Condensed monolayer phases at the air/water interface: phase transitions and structures

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Abstract. A variety of recent measurements demonstrate that a large number of condensed monolayer phases exist. There is a one-to-one correspondence between these phases and known smectic phases in liquid crystals. Several liquid-condensed (LC) phases can coexist with the liquid-expanded phase. The LC phases are hexatics that differ in the orientation of the molecular tilt azimuth. Fluorescence microscope measurements with polarized laser excitation allow these differences in tilt to be seen directly.

1. Introduction

Amphiphiles such as long-chain fatty acids and their methyl and ethyl esters can easily be spread as monolayers on the surface of water (for a general review see [1]; recent developments in experimental methods are discussed in [2]). The thermodynamic state of such a monolayer can be described in terms of the area per molecule, A, the temperature, T, and the pressure, π, which is the difference between the surface tension of pure water γ_0 and that of the surface covered by the film, $\pi = \gamma_0 - \gamma$.

Much has been learned about the phase behaviour of monolayers from isotherm measurements, studies of π as a function of A at constant T. The π–A isotherms of a one-component monolayer are analogous to those of a three-dimensional pure substance. Horizontal portions of the isotherms denote two-phase regions and hence first-order transitions; abrupt changes of slope mark second-order transitions.

Some features of isotherms are very clear, figure 1. At low densities, i.e. at large A, monlayers are highly compressible and their isotherms have the characteristics of a two-dimensional gas. When the monolayer is compressed there is a sharp break in the isotherm at the start of a long horizontal plateau, which is interpreted as a transition to a condensed phase. Another break and relatively flat portion often appears with further compression. A small plateau or kink is seen at still higher pressure.

These features have often been interpreted in terms of four monolayer phases: gas (G), liquid-expanded (LE), liquid-condensed (LC), and solid (S), with the breaks representing G–LE, LE–LC, and LC–S two-phase regions. There has been much controversy about the LE–LC transition. The plateau is never as clearly horizontal as that at the G–LE transition, leading to uncertainty about the order of the transition and even doubts about the existence of the LC phase.
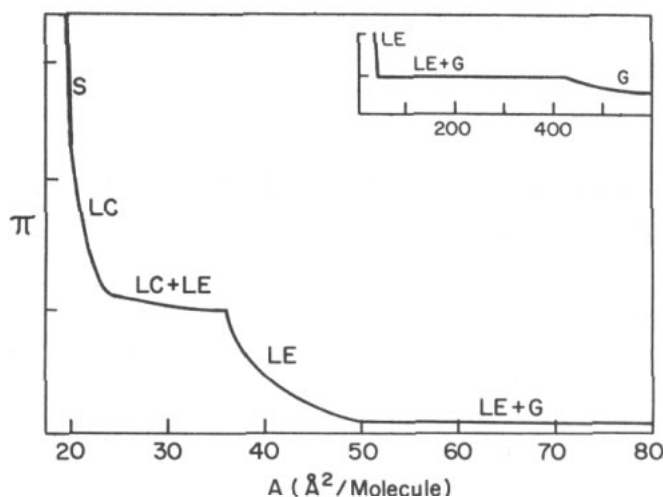
Figure 1. Schematic $\pi-A$ isotherm for fatty acids and esters. The long plateau is associated with the G-LE two-phase region and the smaller one with LE-LC coexistence. The transition to the S phase is shown here as a change in slope, but there may also be a small flat region. The areas per molecule at the transitions are typical of those found for a saturated fatty acid such as pentadecanoic acid.

If very great care is taken to purify the amphiphile, however, the LE–LC plateau is much more convincingly horizontal [3]. Measurements of other monolayer properties such as the surface potential [4] or studies of second-harmonic generation [5] show inhomogeneities in monolayers in the plateau region that can be ascribed to the coexistence of two phases, thereby identifying the transition as first order. To my mind the most convincing evidence of the nature of the LE–LC transition is that obtained with fluorescence microscopy, which allows the monolayer to be observed directly [6–9], but I am not without prejudice in this matter.
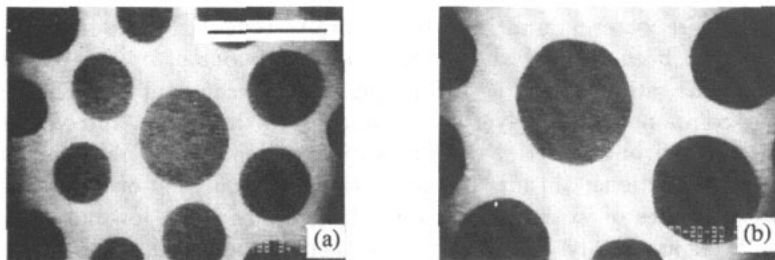

Figure 2. Fluorescence microscope image of a methyl hexadecanoate monolayer in the LE-LC two-phase region. The image is observed with a high-sensitivity television camera. Dark regions are domains of the LC phase, white regions are the LE phase. The bar represents a distance of 200 μm. (*a*) 27 °C; (*b*) 20 °C.

A fluorescence microscope image of a methyl ester monolayer in the LE–LC two-phase region is shown in figure 2. The dark regions are domains of the LC phase; they do not fluoresce strongly because the probe, NBD-hexadecylamine, is not very soluble in this phase. The white background is the LE phase. With compression of the monolayer, the dark LC domains first appear at the phase boundary. The ratio of

dark-to-light regions then increases in accord with the lever rule. If the concentration of the probe is sufficiently low, the LC end of the two-phase region can be observed as the point at which all of the bright LE phase has just disappeared [9].

2. Phase transitions between LC phases

When monolayers of methyl esters in the LE–LC coexistence region are cooled, the circular LC domains undergo a transition in which they become hexagonal, figure 2(*b*) [10, 11]. The hexagons do not have flat faces but show the continuous change in curvature expected [12] for crystals above the roughening transition, which in two dimensions lies at 0 K. The shape change is completely reversible and does not depend on the probe concentration or the rate of cooling and heating. It is clearly an equilibrium phenomenon.

We interpret the circle-to-hexagon transition as a phase transition between LC phases, from a phase in which the line tension is isotropic to one in which it is anisotropic. (Here we use the term LC to indicate any condensed phase that can coexist with the LE phase.) The transition has been observed for all of the esters from methyl tetradecanoate to methyl nonadecanoate, as shown in table 1.

Table 1. Transition temperatures for esters.

Main chain length	Methyl esters T (°C)	Ethyl esters [a] T (°C)
14	10.2	—
15	14.5	—
16	27.0	24.4
17	34.0	28.8
18	44.0	39.2
19	47.0	44.0

[a] L_2'–LS–LE triple point from [13].

Although the observation of the transition came as a surprise, it would not have been if we had been aware of the extensive isotherm measurements carried out by Lundquist [13]. She used these studies to construct π, T diagrams for a large number of ethyl esters. A feature common to all of the diagrams is a triple point at which there is coexistence between the LE phase and two LC phases that she labelled LS and L_2'. The triple-point temperatures for the ethyl esters are listed in table 1. It can be seen that they parallel the transition temperatures that we have determined for the methyl esters.

3. Structures of condensed phases

In Lundquist's phase diagram, the LS (superliquid) phase is the high-temperature LC phase. From packing considerations Lundquist argued that the molecules were tilted with respect to the surface in the L_2' phase and untilted in the LS phase. A precise knowledge of the structure of these phases could be obtained from diffraction studies with synchrotron radiation. Such measurements have been performed on condensed

phases in a number of long-chain fatty acids [14–17], but no esters have yet been studied.

The diffraction studies prompted Bibo and Peterson [18] to initiate a series of careful isotherm measurements on fatty acids. They were able to construct a complex global phase diagram for acids in which there are at least six condensed monolayer phases. The diagram is quite similar to diagrams put forward by Stenhagen [19] forty-five years earlier and to a great extent overlooked.

The global phase diagrams of acids and esters have recently been connected by a miscibility study by Bibo *et al* [20] in which the changes in the boundaries between stability fields have been followed as one progresses from the pure acid to the pure ester through a series of acid-ester mixtures. As a part of this work, connections were also made between most of the phases and structures determined from diffraction measurements. Bibo *et al* argue that the structures of the condensed monolayer phases in the acids and esters can all be related to those of smectic liquid crystals.

The distinctions between the monolayer phases can be made in terms of four types of order: positional order; bond orientational order; tilt order, the relation of the tilt azimuth to the local bond orientation; and broken axial symmetry, the packing of non-rotating hydrocarbon chains in a herringbone pattern. These are known to be features that characterize the order within layers of smectic liquid crystals [21].

A feature of the diagram is that there are four LC phases, each of which is a hexatic phase. Hexatic phases have short-range positional order and quasi-long-range orientational order [21]. (In this context, *short-range* means exponential decay and *quasi-long-range* means power-law decay of correlations.) One of the phases, the LS phase, is untilted and is the analogue of the smectic B_H phase. The others are tilted phases that differ in the relation of the tilt azimuth to the local sixfold orientational order. In one the tilt is towards next-nearest neighbours as in smectic F; in another it is towards nearest neighbours as in smectic I; while in the third it is locked in an intermediate direction, as in smectic L.

4. Fluorescence studies of tilted phases

Moy *et al* [22] demonstrated that regions of monolayer domains with different tilt directions could be detected by stimulating fluorescence with a polarized laser beam that strikes the surface at an oblique angle. The key to the method is the requirement that the chromophore on the probe have a fixed orientation with respect to the amphiphile chain. If this is the case, then the overlap between the electric field of the exciting light and the transition moment of the transition that produces the fluorescence will change with the tilt direction. Regions of differing tilt will then be distinguishable by the variation in fluorescence intensity.

This method has been used by Qiu *et al* [11] to study methyl esters. At temperatures above the circle-to-hexagon transition, the domains have uniform intensity when illuminated by the polarized laser beam. This is in accord with the identification of the high-temperature LC phase as the LS phase, which is untilted. In contrast, remarkable patterns suddenly appear when the monolayer is cooled below the circle-to-hexagon transition, figure 3.

The sixfold pattern of regions of different fluorescence demonstrates that the transition is to a tilted phase. For esters with main chain lengths of 18 or shorter the boundaries between the tilt regions in a domain are curved in either a clockwise or
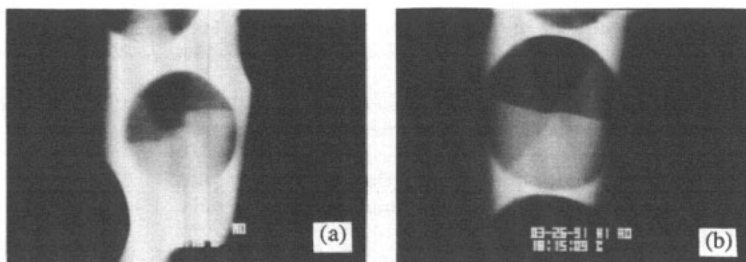
Figure 3. Fluorescence microscope image of hexagonal LC domains obtained with polarized laser excitation. The narrow illuminated strip is the width of the laser beam. Regions with different tilt azimuth fluoresce with different intensity. Each domain is a single six-arm star defect. (*a*) methyl octadecanoate at 31 °C; (*b*) methyl eicosanoate at 20 °C.

counterclockwise sense, figure 3(*a*). The existence of these chiral features in domains built up of molecules that are not themselves chiral shows that this is the L phase, the only one of the smectics that is intrinsically chiral. The boundaries between tilt regions in the longer-chain-length esters are straight, figure 3(*b*), and in these systems the transition is very likely from the B_H to the F or I phase.

A similar pattern of tilt regions has been observed in freely suspended films of hexatic liquid crystals [23]. These so-called, star defects, consist of a pattern of N arms. Selinger and Nelson [24] have developed a theory that explains the structure of such defects. At each of the arms the tilt azimuth jumps by $2\pi/6$. In the regions between the arms the azimuthal angle ϕ is locked to the bond orientation angle θ both change by $(2\pi N)(1 - N/6)$.

For the liquid crystals the energy of the defect is minimum in five-armed structures for all reasonable choices of the elastic constants, in agreement with the observations. If the stars end at the edge of domains, as they do in the monolayers, six arms are optimal.

Acknowledgments

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