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A light scattering study of phase transitions in monolayers of n-pentadecanoic acid

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Abstract. The phase transitions of monolayers of carefully purified n-pentadecanoic acid at the air/water interface have been investigated using both classical and laser light scattering methods. The equilibrium π - A isotherms showed flat coexistence regions between the liquid-expanded and liquid-condensed states. Such clear first-order transitions appear only to be observable for pure pentadecanoic acid. In transitions at temperatures above the triple point ($\sim 17^\circ\text{C}$) the light scattering clearly showed up phase separation within the monolayer, again demonstrating the first-order nature of the transitions. The liquid domains in the liquid/vapour transition were about 1 μm across. In the liquid-expanded/liquid-condensed transition the denser phase regions were of the order of 0.4 μm in size. These estimates are compatible with surface potential fluctuations which have been observed for this system. In the condensed/vapour transition below the triple point the monolayer behaved quite differently, no fluctuations being observed. At a surface concentration such that half of the pentadecanoic acid was in each surface phase, the viscoelastic properties of the film changed abruptly from close to those of the clean subphase to those of a viscoelastic medium. It is hypothesised that the molecular aggregates formed in this transition interact, when sufficiently close together, to form some kind of surface superstructure, which acts as a homogeneous surface phase.

1. Introduction

There has been a considerable resurgence of interest in the phase transitions of monomolecular layers of amphiphilic molecules spread at the air-water interface. This largely stems from the recent demonstration that, at least for certain materials, these transitions are clearly first-order in nature [1, 2], rather than of higher order as had been inferred from the sloping surface pressure-area (π - A) isotherms previously observed. The liquid/vapour transition in such monolayers has been known for some time to be first order (e.g. [3]), but it has only recently been established that this is also the case for the transitions occurring in more compressed monolayers. Following observation of surface potential fluctuations in coexistence regions for pentadecanoic acid monolayers [1, 4], the horizontal isotherms expected for first-order transitions were observed for the liquid/vapour and liquid-expanded/liquid-condensed (LE/LC) coexistence regions [2] for this material and for monolayers of certain synthetic lecithins [5]. Since that time various workers have demonstrated the coexisting phase-separated domains directly, using a variety of techniques. Some of the observations may be open to objection due to the introduction of impurities (fluorophores) in the monolayer, as it has been suggested that the scrupulous purification of all materials is necessary for the observation of true

first-order transitions (inferred via flat coexistence isotherms) [5]. Certain discrepancies in the literature may derive from a history dependence of the phenomena in these transitions, perhaps due to slower equilibration in two dimensions than in three.

The present paper concerns a new approach to studies of transitions in monolayers, involving laser light scattering from thermally excited capillary waves. It has been shown that this scattering is sensitive to the surface viscoelasticity, in particular to the surface dilational modulus. In a few previous light scattering studies of monolayers in transitional states [6, 7] certain fluctuations were reported. Following refinements of the experimental approach and the data analysis, it has proved possible to turn the method into a quantitative probe of phase separation. The effects of the phase-separated domains upon the light scattering depend on their size relative to the illuminated area on the surface or to the wavelength of the surface mode observed, providing a method to estimate that size. This paper examines this novel evidence for coexistence and for the scale of the domains. Many details of the results which are incidental to this purpose are thus omitted here.

The present study involved *n*-pentadecanoic acid (PDA) as this material has come to be regarded as a basic reference material for monolayer studies following the demonstration of flat isotherms in the liquid-expanded/liquid-condensed coexistence region [2]. To ensure that the light scattering data were strictly comparable with other results some considerable effort was devoted to refinements of technique which were ultimately successful in permitting the reproduction of isotherms which were horizontal in this transition. There seems no unanimity concerning the nature of this transition, which is variously referred to as 'fluid/gel', 'liquid expanded/liquid condensed', or simply 'liquid/solid'. Here the rather conventional liquid-expanded/liquid-condensed (LE/LC) usage is followed, without prejudice regarding the exact nature of the phases involved. Careful investigations of surface viscosity and elasticity are needed to settle this point.

2. Experimental methods

2.1. Monolayer formation and classical measurements

Monolayers were formed on a Langmuir trough, machined from solid PTFE, mounted on a substantial metal base. The relatively large subphase area ($18 \times 23 \text{ cm}^2$) ensured that the subphase meniscus was essentially flat at its centre, eliminating problems due to surface curvature. The entire apparatus rested upon a 2.3 tonne optical table with vertical and horizontal vibration isolation, any residual disturbances of the liquid surface being damped out by the rather shallow subphase (depth only $\sim 4 \text{ mm}$). The PTFE barrier was moved very slowly (in one direction during any experiment) by hand, to avoid surface perturbation. The surface tension was measured ($\pm 0.1 \text{ mN m}^{-1}$) using a roughened platinum foil Wilhelmy plate. Precautions were taken to avoid problems due to the tendency of the meniscus to rise up the plate during monolayer expansion [8].

The Langmuir trough was enclosed in a Perspex box, provided with small apertures for passage of the laser beams and the Wilhelmy plate. The walls and base of the enclosure were lined with copper radiators for thermostatted water ($\pm 0.1^\circ\text{C}$) circulation. The temperature of the system was continuously monitored. To assist in equilibration the enclosure and trough were maintained at one temperature for several days. Before each experiment, the subphase was allowed to equilibrate for at least 1 hour, until the tension became constant. Its temperature was uniform to within 0.05°C . Since

evaporation can cause the temperature of the surface layer to differ from that of the bulk by as much as 2°C [9] the humidity within the enclosure was maintained close to 100%. The apertures left for the laser beams avoided condensation on optical windows; any consequent air currents caused no apparent problems.

It has been suggested that ultra-high purity is essential to observation of first-order phase transitions in monolayers [5]. The pentadecanoic acid was over 99% pure as purchased (gas chromatography, Fluka), and was then recrystallised ten times from hexane solution. To avoid trapping impurities during rapid cooling [2], this crystallisation was very slow (45 to 20°C over 18 h). Spreading solutions typically contained 1 mg ml⁻¹ PDA in hexane. The hexane used in all procedures was purified by passage through an alumina column. The absence of surface-active contamination was checked by spreading a quantity of the pure hexane on water; after evaporation the surface pressure remained zero even on compression.

Monolayers were spread on a 0.01N HCl subphase made up just before each experiment with pure HCl (Flucka, puriss grade) dissolved in ultra-pure water from a Millipore Milli-Q water system. The surface tension of the subphase agreed well with accepted values, and did not change measurably on compression after the surface had first been swept and aspirated.

Isotherms generated by compression or continuous addition displayed sloping LE/LC coexistence regions, whereas expansion by small steps ($\Delta A/A \lesssim 3\%$) from a compressed state followed by long equilibration times (≥ 10 min) yielded flat coexistence regions, confirming previous reports [5, 7]. In forming the initial compressed state the spreading solution was dispensed in several small aliquots ($\lesssim 5 \mu\text{l}$) across the subphase, avoiding a pool of solvent which might affect the Wilhelmy plate (cf [10]). On expansion the classically measured tension reacted almost instantaneously, subsequently relaxing relatively quickly to an apparent equilibrium value (cf [10]) at which the tension remained constant over the 10–15 min observation period to within 0.02 mN m⁻¹.

At temperatures below the triple point ($\sim 17^\circ\text{C}$) isotherms were generated by repeated additions of spreading solution. This permitted a large range of surface concentrations ($\Gamma_s \equiv 1/A$) to be covered in a single experiment. Stepwise addition was also used to study very expanded monolayers above T_t .

2.2. Light Scattering

Our surface laser light scattering apparatus closely resembled a system which has been described in detail elsewhere [11]. Photon correlation was used to measure the Fourier transform of the spectrum of thermally excited capillary waves of experimentally selected wavenumber (q). The light scattering system was calibrated by measuring the well established response for the free surface of pure water.

The surface properties that affect the waves constitute two viscoelastic moduli [12]:

$$\gamma = \gamma_0 + i\omega\gamma' \quad (1)$$

$$\varepsilon = \varepsilon_0 + i\omega\varepsilon' \quad (2)$$

where γ describes the response of the surface to shear stress normal to its plane while ε is the in-plane dilational modulus of the monolayer. Here γ_0 is the surface tension, while ε_0 is the dilational elastic modulus ($\equiv d\gamma_0/d \ln A$). The surface viscosities γ' and ε' may be regarded as surface excess properties or as macroscopic properties of the system.

Data analysis is an essential and integral part of surface light scattering experiments. Two approaches to analysis of the correlation functions measured for a particular surface wavenumber were used.

(i) The temporal evolution of the waves (expressed via the complex frequency $\omega = \omega_0 + i\Gamma$) was determined by fitting to

$$g(\tau) = B + A \cos(\omega_0|\tau| + \phi) \exp(-\Gamma\tau) \exp(-\beta^2\tau^2/4) \quad (3)$$

which yielded unbiased estimates of ω_0 and Γ [13].

(ii) The data were analysed directly in terms of the surface properties [14, 15] via

$$g(\tau) = B + A \{ \text{FT} [P(\omega, q | \gamma, \varepsilon)] \} \exp(-\beta^2\tau^2/4) \quad (4)$$

where $\text{FT}[P(\omega, q | \gamma, \varepsilon)]$ indicates the Fourier transform of the spectrum of thermally excited capillary waves of wavenumber q on a surface described by the surface properties γ and ε (NB the density and viscosity of the subphase were assumed to have their accepted values).

The Gaussian term in equations (3) and (4) represents instrumental effects [13, 16].

The effects of the surface properties upon ω are well established (e.g. [17]). Briefly, resonance between the observed capillary waves and dilational monolayer modes causes a maximum in the sensitivity of the capillary waves, and hence the light scattering technique, to the dilational elastic modulus ε_0 . For experimentally accessible q -values this optimal sensitivity occurs at $\varepsilon_0/\gamma_0 \sim 0.16$. The sensitivity to much larger values of ε_0 is greatly reduced.

The light scattering approach is affected by the surface viscoelastic properties across the illuminated region [18]. For a laser beam of diameter D_0 incident on the surface at an angle θ this region will be an ellipse of axes D_0 and $D_0/\cos\theta$: a convenient characteristic dimension is the mean of these (D). Inhomogeneities in a monolayer will affect the observed correlation functions, the precise effects depending upon the magnitude of the typical domain size d relative to both D and the wavelength of the surface waves observed ($\Lambda = 2\pi/q$). Three cases arise.

(i) $D < d$: the monolayer should appear instantaneously homogeneous unless a domain edge crosses the illuminated region. The evolution of the light scattering signal over the duration of an experiment would be governed by motions and/or growth of the domains, leading to fluctuations.

(ii) $\Lambda < d < D$: the light scattering signal will presumably be a weighted average of those from the separate phases, reducing any fluctuations.

(iii) $d < \Lambda$: such small domains should not cause obvious surface inhomogeneities.

Two of these cases involve the capillary waves moving on a surface supporting relatively small inhomogeneities, with effects upon the wave propagation which are not fully understood. These uncertainties will be neglected here.

While fluctuations in the light scattering data have been observed for phase-separated monolayers [6, 7, 9], the long experimental durations caused some temporal averaging. It has recently been shown that statistically significant correlation functions can be recorded in ~ 10 s [19], much faster than usual, considerably reducing this averaging. The data presented here largely derive from single correlation functions rather than averages of several observations.

If the illuminated area of the monolayer is inhomogeneous the observed correlation data might be expected to be an average of functions appropriate to the individual phases. The analysis procedures described above implicitly assume that the surface is uniform, and so may not be appropriate to such inhomogeneous monolayers. The quality of the fits to the data was thus considered: a convenient statistic was the autocorrelation coefficient (r) of the residuals of the fit [20]. Nearly all data observed in the three coexistence regions studied in the present work yielded values of r within the 95% confidence limits [20], indicating the validity of the conventional theory (used in equation (4)). Thus in all cases the data were compatible with the assumption of a homogeneous surface.

It has recently been shown that the relative intensities of the scattered light (I_s) and of the heterodyne reference beam (I_r) can be extracted from the correlation functions [21, 22]. This remains valid for the rapid data acquisition methods [23]. While absolute values of the intensities cannot be obtained, changes in their magnitudes can be followed.

3. Results

Classical isotherms measured at various temperatures (figure 1) were flat through the LC/LE transition, and agreed quantitatively with literature data for both the coexistence pressures and the values of A at which the LE phase adjoins the coexistence region. Recompression of the monolayer above the triple point (T_t) gave isotherms which tended to slope. This has been observed before, being ascribed to the effects of residual impurities [5]. These data permit the triple point to be estimated as $17.4 \pm 1.0^\circ\text{C}$, in good agreement with the accepted value of $\sim 17^\circ\text{C}$. These data suggest that the LC/LE transition in the present monolayers is first order, agreeing with other data for rigorously pure monolayer materials [5, 7]. In the other monolayer transitions, involving condensed/vapour and liquid/vapour coexistence, π also appeared constant within errors, but the data are not shown here.

Light scattering data for the different coexistence regions (LE/LC, liquid/vapour, condensed/vapour) are considered below. In well equilibrated two-phase coexistence regions the surface pressures of the different phases should be identical; γ_0 carries no information regarding phase separation. The surface viscosities may differ between the two phases, but are not very precisely determined by light scattering [15]. In practice the best evidence for phase separation in the monolayer coexistence regions therefore comes from the dilational elastic modulus ε_0 or from the wave damping Γ (which largely reflects ε_0). The present work concentrates upon these quantities.

3.1. Liquid/vapour coexistence region

Monolayers formed in this coexistence state above T_t had $\pi \sim 0.15 \text{ mN m}^{-1}$, in accord with accepted values [24]. The separate phases were of different compressibilities, corresponding to those of the pure phase states at the ends of the coexistence region. For the liquid phase ε_0 ($\sim 13 \text{ mN m}^{-1}$) was very close to that for maximum sensitivity of the light scattering. The damping Γ then essentially amplifies variations of ε_0 (e.g. [17]) so that it should be a convenient probe of the effects of phase separation.

In this coexistence region very evident fluctuations in Γ were observed during monolayer compression. Figure 2 shows the Γ -values observed for a typical monolayer: Γ ranged from close to that observed for the clean subphase to a value typical of the

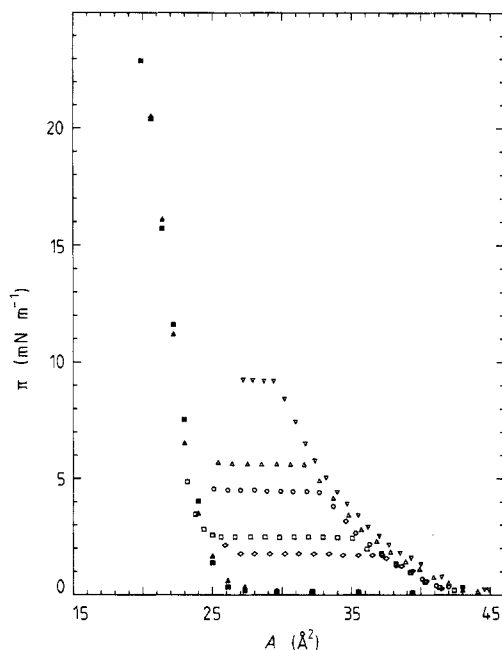


Figure 1. A selection of pressure-area isotherms of PDA measured at various temperatures: ∇ , 27.2°C; \triangle , 23.5°C; \circ , 22.4°C; \square , 19.6°C; \diamond , 19.0°C; \blacktriangle , \blacksquare , 11.5°C. Note the flat LC/LE transition region in those isotherms (open symbols) showing a liquid phase.

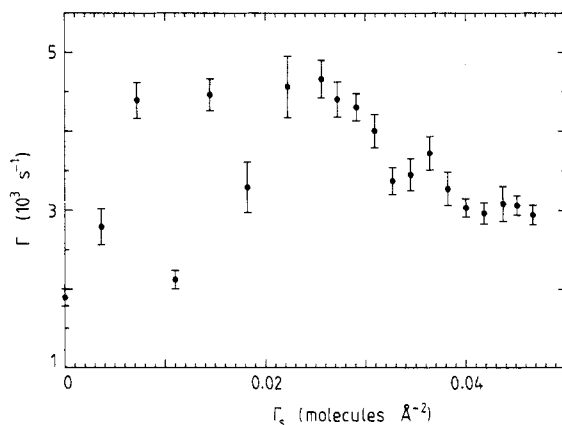


Figure 2. Plot of the damping observed for $q = 322 \text{ cm}^{-1}$ as a function of molecular concentration at 19°C, produced by stepwise addition. Note the large fluctuations for $\Gamma_s \leq 0.02 \text{ molecules } \text{\AA}^{-2}$. At each surface concentration ten correlation functions were recorded in rapid succession; the errors shown are the standard deviations of the individual Γ -values.

expanded end of the liquid region of the isotherm. Similar fluctuations were observed over the entire liquid-gas coexistence region ($42 \text{ \AA}^2 < A < 1500 \text{ \AA}^2$ [24]).

To examine the phase separation more directly, monolayers were studied at fixed A over long periods of time. Figure 3 shows the data for one such run: each point derives from a single correlation function accumulated over 10 s, data being recorded every 100 s for 2.5 h. In most cases the laser beam seems to have illuminated a single-phase

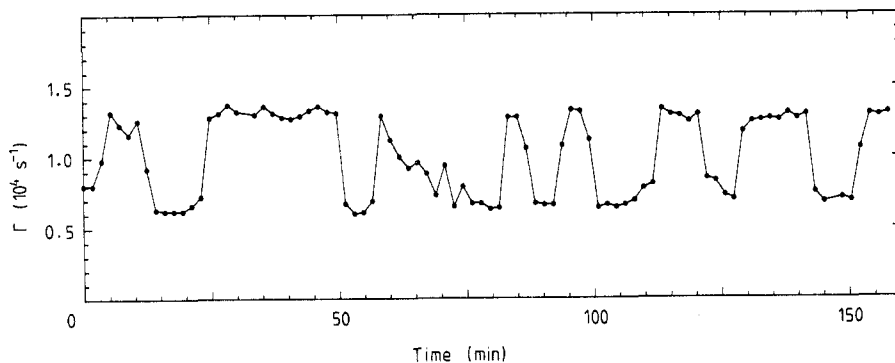


Figure 3. The observed damping ($q = 527 \text{ cm}^{-1}$) as a function of time for a monolayer of surface concentration $0.017 \text{ molecules } \text{\AA}^{-2}$ at 19.0°C . The data cluster about two values: $\Gamma = 6 \times 10^3 \text{ s}^{-1}$, typical of the clean surface, and $1.3 \times 10^4 \text{ s}^{-1}$, typical of the expanded liquid state (the magnitudes of Γ differ from figure 2 because the data derive from different q).

region, although a few intermediate cases were observed, where two different phases were illuminated.

For two phases coexisting at Γ_s the total monolayer area \mathcal{A}_m and the total number of molecules can be expressed in terms of A_l and A_g , the areas occupied by a molecule in the liquid and gaseous phases. Then the fractional area in the liquid phase is

$$\frac{\mathcal{A}_l}{\mathcal{A}_m} = A_l \frac{1 - A_g \Gamma_s}{A_l - A_g} \quad (5)$$

and similarly for \mathcal{A}_g . Using published data ($A_l \sim 42 \text{ \AA}^2$ and $A_g \sim 1500 \text{ \AA}^2$ [24]) and the experimental $\Gamma_s = 0.017 \text{ molecules } \text{\AA}^{-2}$ gives $\mathcal{A}_l/\mathcal{A}_m \sim 70\%$, in reasonable agreement with that proportion of the data of figure 3 having high damping values. Over the 2.5 h experiment the light scattering seems to have sampled a representative proportion of the monolayer phases.

In the experiments for this region the illuminated spot had typical dimension $D \sim 1.8 \text{ mm}$, setting a lower limit on domain size. This was directly confirmed by scanning the laser beam across the liquid surface. The spot could be moved about 1 cm within a 'liquid' domain before the damping of the observed correlation functions decreased, suggesting $\langle d \rangle \gtrsim 1 \text{ cm}$.

The time dependence evident in figure 3 shows that the domains must either be mobile or systematically grow and decay. Fluorescence microscopy experiments show that the number of domains within a phase-separated monolayer appears to be conserved [25], favouring the postulate of domain mobility. The data of figure 3 then permit an independent estimate of the domain size. The transition from one phase to another often occurred within a single 100 s interval, during which time the domain edge must have completely crossed the illuminated area, giving a velocity $> 18 \mu\text{m s}^{-1}$. The average persistence time of the higher values of damping, $\langle t \rangle = 630 \pm 380 \text{ s}$, then suggests $\langle d \rangle \sim 1.1 \pm 0.7 \text{ cm}$. The agreement with the previous result basically supports the assumption of domain mobility.

The light scattering data suggest differences in molecular organisation between the two phases. The scattered intensity (I_s), while subject to error, was highly correlated with Γ (figure 4), values in the liquid domains systematically exceeding those in the gaseous regions by $\sim 12\%$. Scattering by capillary waves depends upon the surface

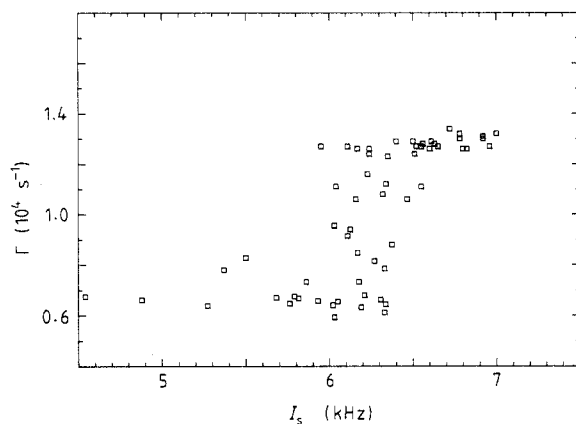


Figure 4. A plot of the scattered intensity versus the capillary wave damping. High damping is correlated with large values of I_s .

reflectivity (R) and tension as [26]

$$I_s \propto R \frac{kT}{\gamma_0 q^2}. \quad (6)$$

However R (assessed by I_r) was less correlated with Γ , values for the two phases differing by $\lesssim 4\%$. The light scattering tension always agreed with the Wilhelmy plate value. Thus the changes in I_s must arise from a separate process, which must, however, be tightly coupled to the capillary waves as I_s is estimated from fits to equation (4) which only accounts for capillary motion. Previous experience [27] suggests that intramonomer molecular modes may be significant. In particular, coupling of molecular splay to the capillary waves [28] can change I_s . The observed small increase in I_s would be consistent with an increase in the combined dielectric anisotropy and order parameter ($\epsilon_a S$) of the PDA in the liquid domains, which seems physically plausible.

3.2. Liquid-expanded/liquid-condensed coexistence region

As the monolayer is compressed through the LE phase the elastic modulus ϵ_0 becomes $\gg 0.16\gamma_0$, the value for maximum sensitivity of light scattering. Thus the damping Γ becomes a poor tool, and ϵ_0 estimated directly from the correlation functions is preferable. Figure 5 shows light scattering ϵ_0 -values for four different surface coverages at 19°C. While the classical ϵ_0 remained constant ($= 0$) as Γ_s was raised, the average light scattering ϵ_0 increased, as did the fluctuations about the average. This is the first time that light scattering fluctuations have been demonstrated in this LE/LC coexistence region. As already noted, the observed correlation functions were well fitted by the direct analysis, the data being indistinguishable from those for homogeneous monolayers. The estimates of the surface properties are thus not meaningless values found by force-fitting an inappropriate form to the data.

In addition to any fluctuations due to phase separation the estimates of ϵ_0 (figure 5) are subject to statistical error. These errors have been estimated from simulations of theoretical correlation functions with random noise similar to that of the observed data. The statistical error upon ϵ_0 was taken as the standard deviation of values found by analysing simulated data. In the LE phase (state 4 in figure 5) this error was essentially the same as the observed spread on the data, indicating the absence of intrinsic

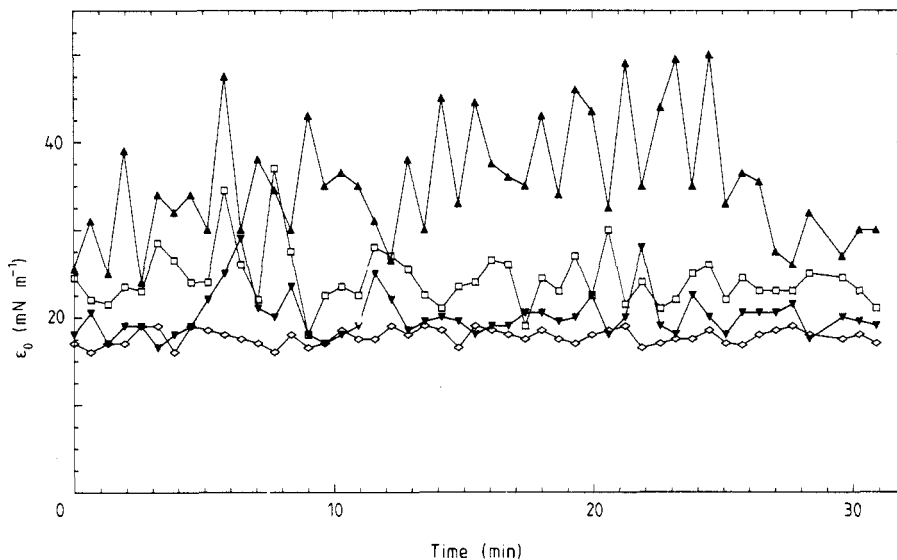


Figure 5. The variation with time of the dilational elastic modulus ($q = 508 \text{ cm}^{-1}$) for four different surface concentrations in a monolayer at 19.0°C : \blacktriangle , 0.025; \square , 0.028; \blacktriangledown , 0.031; \diamond , 0.036 molecules \AA^{-2} . Data were acquired every 40 s over 31 min. The first three values of Γ_s lie in the LC/LE transition, whereas the last is a pure LE state (see figure 1).

fluctuations. However, in the coexistence region the observed fluctuations exceeded the expected statistical errors, permitting the contribution due to phase separation ($\langle \Delta \varepsilon_0 \rangle$) to be estimated (table 1). The simulated data, like the experimental, corresponded well to those expected for an apparently homogeneous monolayer. In deriving these $\langle \Delta \varepsilon_0 \rangle$ values the slow drift in the average ε_0 for the $\Gamma_s = 0.025$ molecules \AA^{-2} data (figure 5) was ignored.

Table 1. The computation of the average domain size at different surface concentrations (see figure 6), using equation (9). $\langle \Delta \varepsilon_0 \rangle$ determined by subtracting $\langle \Delta \varepsilon_0 \rangle_{\text{noise}}$ quadratically from $\langle \Delta \varepsilon_0 \rangle_{\text{obs}}$. See text for details. $\langle \varepsilon_0 \rangle$, $\langle \Delta \varepsilon_0 \rangle_{\text{obs}}$, $\langle \Delta \varepsilon_0 \rangle_{\text{noise}}$ and $\langle \Delta \varepsilon_0 \rangle$ are all in units of mN m^{-1} .

State	Γ_s (molecules \AA^{-2})	$\mathcal{A}_{LC}/\mathcal{A}_m$	$\langle \varepsilon_0 \rangle$	$\langle \Delta \varepsilon_0 \rangle_{\text{obs}}$	$\langle \Delta \varepsilon_0 \rangle_{\text{noise}}$	$\langle \Delta \varepsilon_0 \rangle$	Non-ideality factor	$\langle d \rangle$ (mm)
1	0.036	0.68	35.4	6.9	2.9	6.3	1.43	0.59
2	0.031	0.325	25.5	3.4	2.1	2.8	1.41	0.38
3	0.028	0.085	20.0	2.6	1.6	2.0	1.16	0.43
4	0.025	—	17.5	0.9	0.97	—	—	—

The fluctuations in ε_0 were much more rapid than in the liquid/vapour coexistence region and did not extend to the values for the pure LE and LC phases. The domains must therefore be relatively small compared with D (although fluctuations would be unlikely to be seen if $d < \lambda$). The fluctuations arise from variations in the number of domains in the illuminated surface region, probably due to domain motions, perhaps because of overall surface flow. Using a naive approach the domain sizes $\langle d \rangle$ can be estimated rather crudely from the data.

We assume circular LC domains such as are observed in fluorescence microscopic

studies (e.g. [25]), and that $\langle \Delta \epsilon_0 \rangle \propto \langle \Delta n \rangle = \sqrt{\langle n \rangle}$ where $\langle n \rangle$ is the mean number of domains in the illuminated region (of area = $\pi D^2/4 \cos \theta$). Now $\langle n \rangle$ is related to the fractional monolayer area in the LC phase by

$$\langle n \rangle = (\mathcal{A}_{\text{LC}}/\mathcal{A}_{\text{m}}) \frac{A_{\text{domain}}}{A_{\text{beam}}} \quad (7)$$

where \mathcal{A}_{LC} is the surface area occupied by LC domains. The expected fluctuations in ϵ_0 are then

$$\langle \Delta \epsilon_0 \rangle = \langle n \rangle^{1/2} (\epsilon_{\text{LC}} - \epsilon_{\text{LE}}) \frac{A_{\text{domain}}}{A_{\text{beam}}} \quad (8)$$

which leads to an expression for the average domain diameter $\langle d \rangle$:

$$\langle d \rangle = (\mathcal{A}_{\text{LC}}/\mathcal{A}_{\text{m}})^{-1/2} \frac{D}{\cos^{1/2} \theta} \frac{\langle \Delta \epsilon_0 \rangle}{\epsilon_{\text{LC}} - \epsilon_{\text{LE}}}. \quad (9)$$

This assumes that the light scattering response to a mixed monolayer is a linear summation of the responses to the separate phases (ideal mixing). However, the simulations showed non-ideality (figure 6); the values of $\langle \Delta \epsilon_0 \rangle$ used in this analysis (table 1) were corrected for this.

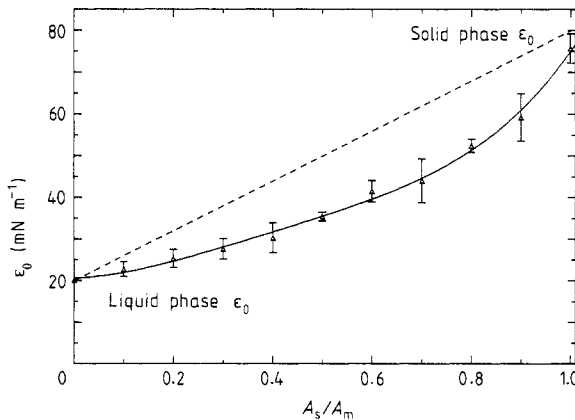


Figure 6. The elastic moduli derived from simple simulations of the LE/LC transitional region. The LE and LC phases were assumed to have $\epsilon_0 = 20$ and 80 mN m^{-1} respectively. The broken curve indicates ideal behaviour; the full curve is a fitted polynomial for interpolation purposes.

In these experiments $D = 2.7 \text{ mm}$. While $\epsilon_{\text{LE}} (= 20 \text{ mN m}^{-1})$ was fairly well determined for the pure LE phase adjoining the coexistence region, ϵ_{LC} was less well established. The values of $\langle d \rangle$ in table 1 were derived for $\epsilon_{\text{LC}} = 80 \text{ mN m}^{-1}$. The value at $\Gamma_s = 0.025 \text{ molecules } \text{\AA}^{-2}$ would tend to be somewhat reduced if the slow drift in $\langle \epsilon_0 \rangle$ were taken into account. Despite the simplicity of this analysis the domains in the LE/LC coexistence region are clearly considerably smaller than in the liquid/vapour region.

3.3. Condensed/vapour coexistence region

Below the triple point, 17.4°C, the transition is from a condensed phase to a gaseous phase, the coexistence region extending from $< 27 \text{ \AA}^2$ to very large areas (see figure 1). The constancy of the classical π in this region implied that the equilibrium $\varepsilon_0 = 0 \text{ mN m}^{-1}$. During the compression the light scattering Γ remained close to that of water until $\Gamma_s \sim 0.012 \text{ molecules \AA}^{-2}$, roughly half-way along the coexistence region, when it increased rapidly (figure 7). In contrast to other coexistence regions, the light scattering data showed no observable fluctuations at any Γ_s . These features of the data were confirmed in several independent experiments.

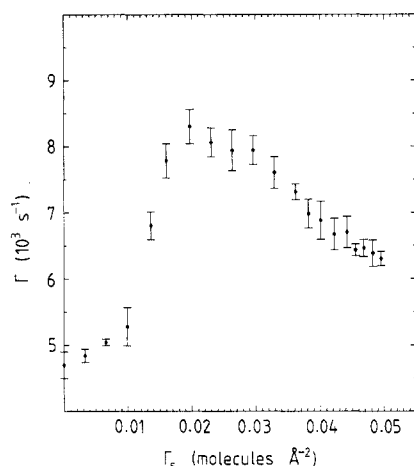


Figure 7. The variation of capillary wave damping for a PDA monolayer compressed by successive additions at 15.0°C. Note the absence of fluctuations compared with figure 2.

The value of ε_0 determined by direct fitting of the light scattering data (using equation (4)) showed a marked increase for $\Gamma_s > 0.012 \text{ molecules \AA}^{-2}$ (figure 8). While ε_0 in the coexistence region ($\sim 40 \text{ mN m}^{-1}$) exceeded the value for maximum light scattering sensitivity, the analysis still yielded relatively precise estimates.

In the coexistence region there must be phase separation. The lack of fluctuations in ε_0 implies that the monolayer was effectively homogeneous. This suggests that $\langle d \rangle < \Lambda$. The average domain size $\langle d \rangle$ must certainly be much less than D or fluctuations between condensed and gaseous behaviour would be observed, due to the very different ε_0 in the two phases. While the effects of small domains upon the propagation of the capillary waves are not fully understood, simulations confirmed that the observed data were incompatible with an inhomogeneous surface. Correlation functions were simulated for a surface comprising solid and gaseous monolayer regions of the appropriate properties (γ_0 as that of the subphase and $\varepsilon_0 = 80$ and 0 mN m^{-1} respectively) with added random noise comparable with experimental values. In general the estimate of ε_0 for the simulated data depended upon the starting point of the fitting process, the fitted surface tension deviated from the value used to generate the data, and the residuals were strongly correlated. None of these problems occurred for experimental data: ε_0 and γ_0 were always uniquely determined, independent of the initial values of the fitting parameters, while the residuals were uncorrelated for all Γ_s . The monolayer thus behaved as a homogeneous system with well defined surface properties rather

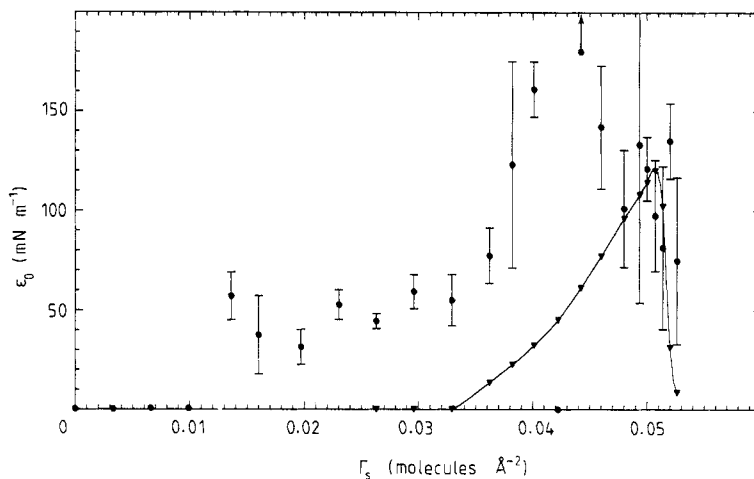


Figure 8. The classical (\blacktriangledown) and light scattering (\bullet) estimates of the dilational elastic modulus for a monolayer at 15.0°C. (Light scattering at $q = 617 \text{ cm}^{-1}$.)

than as a mixture of two separate phases.

4. Discussion

There have been several previous light scattering studies of pentadecanoic acid monolayers [6, 7, 9, 29]. These studies have not concentrated upon the monolayer transitions, but in several cases [6, 7] fluctuations in the light scattering results (commonly the wave damping) in the liquid/vapour region have been identified with phase separation in the monolayer, although no quantitative analysis was attempted. The absence of fluctuations for the LC/LE transition in these studies is not surprising, due to temporal integration. It has been suggested that Γ might be a more informative indicator of phase separation than π [7].

The present advances undoubtedly stem from improvements in experimental technique. Firstly the monolayer materials were highly pure, leading to flat first-order LE/LC coexistence isotherms with larger domains. Secondly rapid data acquisition [19] considerably reduced averaging of the fluctuations. Finally the direct analysis of the observed correlation functions in terms of the relevant surface properties reduced the uncertainties of these parameters. The working temperature of 19°C further enhanced the fluctuations in the LE/LC region, since light scattering is more sensitive to the relatively low value of ε_0 in the LE domains ($\sim 20 \text{ mN m}^{-1}$) compared with that at higher T .

The light scattering approach has its limitations, particularly in determining the dilational modulus ε . When ε_0 is large, its precision falls considerably. Further difficulties arise from the present uncertainties in our understanding of capillary wave propagation upon a surface supporting an inhomogeneous film. These difficulties do not obscure the principal present results: in the liquid/vapour and LC/LE transitions the mechanical properties of the monolayer displayed considerable fluctuations, indicative of phase coexistence, whereas in the condensed/vapour region no such fluctuations were apparent, although the data differed considerably from classical expectation.

The dilational modulus of PDA monolayers displays viscoelastic relaxation [30], resulting in an increase in ε_0 relative to its equilibrium value, associated with a decrease

in ε' . It is the high-frequency surface viscoelastic modulus which has been shown to vary from one phase to the other in a coexistence region: the classical, equilibrium elastic properties must, by definition, be equal in the two phases. There is no evidence of differences of the surface viscosities between phases.

Such relaxation has been observed for single-phase states of PDA monolayers as well as in the coexistence regions [30, 23]. It is thus difficult to interpret the difference between the classical equilibrium value and the light scattering value of ε_0 in the latter case simply. There is most likely more than one relaxation process involved: in addition to other processes (present in the single-phase regions), molecules will exchange between the coexisting phases. No evidence for frequency dependence of ε was found over the range of ω_0 probed, suggesting that the inverse timescales of the relaxation are well below the capillary wave frequencies.

4.1. Liquid/vapour and LC/LE transitions

4.1.1. Flat isotherms. The present classical surface pressure data in the LC/LE transition confirm previous reports [5, 7] that flat isotherms are observable in coexistence regions for sufficiently pure PDA. Because of the significance of this result special care was taken to exclude possible experimental artifacts contributing to the production of an apparently flat isotherm. In particular, in generating an isotherm by expansion, a minor decrease in π could be offset by systematic slight increases of either T or impurity concentration. However, studies of the T equilibration process and of the subphase tension after cleaning confirmed that these contributions were negligible. The quantitative agreement with literature values [5] of both the transitional π and the molecular areas at the expanded ends of the horizontal isotherms strengthens this conclusion.

The most obvious interpretation of such flat coexistence isotherms is that the transitions involved are simple first order, as suggested after observations of surface potential fluctuations [1, 4]. This is not universally accepted: the flatness has recently been ascribed to solvent (hexane) retention within the monolayer [31]. However, the retention of alkane solvents has been stated to be negligible [10]; also the transitional π for PDA is the same whether spread from hexane solution or from crystals from which solvent has been scrupulously removed [32]. It seems unlikely that the commonly reported sloping coexistence regions of isotherms can arise solely from electrical forces between phase-separated domains [25], as it appears that flat isotherms have been observed whenever investigators have used critically purified material [5, 7, 33]. However, the matter cannot yet be regarded as non-controversial.

We take the view that the observed flat coexistence isotherms demonstrate the purity of our PDA samples, and consider the light scattering data as representative of two-phase states of pure PDA monolayers. As the same material was used for all the present work, the liquid/vapour and condensed/vapour transitions are also taken to be simple first order, although the precision of our surface manometry was not adequate to demonstrate this explicitly.

Pethica and co-workers have shown that even for 99.85% purity, the PDA transitions appear slightly degenerate [32], whereas after purification to a level in excess of 99.95% the LE/LC coexistence regions of the isotherms become essentially flat, provided that sufficient time is allowed for equilibration. Even at these purity levels the sharp change from coexistence region to dense phase at small A was found to be somewhat blurred (cf 19.0°C data of figure 1), apparently due to residual impurities. Unfortunately most

previous investigations of the transitions of fatty acids have not been performed upon such highly purified materials, and in few cases are isotherms demonstrating simple first-order changes presented.

4.1.2. Surface potential fluctuations. Fluctuations of surface potential (V) have been observed in the liquid/vapour and LC/LE transitions of PDA [1, 4] whereas in pure-phase regions the V was steady and reproducible. The probes used were 3 mm [4] and 1 cm [1] in size. In the liquid/vapour region the fluctuations of V were similar in both experiments, ranging between values appropriate to the pure vapour phase and the pure liquid phase. This suggests that the domains were $\gtrsim 1$ cm across as smaller structures would have been spatially averaged to different extents by the two probes. However, in the LC/LE case such averaging seems to have occurred: the fluctuations with the 3 mm probe were roughly twice as large as for the 1 cm probe; in neither case did they seem to include the pure phase values. The domains appear to be less than 3 mm in size in this case.

The fluctuations determined using light scattering suggest liquid domains in the liquid/vapour transition which are of the order of 1 cm in dimension, whereas in the case of the LC/LE transition the size of the condensed domains was much smaller, about 400 μm . The crudeness of the analysis in the latter case should not affect the order of magnitude of this value. These conclusions exactly parallel those drawn here from the reported fluctuations of V [1, 4]. The region illuminated by the laser beam was comparable in size with the potential probes. In the latter experiments the monolayer was circulated across the surface by air currents prior to observation [1], so that the surface phases were moving under the probe. Now the time evolution of the present fluctuations in the LC/LE region was very similar to that for V (N R Pallas, private communication), confirming that the present data also arose from mobile domains, as inferred above. In every respect then, the light scattering data for the liquid/vapour and the LC/LE transitions quantitatively support the conclusions of the surface potential work.

Light scattering results from several monolayers are collated in figure 9, where the extents of the fluctuations observed in time-dependence experiments at various surface concentrations are indicated. This presentation of the results resembles similar plots of surface potential [1, 4].

4.1.3. Microscopic observations. There have recently been many studies of the microscopic structure of monolayers, with considerable emphasis on transitional states. Some of these investigations have concerned monolayers transferred to a solid substrate using Langmuir–Blodgett techniques [33, 34], whilst others have used epifluorescence microscopy to study spread monolayers [25, 35, 36]. Some of these studies have involved fatty acids, with some work on PDA [25]. All studies confirm that monolayers in coexistence regions show inhomogeneous structures on a microscopic scale, whereas in the single-phase region the films are featureless. Unfortunately it is not entirely clear how the beautiful and suggestive coexisting structures revealed by these techniques relate to states existing in Langmuir films of highly purified amphiphiles.

In none of these studies was a horizontal coexistence isotherm demonstrated, even before addition of fluorescent probe molecules. Indeed it has been shown that reduction of probe concentration leads to a reduction in slope of the LC/LE transitional portion of the isotherm [35]. The residual slope for zero probe concentration was shown to be compatible with an intrinsic impurity concentration of 1 or 2%, although an

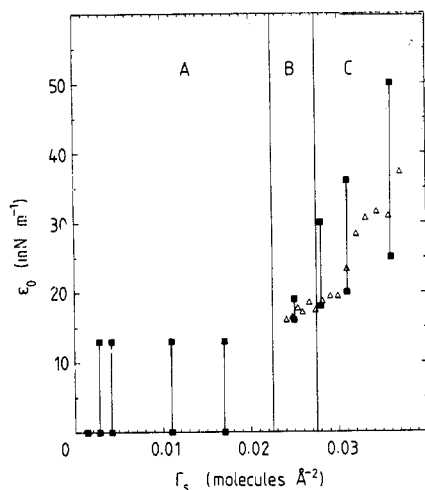


Figure 9. Light scattering estimates of ϵ_0 for PDA monolayers at 19.0°C. The different phase regions are indicated: (a) liquid/vapour, (b) liquid, (c) LC/LE. Average values of ϵ_0 are shown (Δ) for various surface concentrations in the liquid and LC/LE regions, as well as the spread of the fluctuations observed (\blacksquare and vertical lines). The data for the liquid/vapour transition derive from a different monolayer. The spread shown at $\Gamma_s = 0.025$ molecules \AA^{-2} indicates the inherent precision of ϵ_0 .

explanation of the slope involving electrical effects between phase-separated domains was also advanced. This hypothesis may be questionable, as flat isotherms appear to be associated with sufficiently pure monolayer materials (fatty acids, lecithins) and careful techniques [5, 7, 33].

While phase separation clearly does occur during monolayer transitions [1] the scale of the microscopic structures observed by the fluorescence methods (for example) appears to conflict with the surface potential fluctuations [1, 4], at least in the liquid/vapour case. In the LE/LC region $\langle d \rangle$ for the more condensed domains ranged from 35 μm to perhaps 80 μm as Γ_s was increased, less than the values found here (table 1). The scale of the structures seen in the liquid/vapour coexistence region is less than a few hundred μm . While the fluorophore concentration does not appear to alter the structures markedly, the microscopic structure of the film may well be determined by the intrinsic impurities, if their levels are of the order of one or two per cent [35, 37]. It is regrettable that there do not appear to have been parallel studies of (say) surface potential fluctuations and microscopic structure, nor do experiments seem to have been performed involving very low concentrations of probe molecules added to a monolayer of high intrinsic purity. Comparisons between the present results and this work may not be very meaningful. It is apparently commonly observed that the films are very inhomogeneous (C M Knobler, private communication), the well defined structures only occupying part of the trough surface. The structures observed microscopically are also apparently history dependent. It is not at all clear that there is a real conflict between the results of the microscopic studies and the present data.

4.2. Condensed/vapour transition: $T < T_i$

In the vapour phase the dilational elastic modulus is essentially zero; the presence of a few very small domains or aggregates of molecules in a condensed phase would not be expected to increase the measurable value of ϵ_0 markedly. The observed increase

occurs at A almost exactly equal to the area of a straight PDA molecule lying upon the liquid surface; at this point about half of the PDA molecules are in the condensed phase. The change is both substantial and abrupt, indicating a dramatic change in the film behaviour or structure. The only conceivable experimental origin is in the monolayer deposition procedures: in this region the PDA solution was always added close to the illuminated spot, perhaps promoting monolayer structure in that region. This did not occur in the liquid/vapour region, so the manner of formation of the domain structures and the film mobility must be assumed to be very different in the two cases. The simplest hypothesis is that the film behaviour really does change at $\Gamma_s \sim 0.012$ molecules \AA^{-2} .

The jump in monolayer properties at this Γ_s might arise from a single very large condensed domain settling under the laser beam. However, in several experiments the abrupt increase of ε_0 occurred at essentially the same surface concentration. The effect must be intrinsic to the low-temperature PDA monolayer and seems unlikely to be a chance observation.

The change cannot arise from incoherent contributions due to a large number of independent solid domains, very much smaller than those in the LE/LC transition. This would cause a smooth variation of ε_0 with Γ_s , due to an increase in the density of domains, rather than the abrupt change which is observed.

Now aggregation must set in at large areas in such films: in the absence of attractive van der Waals interactions π would increase well before the observed transition. The observed data could arise from the formation of some kind of 'superstructure' within the monolayer which then acts as a homogeneous viscoelastic phase. Any such superstructure must apparently occupy the entire monolayer area as fluctuations were never observed, and the jump in ε_0 occurred reproducibly at the same Γ_s . This suggests that the situation may not be exactly as that observed in certain microscopic studies in which very inhomogeneous superstructures of many small domains are observed [38]. Two possible superstructures suggest themselves, which cannot at present be distinguished experimentally.

(i) A foam structure, as observed in fluorescence microscopy for stearic acid [38]. As discussed above, the exact status of the structures observed with fluorescence microscopy is somewhat unclear although it was suggested that this foam is intrinsic to the monolayer. It may be significant that the foam structure showed a change in appearance at Γ_s such that about half of the monolayer was likely to be in each phase.

(ii) A super-lattice of molecular domains arising from interactions between the dipole moments of the PDA molecules (e.g. [39]). The dipole moments of the molecular aggregates could suffice to cause repulsion, leading to a regular array or superlattice of aggregates. Such regular superlattices of domains have been observed in certain microscopic studies of phospholipid monolayers (e.g. [40]).

At present the viscoelastic responses of these surface structures have not been analysed. It seems possible that they could well be relatively 'soft' in their response to low-frequency applied stress, leading to the classical (zero) values of ε_0 , while appearing relatively solid to high-frequency perturbation, as shown by the light scattering values of ε_0 . The regular arrays of domains which have been observed under certain conditions in microscopic studies are susceptible to compression by electric fields [41], indicating that the compression modulus for slow perturbations is indeed rather low.

Without dwelling upon the surface viscosities determined in the light scattering experiments, it is pertinent to comment upon the variation of ε' for these low-temperature

monolayers. At or close to the surface concentration at which ϵ_0 increases abruptly, this surface viscosity becomes non-zero, although of small magnitude. Its zero value at larger Γ_s , where ϵ_0 agrees with its equilibrium value of zero, indicates that the monolayer is there not viscoelastic in nature. The small value of ϵ' for monolayer states where ϵ_0 exceeds its classical value indicates that viscoelastic relaxation is involved in that case. Regrettably there is no information available on the low-frequency viscosity of such monolayers.

Unfortunately there have been few previous studies of this transition in PDA, so comparisons must be made with other fatty acids which transform directly from the condensed to the vapour phase. Stearic acid, which should have a triple point $\sim 35^\circ\text{C}$ (based on the crude approximation that one additional CH_2 unit in the chain corresponds to an $8\text{--}10^\circ\text{C}$ rise in T_t [8]), has been studied extensively. No abrupt change was observed in the surface potential for stearic acid, but fluctuations of V were observed [1] throughout the solid/vapour coexistence region (at 25°C). The potential fluctuations would suggest that, at least for stearic acid, the monolayer remains mobile in the condensed/vapour coexistence region. A light scattering study of surface waves on a stearic acid monolayer [9] has reported fluctuations of capillary wave damping over a limited portion of the transition region ($60 \text{ \AA}^2 < A < 130 \text{ \AA}^2$ at 21°C). It thus appears that for stearic acid the coexisting domains are of the order of a millimetre in size. This contrasts with PDA, where the absence of significant fluctuations in the present data suggests smaller domains, and that an effectively homogeneous monolayer forms at Γ_s above a critical value. The difference may arise from the different materials or the T used in the present work might be significant, perhaps because of the increased subphase viscosity or because of the proximity of T_t .

Qualitatively the main features of our data are similar to those found in an ellipsometric study of arachidic acid [42], where an abrupt change in monolayer properties was found at surface concentrations within the coexistence region.

5. Conclusions

The π - A isotherms determined here for pentadecanoic acid confirm that flat LE/LC coexistence regions are observed when care is taken to permit full equilibration of pure samples of this amphiphile [5, 7]. To within the precision of measurement the isotherms were also horizontal in the liquid/vapour and condensed/vapour ($T < T_t$) transitions.

The light scattering experiments, carried out on the same material as the Wilhelmy plate surface pressure measurements, demonstrated clear evidence for phase separation in both transitions observed at temperatures above T_t . In both cases the monolayer appeared to be mobile, so that fluctuations were apparent as the separate phases passed through the surface area illuminated by the laser beam. In the liquid/vapour transition the size of the liquid domains was estimated to be $\sim 1 \text{ cm}$, whereas in the LE/LC case the regions of denser phase were rather smaller, $\sim 0.4 \text{ mm}$. In the former case there were indications, from the scattered intensities, that the PDA molecules were more ordered in the liquid-phase domains. In all respects these results seem to be in complete agreement with conclusions which can be drawn from observations of surface potential fluctuations in pure PDA monolayers [1, 3]. It is not obvious that the present data are really in conflict with certain results from microscopic studies of monolayers [25], which involved insertion of molecular probes into films of PDA which had not been

as extensively recrystallised as in the present work or that of Pethica and co-workers [1, 5].

An unexpected feature of the present results is the observation that at low temperatures ($< T_1$) the expanded monolayer does not display apparent phase separation, as is observed for stearic acid [1, 9], but rather shows an abrupt change in elastic modulus at an area per molecule closely approximating the area of a recumbent, straight PDA molecule. At larger areas within the coexistence region, although phase separation must be present, the viscoelastic properties are very close to those of the clean subphase. In the more compressed coexistence state the elastic modulus is rather large and essentially independent of A . It appears that for $\Gamma_s < 0.012$ molecules \AA^{-2} the molecular aggregates are basically independent of each other, whereas when closer together at larger Γ_s the aggregates interact to form some form of superstructure in the monolayer. This observation is rather remarkable, as it seems to find no parallel in other studies of condensed/vapour transitions, albeit in monolayers of stearic acid rather than PDA.

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