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Novel phase diagram of a mixed Langmuir monolayer of octylcyanobiphenyl and stearic acid

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Abstract. – We have studied the phase diagram of a mixed monolayer system of 4'-*n*-octyl-4-cyanobiphenyl (8CB) and stearic acid (SA) at the air-water interface by surface manometry and optical microscopic techniques. We found that in the mixture, a liquid condensed phase (also known as L_2) was induced which does not occur in the monolayers of the individual components. The induction occurs over a large range of molar concentrations *viz.* 3% to 95% of SA in 8CB. More interestingly, we observed a phase separation of the liquid expanded (LE) phase (also known as L_1) into an 8CB-rich LE phase and an SA-rich LE phase for molar concentrations in the range 55% to 95% of SA in 8CB. We also observed a co-existence of three stable phases.

Amphiphilic molecules spread spontaneously on water surface to form stable Langmuir monolayers at the air-water interface. Generally, on compression, a monolayer exhibits the phase sequence: gas \rightarrow liquid expanded (LE) \rightarrow liquid condensed (LC) \rightarrow solid \rightarrow collapsed state. In recent times, detailed phase identifications [1]-[7] of monolayers have been carried out mainly based on miscibility and X-ray diffraction studies. In this classification, the LE phase is called L_1 . The LC phase is generally called L_2 and is further classified into L_{2d} , L_{2h} etc. There are some cases in which a monolayer has only one liquid phase, for example, stearic acid (SA) [8]. There are also systems where a monolayer in the LE phase goes directly to multilayer structures [9]. This is seen in a monolayer of 4'-*n*-octyl-4-cyanobiphenyl (8CB). We have investigated a monolayer of a mixed system of these two components *viz.* 8CB and SA and studied its phase diagram. In this paper, we use the broad nomenclature LE and LC since the nomenclature L_1 , L_{2d} , L_{2h} etc. requires detailed structural identification. The same mixed system has also been studied by Enderle *et al.* [10]. Interestingly, our epifluorescence studies showed a hitherto unobserved induced LC phase in the mixed monolayer on compressing it from the LE phase. In addition, at high concentrations of SA, we found that the LE phase separated into an 8CB-rich LE phase (LE_1) and an SA-rich LE phase (LE_2). The LE_1 and LE_2 phases were seen in co-existence with the gas phase at high area per molecule (A/M) and with the LC phase at low A/M. Further, multilayer domains and LC phase co-existed

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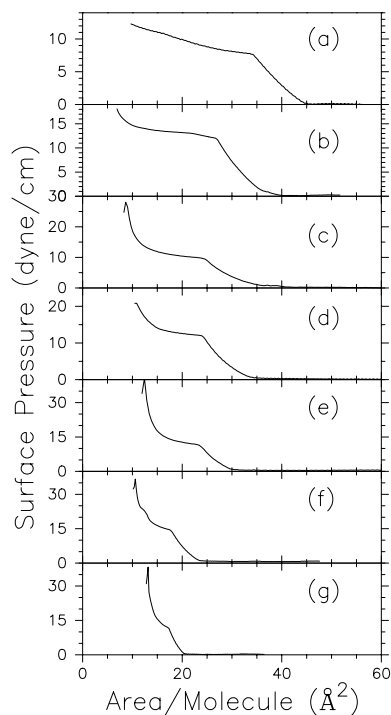


Fig. 1

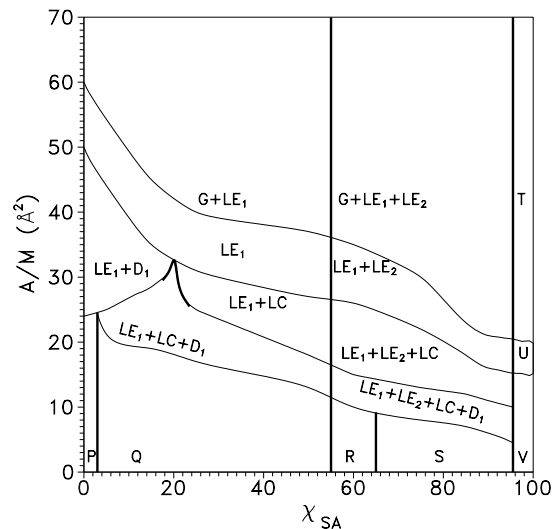


Fig. 2

Fig. 1. – Surface pressure-area isotherms for mixed monolayers of SA and 8CB obtained from surface manometry. The molar concentrations of SA are (a) 15%, (b) 25%, (c) 50%, (d) 60%, (e) 75%, (f) 85%, (g) 90%. The compression rate was $0.05 \text{ \AA}^2/\text{molecule}/\text{second}$. The kink at $12 \text{ \AA}^2 \text{ A/M}$ in (f) corresponds to the onset of the D_1 domains and was not apparent at other concentrations. While comparing the surface pressures, the different scales in the y -axis may be noted.

Fig. 2. – Phase diagram at a temperature of $23 \text{ }^\circ\text{C}$ for the mixed monolayer system. The thin lines indicate the actual phase boundaries. The thick lines indicate approximate boundaries. (Key: G = gas phase, P = $LE_1 + D_1 + D_2$, Q = $LE_1 + LC + D_1 + D_2$, R = $LE_1 + LE_2 + LC + D_1 + D_2$, S = $LE_1 + LE_2 + LC + D_1 + D_3$, T = gas + LE_2 , U = LE_2 , V = collapsed state.) χ_{SA} = molar concentration of SA in 8CB expressed as a percentage.

with the LE_1 and LE_2 phases. The phenomenon of co-existence of three stable phases can be understood in terms of Crisp's phase rule [11].

The materials 8CB (BDH) and SA (Aldrich) were used as received. The technique used for forming a monolayer has been described elsewhere [9]. The subphase was maintained at a temperature of $23 \pm 1 \text{ }^\circ\text{C}$. To construct the phase diagram, we studied mixtures with different concentrations of SA in 8CB. The surface pressure (π)-area (A) isotherms obtained from surface manometry showed kinks and plateaus (fig. 1) indicating structural changes. To investigate these changes we employed fluorescence microscopy [9], [12]. The monolayer was directly observed under the microscope (Leitz, Metallux 3). In our experiments, we used either of the two fluorescent dyes 4-(hexadecylamino)-7-nitrobenz-2-oxa-1,3 diazole (NBD HDA) and 12-*n*-methyl-*n*-((7-nitrobenz-2-oxa-1,3 diazol-4-yl) amino) octadecanoic acid (NBD SA) (both from Molecular Probes) at a molar concentration of 0.5% in the monolayer. This was undertaken to rule out any artifact in the fluorescence intensity arising out of a particular

dye in the monolayer. We used a reflection microscope to study the surface topography of the multilayer domains and a polarising microscope to characterise their phases [9].

In general, under a fluorescence microscope, the LE phase appears bright and the gas phase appears dark in the two-phase co-existence region. This is attributed [12] to the difference in densities of the phases and the quenching of the dye in the gas phase. On compression, the two-phase monolayer becomes uniformly bright, indicating an onset of a pure LE phase. At higher compression, one gets the LC phase which appears dark due to expulsion of the dye [13]. In case of certain liquid crystal forming molecules like 8CB one observes even brighter domains (D_1) corresponding to a three-layer structure growing in the bright LE phase. Under further compression the D_1 domains transform into either flat smectic domains (D_2) or lens shaped nematic or isotropic domains (D_3) depending on temperature [9].

The π -A isotherms for seven different molar concentrations of SA in 8CB are shown in fig. 1. At high concentrations of SA, the isotherms resembled those of pure SA while at high concentrations of 8CB, the isotherms resembled those of pure 8CB. This indicated a good mixing of the two species of molecules [14]. The SA monolayer can be compressed to very high surface pressures (65 dynes/cm) before it collapses. This value gradually decreases with increase in 8CB concentration. We suggest that this is due to the formation of three-dimensional D_1 and D_2 (or D_3) domains in 8CB-rich monolayer.

From our studies we have constructed the phase diagram depicted in fig. 2. In the mixtures with up to 3% of SA in 8CB, the phase sequence on compression was that of pure 8CB: gas + $LE_1 \rightarrow LE_1 \rightarrow LE_1 + D_1 \rightarrow LE_1 + D_1 + D_2$. In the mixtures with 3% to 20% of SA in 8CB, on compressing the monolayer in the $LE_1 + D_1$ co-existence region, the LC phase appeared. This was followed by D_2 domains. Here the phases LE_1 , LC, D_1 and D_2 co-existed. The D_2 domains were flat with smectic A order, as found by reflection and polarising microscopy [9]. In the isotherm for 15% SA in 8CB, a slight change of slope at $30 \text{ \AA}^2 \text{ A/M}$ (fig. 1(a)) corresponds to the appearance of the LC phase.

For 20% to 55% of SA in the mixture, the LC phase appeared before the onset of the D_1 domains. Here the phase sequence was: gas + $LE_1 \rightarrow LE_1 \rightarrow LE_1 + LC \rightarrow LE_1 + LC + D_1 \rightarrow LE_1 + LC + D_1 + D_2$. For 25% SA in the mixture, the isotherm exhibits a change of slope at $22 \text{ \AA}^2 \text{ A/M}$ (fig. 3). This corresponds to the appearance of D_1 domains.

At SA concentrations between 55% and 65%, an SA-rich liquid expanded phase (LE_2) separated from the LE_1 phase. The phase sequence was: gas + $LE_1 + LE_2 \rightarrow LE_1 + LE_2 \rightarrow LE_1 + LE_2 + LC \rightarrow LE_1 + LE_2 + LC + D_1 \rightarrow LE_1 + LE_2 + LC + D_1 + D_2$. The LE_2 phase was not as bright as the LE_1 phase but was brighter than the gas phase. The co-existence is shown in fig. 4. These three phases co-existed even for A/M as large as 200 \AA^2 . The LE_1 and LE_2 phases also co-existed with the LC phase at low A/M (fig. 5). In the range 65% to 95% of SA in the mixture, we found the same phase sequence except that D_3 domains appeared in place of D_2 domains. The D_3 domains were lens-shaped with nematic order [9]. Beyond this concentration, the behaviour was like that of pure SA.

Under fluorescence microscope, we observed that in the LE_1 phase, the D_1 domains appeared first and were followed by the D_2 or D_3 domains. On the other hand, the LE_2 phase transformed into the D_3 domains directly and rarely transformed into the D_1 domains. Also the D_3 domains in the LE_2 phase moved much faster than those in the LE_1 phase, indicating more fluidity in the LE_2 phase.

An important result is the observation of an induced LC phase which does not occur in the monolayer of either component. It occurs in mixtures with molar concentrations of 3% to 95% SA in 8CB. Under the fluorescence microscope, this induced phase appeared dark due to expulsion of the dye. This showed it to be a dense phase. Also the monolayer was less mobile. Hence we identify this as the LC phase. This could be L_{2h} , L_{2d} or the fluid lamellar phase [15].

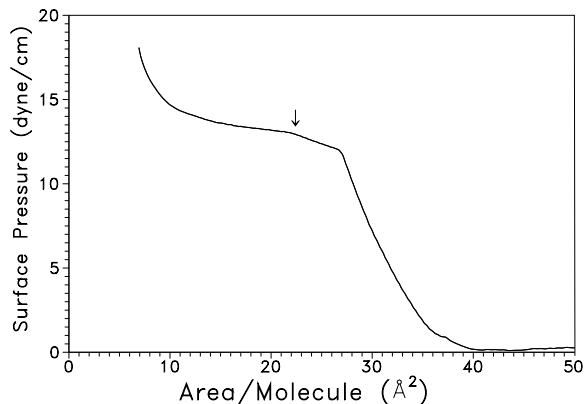


Fig. 3

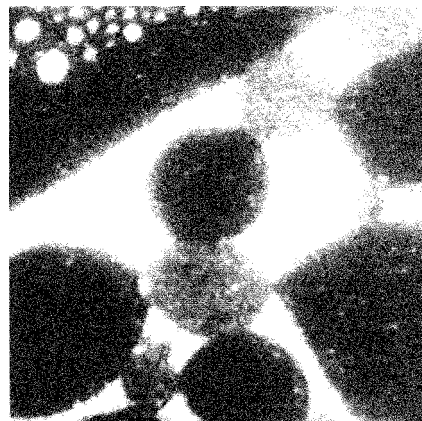


Fig. 4

Fig. 3. – An enlarged plot of the isotherm for 25% SA in 8CB shown in fig. 1(b). The plateau at A/M greater than 40 \AA^2 is the gas + LE₁ two-phase region. The region with steeply increasing π corresponds to pure LE₁ phase. The change of slope at 27 \AA^2 indicates the onset of LC phase. The change of slope indicated by the arrow is the onset of the D₁ domains. This change of slope was most prominent at this molar concentration. The D₂ domains appeared at 16 \AA^2 A/M.

Fig. 4. – Fluorescence image of the co-existence of gas (black domains), LE₂ (grey domains) and LE₁ (small bright domains and the bright background) phases. The molar concentration is 75% SA in 8CB and A/M is 50 \AA^2 . Scale of the image: $1020 \mu\text{m} \times 1020 \mu\text{m}$.

X-ray [2] or miscibility [3] studies can reveal the exact phase. Further, our results along with second-harmonic generation can yield quantitative information on the order of these phases at the molecular level. Dupin *et al.* [16] attribute the absence of two liquid phases in SA, as opposed to myristic acid, to the long chain length of SA molecules. We suggest that the smaller chain length of 8CB molecules brings the effective chain length of the mixture to an appropriate range. Also, Schmid and Schick [17] have pointed out that two liquid phases can be formed due to stiff chains. Hence, the formation of LC phase is further aided by an increase in the chain stiffness, due to the biphenyl group of 8CB. Therefore the mixed monolayer may be considered to be effectively like the monolayer of a fatty acid with shorter and stiffer chains. Another interesting observation is that for SA molar concentration up to 20%, the D₁ domains appeared first and the LC phase appeared later. On the other hand, at higher SA concentrations, the LC phase preceded the D₁ domains. This behaviour is obviously a result of the subtle nature of the hydrophobic chain—subphase and polar headgroup—subphase interactions involved in the formation of LC and D₁ phases.

An interesting new result is the phase separation of the LE phase into LE₁ and LE₂ in the mixed monolayer. Both phases were highly mobile and the dye dissolved in them easily. Hence we broadly identify them as LE phases. The LE₁ phase is definitely the L₁ phase (like smectic A). The LE₂ phase is more mobile than the LE₁ phase and is likely to be a modified form of the L₁ phase. However, the two phases are distinct as indicated by the clear phase separation. Again a detailed structural identification of the phases is required. Also, transferring the monolayer onto a solid substrate and studying it by atomic force microscopy and X-ray diffraction can give valuable information. To confirm the phase separation, we repeated the experiments with two different dyes. The phase separation and the relative areas occupied by the LE₁ and LE₂ phases at any concentration were independent of the particular

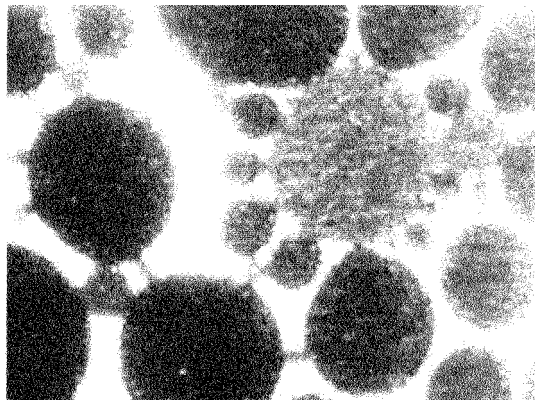


Fig. 5

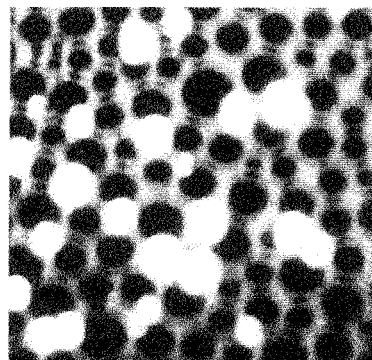


Fig. 6

Fig. 5. – Fluorescence image of the 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 \AA^2 . Scale of the image: $960 \mu\text{m} \times 1280 \mu\text{m}$.

Fig. 6. – Fluorescence image of the D_2 domains (bright) entering into the LC domains (black). The grey background consists of the LE_1 phase and the D_1 domains, whose difference is not very apparent. The molar concentration is 25% of SA in 8CB, A/M is 10 \AA^2 . Scale of the image: $860 \mu\text{m} \times 920 \mu\text{m}$. The fluorescence images shown in figs. 4, 5 and 6 were obtained using the dye NBD HDA.

dye used. The phase separation started only on increasing SA beyond 55%. At still higher concentrations, the LE_2 phase increased in area at the expense of the LE_1 phase. Further, the multilayer domains, which are characteristic of pure 8CB, always appeared first in the LE_1 phase. In addition, the LE_1 phase had a lower fluidity compared to the LE_2 phase. This indicated a higher proportion of 8CB in LE_1 phase, as the larger head-group of 8CB impedes movement. Based on these results, we conclude that the LE_1 phase is 8CB rich while LE_2 is SA rich.

The co-existence of three stable monolayer phases, such as gas, LE_1 and LE_2 (fig. 4) and LE_1 , LE_2 and LC (fig. 5) can be accounted for by Crisp's phase rule [11] for two-dimensional systems. For a single interface with q surface phases, the number of degrees of freedom at any given temperature and pressure is given by

$$F = C^B + C^S - P^B - q + 1, \quad (1)$$

where C^B = total number of components in the bulk phases, C^S = number of components in the monolayer on the interface, P^B = total number of bulk phases separated by the interface. In our case, $C^B = 2$ (air and water), $C^S = 2$ (8CB and SA) and $P^B = 2$ (gas and liquid). So, eq. (1) gives

$$F = 3 - q. \quad (2)$$

Thus, at any fixed temperature, a two-component monolayer system can have a maximum of three stable phases. The D_1 , D_2 and D_3 domains are three-dimensional structures and hence cannot be considered under this phase rule.

It was mentioned earlier that we got the lens-shaped D_3 domains in mixtures with SA concentration above 65% and flat D_2 domains at lower concentrations. This indicates that the large amount of SA present in the monolayer lowers the smectic A-nematic transition temper-

ature of 8CB-SA mixture to sub-ambient levels, as confirmed by polarisation microscopy.

We may mention that apart from being of interest to theoreticians in condensed-matter physics, our phase diagram studies of SA and 8CB showing new phases and co-existence of different phases should have an impact in the understanding of the formation of Langmuir Blodgett (LB) films. It is known that though SA is one of the best LB materials, it is difficult to deposit it in a pure form [1].

We observed some D_2 domains entering into the LC areas of the monolayer (fig. 6). This may be due to the expulsion of some 8CB molecules which form a D_2 domain over the monolayer. According to Enderle *et al.* [10], all the 8CB molecules are squeezed out of the monolayer and they settle above the SA monolayer. But if there is such a total expulsion of 8CB molecules, the A/M value at the peak surface pressure should decrease with higher concentration of 8CB. No such trend was seen by us. Also, the π value at the onset of collapse for the mixed monolayer was less than that for a pure SA monolayer [10]. Therefore, we conclude that a partial squeezing out of 8CB molecules is more likely, as seen in 8CB-pentadecanoic acid system [14].

The partial squeezing-out of 8CB molecules from the monolayer at very low A/M can be attributed to the weak anchoring of 8CB molecules to water as compared to that of SA molecules. On the other hand, the phase separation of the 8CB-rich LE_1 phase and the SA-rich LE_2 phase is not easy to understand.

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