Surprises on a surface

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Two-dimensional (2D) systems have been theoretician's paradise and experimentalist's obsession! These are interesting and intriguing because there is no true long-range positional order. In 2D systems, thermal fluctuations are strong enough to prevent the existence of conventional long-range positional order. Also thermal fluctuations lead to algebraic correlation in the positions of atoms or molecules. Another feature of these systems is the spontaneous formation of unbound dislocations (topological defects) in equilibrium leading to the destruction of lattice order. Such topological defects are important in the Kosterlitz–Thouless theory of 2D melting. Though 2D systems lack true long-range positional order, they can be endowed with the true long-range orientational order as seen in hexatic liquid crystals[1].

Invariably 2D systems are hard to realize in the laboratory. This is where Langmuir monolayers become very relevant and have understandably attracted the attention of physicists and chemists alike. A Langmuir monolayer is a layer of amphiphilic molecules formed at the air–water interface. These monolayers act as good models for research in 2D systems. Even relatively simple experiments reveal their main features and properties. Further, they lend themselves easily to tuning of experimental parameters. Their wide applications in reducing friction, wear, rust and evaporation losses, to name a few, are too well known to be stressed here. In some cases such as emulsions, foams and solid dispersions, these monolayers are used to stabilize the system. The wave-guiding and nonlinear optical properties of Langmuir–Blodgett films serve to enhance the interest in the subject for potential applications[2,3]. These systems are more than of an academic interest since they often mimic the features of biological membranes. In fact, it has been known for a long time in physiology that the human lung uses amphiphilic molecules to reduce surface tension of alveolar fluid, a necessary process for breathing[4].

A proper understanding of Langmuir monolayers calls for a study of their phases and phase transitions. Though the phases and phase transitions in 3D are well familiar, such studies in 2D systems are still in a nascent state. Phase transitions in Langmuir monolayers can be pretty complex. Surprisingly even a simple Langmuir monolayer system can sometimes exhibit as many as 17 phases[5]. Occasionally, we even find multilayered structures co-existing with 2D phases. Interestingly some of these multilayers at air–water interface exhibit liquid crystalline order (Figure 1) as well[6]. These 2D phases are thermodynamically stable and interesting from the point of view of physics. They exhibit the familiar first-order transitions, second-order transitions, critical points and so on.

There can be other exotic possibilities like induced phases. Literature to this date is scanty on such phenomena. It is

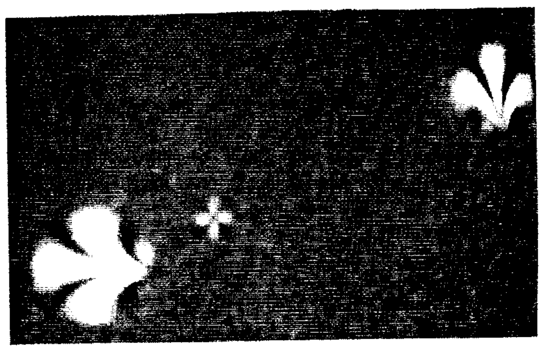

Figure 1. Images of 8CB domains at 30°C around 10 Å² A/M under polarizing microscope, showing point defects characteristic of liquid crystalline ordering. Scale of image: 65 μm × 110 μm (Private communication: A. Bhattacharyya and K. A. Suresh)

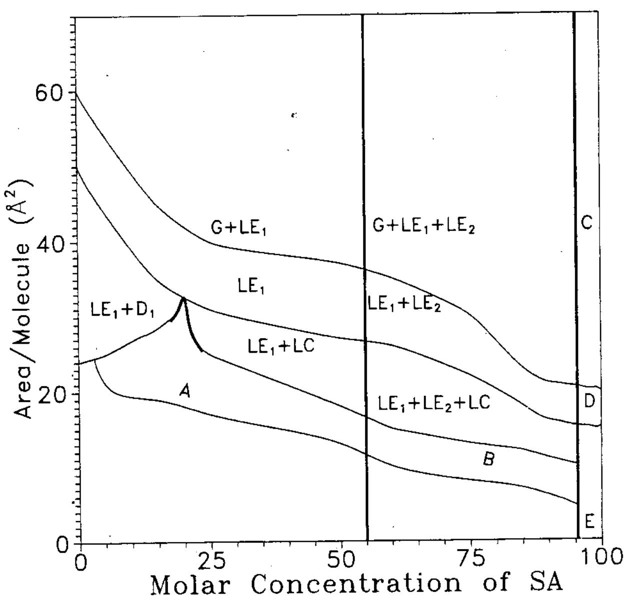

Figure 2. Phase diagram at temperature 23°C for mixed monolayer system. The thin lines indicate actual phase boundaries. The thick lines indicate approximate boundaries (G, gas; A = $LE_1 + LC + D_1$; B = $LE_1 + LE_2 + LC + D_1$; C = Gas + LE_2; D = LE_2; E = collapsed state; D_1, Multilayered structures.) (Private communication: A. Bhattacharyya and K. A. Suresh). The molar concentration of SA in 8CB is expressed as a percentage.

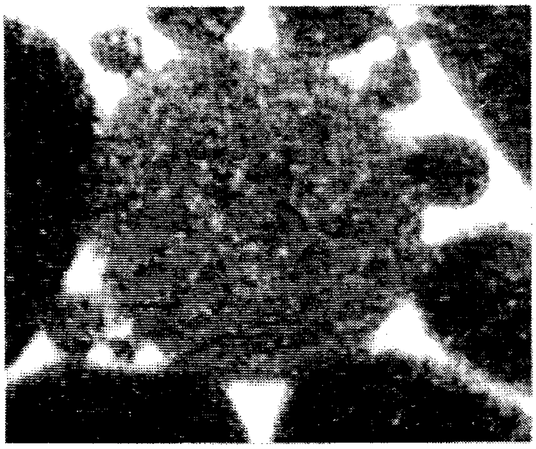

Figure 3. Fluorescence image of co-existence of LE_1 (bright background), LE_2 (grey domains) and LC (black domains) phases. The molar concentration is 75% of SA in 8CB and A/M is 15 $Å^2$. Scale of image: 960 μm × 1280 μm. (Private communication: A. Bhattacharyya and K. A. Suresh)

in this context that the recent study of a mixed Langmuir monolayer system, by A. Bhattacharyya and K. A. Suresh is relevant and significant[7]. It is a well known fact that on compression a monolayer generally exhibits the phase sequence: Gas ⇒ liquid expanded (LE) ⇒ liquid condensed (LC) ⇒ solid ⇒ collapsed state.

We may briefly describe here the structure of these phases. In the gaseous phase, the amphiphilic molecules are quite far apart with no interaction between them. In the two liquid phases, viz. LE and LC, they have liquid-like short-range positional order but with different molecular surface densities. Generally the surface density of the LC phase is almost double that of the LE phase. This is due to the fact that in the LC phase, the molecules stay upright on water whereas in the LE phase they stay nearly flat on water. Such liquid–liquid transitions are a common phenomenon in monolayers. It is almost non-existent in 3D liquids. Incidentally, there have been claims of late of liquid–liquid transitions in water[8]. The solid phase is either in an amorphous state or in a crystalline state possessing quasi-long-range positional order. At surface density beyond a certain limit, the monolayer collapses into a mixture of 2D and 3D phases. There are some cases in which a monolayer has only one of the two liquid phases. For example, stearic acid (SA)[7] has the phase sequence: gas ⇒ LE ⇒ collapsed state.

Against this background, we can appreciate the novel phase diagram (Figure 2) of a Langmuir monolayer of a mixed system obtained by Bhattacharyya and Suresh. They considered a mixture of SA and 4′-*n*-octyl-4 cyanobiphenyl (8CB). The interest in this system arises from the fact that the binary liquid systems are ideal testing grounds for various theories and applications. Their study indicates the existence of a hitherto unreported induced LC phase in the said mixed monolayer. This is seen over a range of compositions, on compressing the LE phase. It should be pointed out that neither of the two pure components exhibits an LC phase. It is important to know why monolayers of some amphiphilics only exhibit LC phase and not others. This is still an open question in this area of research. Some investigators attribute the absence of LC in SA to the long chain length of SA molecules[9]. Others argue that the existence of the LC phase in addition to LE phase in a pure component system can be due to stiff chains[10]. In the case of 8CB and SA mixture, 8CB effectively decreases the mean chain length. Also 8CB has a stiff biphenyl ring which may also contribute to the induction of the LC phase.

Another important result in this mixed system is the phase separation of the LE phase into an 8CB-rich LE phase (LE_1) and SA-rich LE phase (LE_2). The two phases are distinct as indicated by the clear phase separation seen in Figure 3 under different experimental situations. The occurrence of the two distinct LE phases is probably due to some subtle differences in the structure of the two phases. This calls for a detailed study of this phenomenon. The mechanism driving this phase separation is an interesting process to be resolved. Incidentally, a detailed study of this phase diagram reveals the existence of multilayer structures with reversible phase sequence: smectic-A ⇒ nematic ⇒ isotropic. The richness of the phase diagram and their uniqueness should lead to a more vigorous activity in the field.

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