

# Optical measurements of the phase diagram of Langmuir monolayers of fatty acid–alcohol mixtures

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The surface pressure-temperature diagram of Langmuir monolayers of mixtures of heneicosanoic acid with heneicosanol has been determined from 10 °C to 40 °C by direct observation with Brewster angle microscopy. The measurements focused on the way in which the boundary between the  $L_2'$  and  $L_2$  phases change with composition. As previously observed by Shih *et al.* [J. Chem. Phys. **101**, 9132 (1994)], it moves to lower pressure and higher temperature with increasing concentration of alcohol. We have discovered that the boundary between the Ov and  $L_2$  phases, which had not been studied before, moves in the opposite direction and that the  $L_2'$  and Ov phase regions merge, an unanticipated result. © 1995 American Institute of Physics.

## I. INTRODUCTION

The complexity of the phase diagrams of monolayers of simple amphiphiles at the air/water interface has been revealed by a variety of investigations of fatty acids, alcohols, and esters. In this work, x-ray studies, which provide information about the molecular structures of the phases, have been complimented by optical measurements with polarized fluorescence microscopy (PFM) and Brewster-angle microscopy (BAM), which allow phase boundaries to be determined directly with high precision and which also provide information about the orientation of the molecular tilt azimuth and the molecular tilt angle. It is clear from the x-ray measurements that the packing of the hydrocarbon chains, which constitute the tails of the amphiphile, plays an important role in determining the structures of the phases. The interactions between head groups also play a role, in great part because the chain tilt depends on the mismatch between the head-group spacing and the chain diameter.

In a recent paper, Shih *et al.*<sup>1</sup> have examined the interplay between the effects of head group and tail by studying the phase behavior of mixtures of heneicosanoic acid and heneicosanol. They determined the phase diagrams from pressure-area isotherms of the pure components and four mixtures and they examined the structures of the phases by performing x-ray measurements along one isotherm at three compositions along an isobar for one mixture. Their results are summarized in Fig. 1, which, with the exception of the labeling of the phases, is identical to their Fig. 1.

The phases S, LS, and RII are untilted, i.e., the molecules are normal to the surface. There are two tilted phases shown in the diagram,  $L_2$ , in which the molecules are tilted toward their nearest neighbors, and  $L_2'$ , in which they point in the next-nearest neighbor direction. The absence of the  $L_2$  phase in the alcohol had been known<sup>2</sup> and a major goal of the measurements by Shih *et al.* was to trace the path of the  $L_2/L_2'$  phase boundary from the pure acid to the alcohol. This transition is called the “swiveling transition” because it represents a rotation of the molecular tilt azimuth by 30°. As shown in the figure, the phase boundary moves toward lower pressure and higher temperature as the alcohol concentration

increases and vanishes somewhere between 30 and 50 mol% alcohol.

It is not evident how the  $L_2/L_2'$  boundary disappears from the phase diagram and we therefore set out to determine the phase diagrams of acid/alcohol mixtures by PFM and BAM, techniques that are more rapid than x-ray analysis and generally easier to interpret than pressure-area isotherms. A recent study<sup>3</sup> has shown that the phase boundaries in acid monolayers can be directly located with high precision by these optical methods.

## II. EXPERIMENT

Heneicosanoic acid and heneicosanol, both claimed to be 99+% pure, were obtained from Nu-chek Prep and were used without further purification. They were spread from

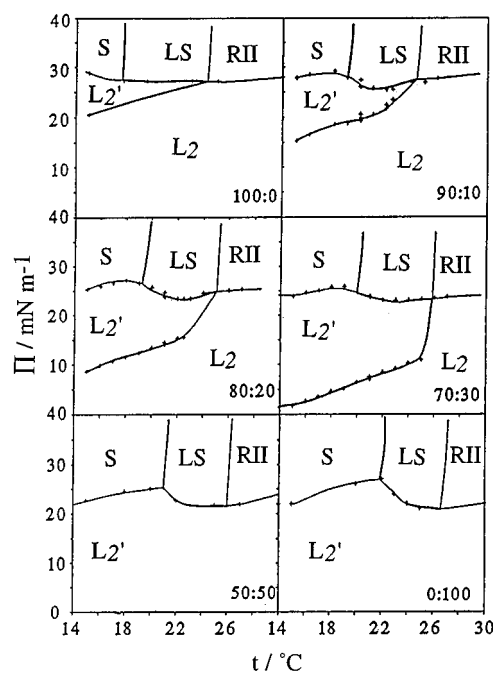


FIG. 1. Surface pressure-temperature phase diagrams for acid–alcohol mixtures determined from isotherm measurements. The ratio of acid to alcohol is given at the lower right of each diagram. The  $L_2'/S$ ,  $LS/RII$ , and  $L_2/RII$  transitions are second order. Adapted from Shih *et al.* (Ref. 1).

chloroform (Fischer spectranalyzed) onto pure water (Millipore Milli-Q) contained in custom-built Teflon troughs. Acid-alcohol solutions were prepared by mixing solutions of the pure components and new mixtures were prepared for each run. For the fluorescence measurements 0.7 mol% of the probe NBD-hexadecylamine was added to the solutions. The details of the PFM<sup>4</sup> and BAM<sup>5</sup> measurements have been described previously. In both cases the cover glass was heated during experiments carried out at temperatures other than ambient in order to prevent fogging by condensation from the monolayer or the surrounding air. Thermocouples immersed in the subphase were used to measure the temperature and the pressure was measured with a filter paper Wilhelmy plate in conjunction with an R&K transducer. The observations were generally begun one hour after the monolayer was spread, which allowed the mosaic textures to develop into larger, more regular shapes that allowed the transitions to be seen more readily.

### III. RESULTS AND DISCUSSION

The initial studies of the phase diagram were carried out by PFM. The transition from the tilted to the untilted phases was easily observable and changes from a continuous transition to a first-order transition could be distinguished. It had previously been reported<sup>3,4</sup> that the swiveling transition between the  $L_2$  and  $L'_2$  phases was difficult to observe by PFM but was readily seen by BAM. We found that it is much more apparent in fluorescence measurements when the mosaic texture in the monolayers consists of large domains. Although the textures that we observed by the two imaging methods generally differed very little, some of the phase changes occurred less sharply when there was probe present, particularly in regions of the diagram where phase boundaries intersect. For this reason we focused on the BAM studies and it is these results that we report below.

Figure 2(a) shows the surface pressure-temperature phase diagram for heneicosanoic acid in the temperature range 10 °C–40 °C determined by visual observations with BAM. The measurements were performed by compressing (full symbols) or expanding (open symbols) the monolayer at constant temperature. The swiveling transition is seen as a sharp change in the texture and the transition from a tilted to an upright phase by a loss in contrast.<sup>3</sup> Isotherm data points taken from Fig. 1 in the Shih *et al.* paper are indicated by crosses in Figs. 2(a), 2(b), and 2(f). In general, the phase boundaries that we have determined lie higher in pressure by about 1 mN m<sup>-1</sup>. The transition at high temperature between the  $L_2$  and Ov phases would not have been detected in the isotherm measurements. It was discovered by BAM<sup>6</sup> and its existence was verified by PFM.<sup>4</sup> The phase was then detected by x-ray measurements,<sup>7</sup> which showed that it is a rotator phase in which the molecular tilt is toward next-nearest neighbors. There is no evidence of it in isotherms because the molecular areas in  $L_2$  and Ov phases are essentially identical.

Figures 2(b)–2(h) show how the phase diagram evolves with the concentration of alcohol. In agreement with the observations of Shih *et al.* the  $L_2/L'_2$  phase boundary moves to higher temperature and lower pressure with increasing alco-

hol concentration and the transition between the tilted and untilted phases moves to lower pressure, although less dramatically. What was not observed by them is the behavior of the  $L_2/Ov$  boundary. It moves to lower temperature and lower pressure and merges with the  $L_2/L'_2$  transition at a composition near 23 mol%. The merged boundary then moves rapidly to lower pressure. The variation of the maximum in the boundary with concentration is linear and it extrapolates to zero pressure at 37 mol%. We could not detect it in a brief study at 36% mixture (not shown).

The phase diagrams of the mixtures are projections on the composition axis. At first-order transitions the coexisting phases will not be identical in composition and the transitions will occur over a range of pressure and temperature. Our measurements do not allow us to determine the compositions of the coexisting phases so we cannot construct the complete phase diagram. We see evidence of two phases during some of the measurements. The change in texture sweeps across the image as the pressure is altered and, if the pressure is held constant, the front can be stopped. The differences between the phase boundaries determined by raising or lowering the pressure can be attributed to hysteresis.

Although one expects to observe slight differences in texture between the untilted phases because of the anisotropy of the molecular chain cross section,<sup>3</sup> we did not detect them. The phase boundaries can be determined, however, by the changes in the order of the tilted-to-untilted transition. As shown in Fig. 1, Shih *et al.* observed that the transition from a tilted phase to the S phase is second order, the transition to LS is first order, and that to RII is second order. If we take the low-temperature end of the region of first-order transitions that we have observed as an indication of the S/LS phase boundary, and the high-temperature end as an indicator of the LS/RII phase boundary, we find that the LS phase exists between 18 °C and 25 °C, with no significant dependence on the composition. This is in reasonable agreement with these phase boundaries determined by Shih *et al.*

The  $L'_2$  and Ov phases differ only in the extent of rotational freedom of the chains. Thus, one might expect that a rotator transition might be found at pressures above the swiveling transition in mixtures with alcohol concentrations in excess of 23 mol%. We have carried out temperature scans at constant pressure in an effort to observe such a transition, but we have found no clearcut evidence for one. The transition would almost certainly be continuous. We observe changes in texture as the temperature is varied, but there are no obvious features that one could associate with a transition. Although it has been argued<sup>8</sup> that the field of the  $L_2$  phase must also consist of both rotator and nonrotator phases, we have seen no evidence for a transition in temperature scans.

While in most respects our results agree with those of Shih *et al.*, there is one significant discrepancy. In isobaric measurements at 17 mN m<sup>-1</sup> on a 30 mol% alcohol mixture, they observed that the  $z$  component of one of the diffraction vectors fell to zero at 28 °C, evidence of a transition to the  $L_2$  phase and in accordance with the steep rise in the  $L'_2/L_2$  phase boundary drawn in Fig. 1. This is inconsistent with our measurements, which show that the boundary would not be observed at the pressure for mixtures richer than 23% in alcohol. We have no explanation for this difference other

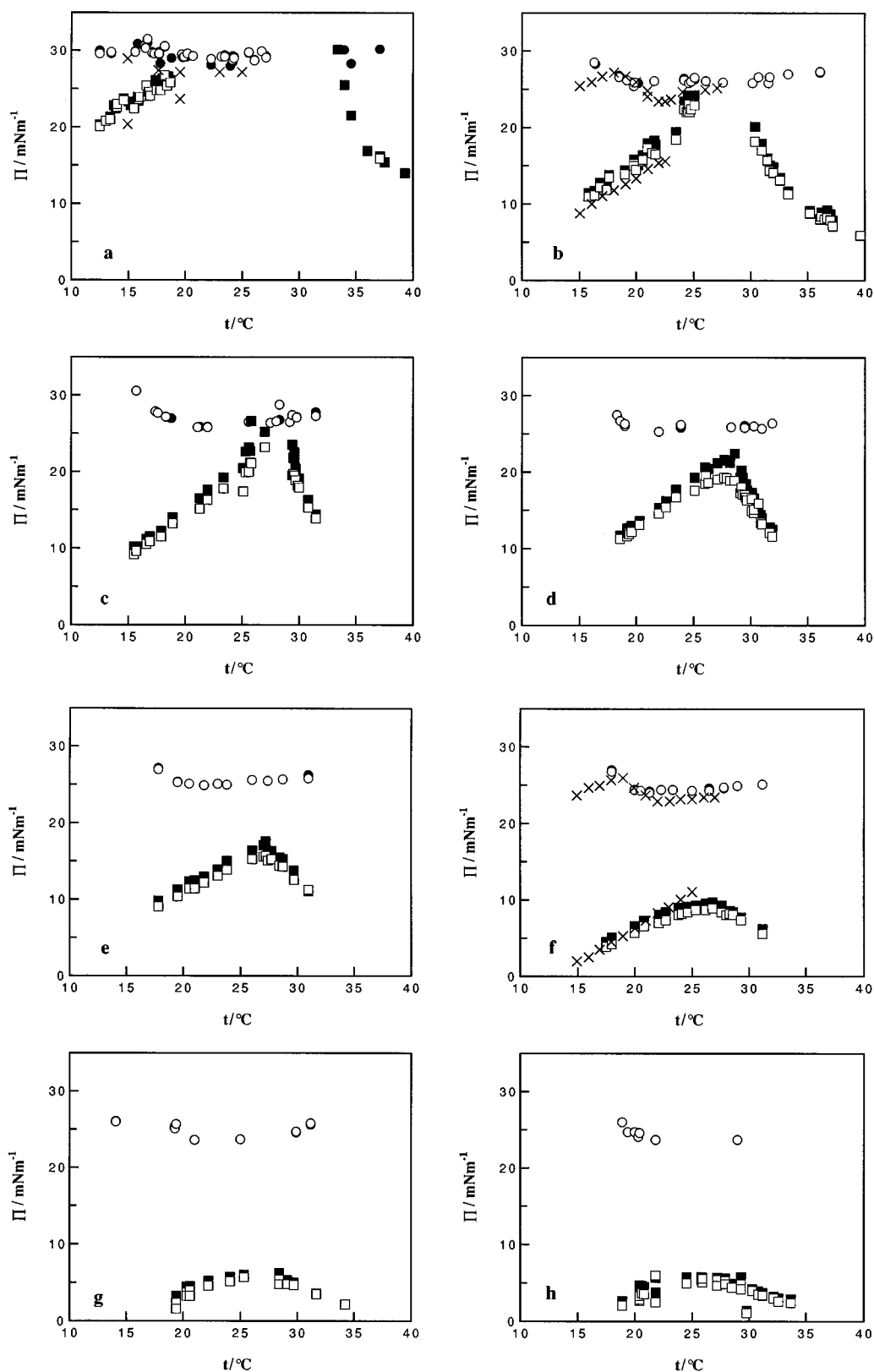


FIG. 2. Surface pressure-temperature phase diagrams for acid-alcohol mixtures determined by BAM at different concentrations of alcohol. The open symbols represent observations made with increasing pressure and the closed symbols are observations made with decreasing pressure. Squares indicate transitions between tilted phases and circles indicate transitions between a tilted and an untilted phase. The crosses in (a), (b), and (f) are experimental points taken from Fig. 1 of Shih *et al.* (Ref. 1). Alcohol concentrations in mol% (a) 0; (b) 20; (c) 22; (d) 23; (e) 25; (f) 30; (g) 33; (h) 35. The S, LS, and RII phases could not be distinguished from each other, but the tilted/untilted transition appears to be first-order between 18 °C and 25 °C and continuous elsewhere.

than the possibility that either we or Shih *et al.* have made an error in the composition. The boundary moves rapidly with composition and as little as a 5% change in the concentration of the alcohol could account for the difference.

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