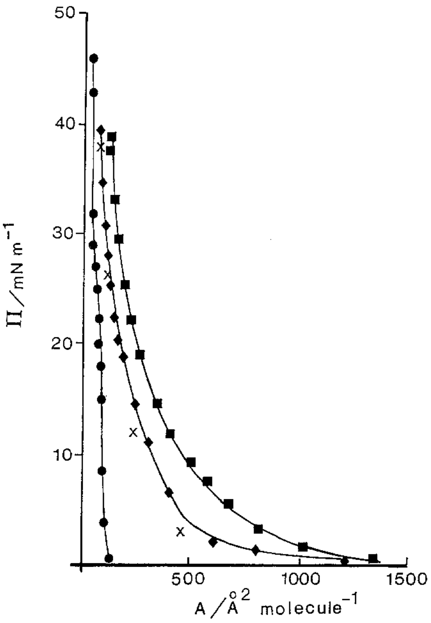

Fig. 10 B246 - Soya bean lecithin (SBL) mixed monolayer isotherms at the W/A interface at 25 °C. From left to right $x_{B246} = 0.0$, 0.48 and 1.0. The theoretical positions for the isotherms are indicated (X) Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

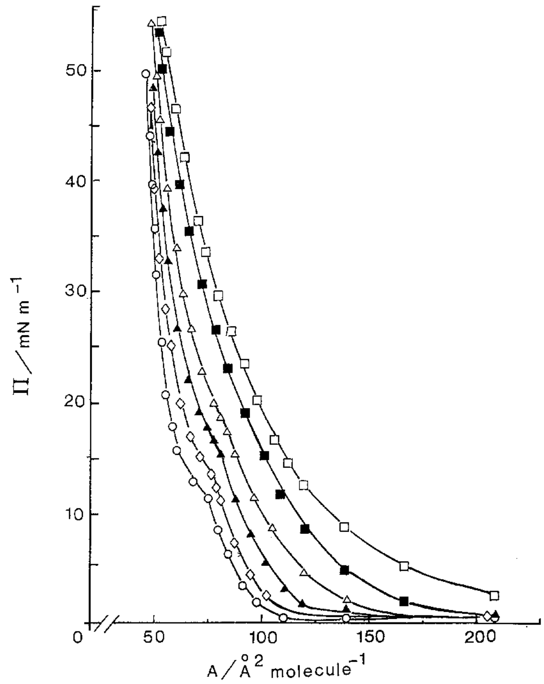

Fig. 11 The effect of NH_4NO_3 on the L,α-dipalmitoyl lecithin (DPL) W/A isotherms at 25 °C. The concentration of NH_4NO_3 is ○ 0 % w/v, 0 mol dm^{-3}; ◇ 1 % w/v, 0.13 mol dm^{-3}; ▲ 10 % w/v, 1.25 mol dm^{-3}; △ 30 % w/v, 3.75 mol dm^{-3}; ■ 50 % w/v, 6.25 mol dm^{-3}; □ 70 % w/v, 8.75 mol dm^{-3}; Ordinate: π/mN m^{-1} Abscissa: A/Å^2 molecule^{-1}

B246 polymer assists a preferred horizontal orientation, increasing the net molecular area at the lower surface pressures. The positive ΔA at low surface pressures implies the absence of domains; it is difficult to visualize these forming simply by increasing the pressure, thus the zero ΔA values at high surface pressure imply ideal mixing.

The effect of electrolyte upon the single component monolayer

The π-A isotherms for DPL at the ammonium nitrate solution/air interface are shown in Fig. 11. The DPL monolayer apparently becomes more expanded as the electrolyte concentration is raised. The collapse pressure is also raised. The DPL transition is still present at a concentration of ammonium nitrate as high as 3.75 mol dm^{-3} (Fig. 11). Cadenhead et al. [17] also studied the effect of varying the substrate ionic strength (and pH) on a lecithin monolayer, using sodium chloride concentrations up to 0.15 mol dm^{-3} (pH 5.3) (also calcium chloride and versene concentrations up to 10^{-5} mol dm^{-3} (pH 5.7) were used). "Variations of 3 to 4 Å molecule^{-1} and 2.3 dynes cm^{-1} were observed even though the "lift-off" and collapse points of the isotherm remained invariant." Their observation is in agreement with our isotherm of 0.13 mol dm^{-3} NH_4NO_3 (Fig. 11) in which we observe an expansion of 8 Å^2 molecule^{-1} at the transition point.

In ref. [2] it is shown that in experiments with electrolyte in the sub-phase, the π-A isotherm is open to misinterpretation. It is clear that an expansion of the isotherm must occur, even if there is no interaction of the surfactant with the electrolyte, and a more satisfactory method of displaying the results is a γ-A plot.

Ammonium nitrate interacts strongly with the ionic DPL causing a dramatic expansion of the monolayer (Fig. 12). Salting-out is unlikely to be responsible as the lecithin headgroup is already horizontally oriented at low surface pressures. Anions are generally more surface active than cations [18], so that the zwitterionic head group of lecithin could become anionic in the presence of the electrolyte, whereas the cationic trimethylammonium ion is

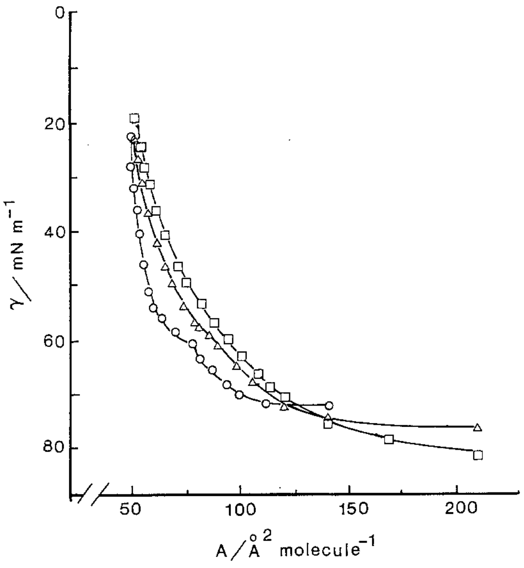

Fig. 12 The effect of NH_4NO_3 on the L,α-diplamitoyl lecithin (DPL) W/A γ/A isotherm at 25 °C. The concentration of NH_4NO_3 is ○ 0 % w/v, 0 mol dm^{-3}; △ 30 % w/v, 3.75 mol dm^{-3}; □ 70 % w/v, 8.75 mol dm^{-3}; Ordinate: γ/mN m^{-1} Abscissa: A/Å^{2}molecule^{-1}

partially neutralised by the excess of nitrate anions present at the surface; the resulting charged layer would be more expanded due to ionic repulsions.

Conclusions

Single component monolayers

The lecithin W/O π-A isotherm is more expanded than the W/A isotherm at low surface pressures due to reduced van der Waals attraction between the surfactant hydrocarbon chains. The apparent condensation of SBL above 8 mN m^{-1} is probably attributable to the dissolution of impurities (SBL) into the oil phase, combined with improved packing of the variable alkyl chains. The equation $\pi A = ikT$ was only obeyed by lecithin at the W/O interface ($\pi < 13$ mN m^{-1}) confirming the reduced van der Waals attraction in the presence of the oil. The equation $\pi(A - A_0) = ikT$ adequately described the W/A isotherms although A_0 values were often larger than the close packed areas. (The results are summarised in Table 3). The discrepancies were interpreted in terms of changes in headgroup hydration and/or headgroup re-orientation on compression. The i values give an indication of the homogeneity of the films, with low values (≤ 0.2) suggesting the presence of islands at the W/A interface. Higher values of i (≥ 1.3) at the W/O interface are in accordance with more fluid films. Further work to assess the homogeneity of the films using surface potential measurements should throw light on this interpretation of i values.

The Gaines' equation of state, which takes explicit account of the subphase, was remarkably successful in describing the π-A isotherms, and predicted area per molecule values consistent with a horizontal-to-vertical headgroup transition at the W/A interface.

Mixed monolayer isotherms

The block copolymer and DPL showed efficient packing when the headgroups were forced into a closed-packed arrangement (≥ 25 mN m^{-1} – W/A; ≥ 35 mN m^{-1} – W/O). At lower surface pressures inefficient packing was attributed to re-orientations of the lecithin headgroup by the cosurfactant. The same effects were observed using the impure lecithin.

Table 3 Summary of lecithin monolayer results

	DPL		SBL	
Method	$A_{W/A}$/Å^2 molecule^{-1}	$A_{W/O}$/Å^2 molecule^{-1}	$A_{W/A}$/Å^2 molecule^{-1}	$A_{W/O}$/Å^2 molecule^{-1}
Molecular model				
Hd. grp. vertical	51.6 ± 2.2	51.6 ± 2.2	—	—
Hd. grp. horizontal	85.5 ± 5.4	85.5 ± 5.4	—	—
Conventional extrapolation of the π-A isotherm (A_c)	53.0 ± 2.5	65 ± 15	51.7 ± 2.2	41.1 ± 3.6
A_0 in $\pi(A - A_0) = ikT$				
pre-transition	77.1 ± 2.4	26.7 ± 1.8	81.9 ± 1.3	13.8 ± 0.9
post-transition	39.7 ± 1.1	—	—	—
ω_2 in Gaines' equ.				
pre-transition	60.5 ± 0.5	44.0 ± 1.2	70.0 ± 0.8	23.7 ± 2.0
post-transition	42.5 ± 0.5	—	24.5 ± 0.5	—

See text for values of i and f_1^s

The effect of electrolyte in the subphase

DPL showed a strong interaction with ammonium nitrate leading to a relatively large expansion of the monolayer, even when this was closely-packed.

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Glossary of symbols

W/A	Water-air interface
W/O	Water-oil interface
E/A	Electrolyte-air interface
L-C	Liquid-condensed
A_c	Area per molecule obtained by conventional extrapolation of the π-A isotherm at close-packing
A_e	Experimentally determined area per molecule
A_t	Theoretically predicted area per molecule
A_v	Area per molecule obtained by vertical extrapolation of the π-A isotherm at close-packing
A_0	Head group area term
f_1^σ	Activity coefficient of water in surface region
i	Constant
x_i	Mol fraction of component i
Z	Compressibility factor $= \pi A/kT$
γ	Interfacial tension
π	Surface pressure
ω_i	Partial molar area of component i

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