

# Transition between two next-nearest-neighbor phases in a mixed Langmuir monolayer. A study by grazing-incidence x-ray diffraction and Brewster-angle microscopy

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Grazing incidence x-ray diffraction and Brewster-angle microscopy measurements have been undertaken for a mixed Langmuir monolayer of octadecanoic acid and methyl octadecanoate. For the composition studied (49.7 mol % ester) there are two noncrystalline tilted phases, one at low pressure in which the chains point to their nearest neighbors ( $L_2$  phase) and a higher-pressure phase in which the tilt is toward next-nearest neighbors. The higher-pressure phase arises from a merger of the  $L'_2$  and  $OV$  phases, which are separated in the pure acid. A continuous change between the two regions is observed rather than a first-order transition, as had been suggested. The results are discussed with reference to different proposals for the origin of two distinct next-nearest neighbor tilted mesophases: the presence of one-dimensional chain backbone order [V. M. Kaganer and E. B. Loginov, *Phys. Rev. E* **51**, 2237 (1995)] and a coupling between tilt and distortion [E. Sirota, *Langmuir* **13**, 3849 (1997)]. © 2000 American Institute of Physics. [S0021-9606(00)70631-3]

## INTRODUCTION

Grazing-incidence diffraction (GID) and Brewster-angle microscopy (BAM) studies have shown that insoluble monolayers of simple amphiphiles such as the long-chain fatty acids, alcohols and esters at the air–water interface have complex phase diagrams.<sup>1</sup> At least eight condensed phases have been identified. In the high-surface-pressure phases the molecules are untilted, i.e., their chain axes are perpendicular to the water surface; in the other condensed phases they are inclined with respect to the surface normal. In these “tilted” phases the tilt angle increases with decreasing surface pressure. The phases can further be distinguished by the degree of chain backbone order, which generally increases with decreasing temperature, and, in tilted phases, the direction of the molecular tilt azimuth. Phases have been identified in which the tilt is toward nearest neighbors (NN), next-nearest neighbors (NNN) or in an intermediate direction. The degree of translational order can be determined from the width of the x-ray diffraction peaks. Two of the phases have the quasi-long-range translational order of a two-dimensional crystal. The others have shorter translational correlation lengths but, as shown by the macroscopic organization of the tilt azimuth discovered in imaging studies,<sup>2</sup> these mesophases have quasi-long-range orientational order.

Early surface pressure-area isotherm studies<sup>3–5</sup> showed

that the phase diagrams for the simple amphiphiles such as saturated fatty acids and their esters have similar topologies but there is no “universal” diagram. This is borne out by recent diffraction and imaging measurements in which two general types of diagrams have been found for simple systems. In the diagram for the linear saturated acids and acetates there are three major noncrystalline tilted phases.<sup>6</sup> In two of them, denoted  $L'_2$  and  $OV$ , the tilt is toward next-nearest neighbors while in the other phase, denoted  $L_2$ , it is toward nearest neighbors. On the other hand, in the corresponding alcohols and esters there is generally only a single noncrystalline tilted phase and in it the tilt is toward next-nearest neighbors.<sup>7</sup>

To understand the dependence of the phase behavior on the head group, Shih *et al.*<sup>8</sup> employed isotherm measurements and GID to study the way in which the phase diagram evolved when heneicosanol was mixed with heneicosanoic acid. Their measurements were incomplete, however, because they were unable to observe the  $L_2$ – $OV$  phase boundary for which there is no signature in pressure-area isotherms. Both tilt transitions can be observed by BAM and Fischer *et al.*<sup>9</sup> used this technique to examine the entire phase diagram. Like Shih *et al.*, they found that with increasing concentration of the alcohol the  $L_2$ – $L'_2$  phase boundary moves to lower pressure and higher temperature. What had not been observed earlier was the simultaneous movement of the  $L_2$ – $OV$  boundary to lower pressure and lower temperature.

Similar behavior was found in BAM studies of mixtures

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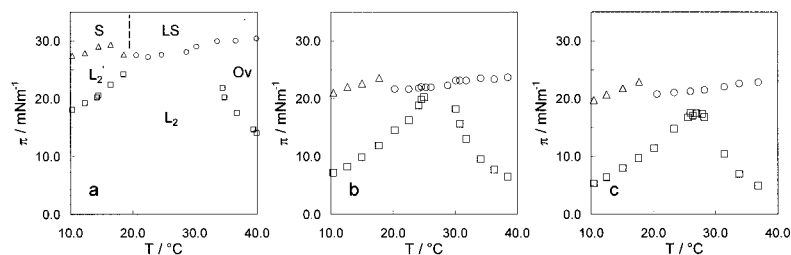


FIG. 1. Surface pressure-temperature phase diagrams for the system heneicosanoic acid+methyl heneicosanoate. The phase boundaries were determined from BAM measurements. Concentration of ester in mole percent: (a) 0; (b) 27.2; (c) 32.0. The squares represent boundaries between NN and NNN phases, the circles are transitions from tilted phases to the LS phase, and the triangles transitions to the S phase. Adapted from Ref. 10.

of fatty acids with methyl, ethyl and propyl esters of the same chain length.<sup>10</sup> As can be seen in Fig. 1, which shows phase diagrams for mixtures of methyl heneicosanoate with heneicosanoic acid, the  $L_2'-L_2$  and  $Ov-L_2$  phase boundaries eventually meet and the two NNN phases appear to merge. With the addition of more ester, the field of this combined  $L_2'-Ov$  phase moves down in pressure and displaces the  $L_2$  phase, which finally disappears. Beyond this concentration all the mixtures have phase diagrams with the same topology as that of the pure ester. The various mixtures differ primarily only in the concentrations at which the  $L_2'$  and  $Ov$  boundaries just touch and the last trace of the  $L_2$  phase vanishes.

Kaganer and coworkers have formulated a Landau theory that quite successfully describes the phase diagrams of the long-chain fatty acids.<sup>1,11</sup> In the theory the phase diagram is divided into low-temperature phases in which there is chain backbone (herringbone) order and high-temperature phases in which it is absent. Kaganer and Loginov<sup>11</sup> postulated that one-dimensional herringbone order exists in the high-pressure untilted S phase but not in the neighboring LS phase. Symmetry requirements also led them to a division of the  $L_2$  phase into two phases,  $L_{2h}$ , which has herringbone order, and  $L_{2d}$ , which does not. For the contribution of the herringbone order to the free energy they wrote

$$\Phi_\varphi = F\varphi^2 - G\varphi^4 + H\varphi^6. \quad (1)$$

Here  $\varphi$  is the herringbone order parameter. Since the  $S-LS$  transition is known from experiment to be first order, they took the coefficients  $F$ ,  $G$ , and  $H$  to be positive. In the theory, the  $L_{2h}-L_{2d}$  transition line is an extension of the  $S-LS$  transition, which under these assumptions should be first order as well. There has been no direct evidence of a first-order transition between  $L_{2h}$  and  $L_{2d}$  phases, however. This has been reconciled in the most recent discussion of the Landau theory<sup>1</sup> by arguing that in mean field the transition to one-dimensional herringbone order is second order [ $G < 0$  in Eq. (1)] and that it is first order in the case of the S and LS phases only because of the presence of fluctuations. The fluctuations are assumed to be damped by the presence of tilt so that the  $L_{2h}-L_{2d}$  transition remains second order.

An alternative view of the phase transitions in monolayers has been suggested by Sirota<sup>12</sup> on the basis of analogies between monolayer phases and rotator phases in alkanes. He postulates that the key distinction between the S and LS phases is one of lattice distortion within the horizontal plane and, similarly, that the  $L_{2h}$  and  $L_{2d}$  phases can be distinguished by the distortion in a plane perpendicular to the chain direction. The  $S-LS$  transition is then first order be-

cause of the presence of a cubic term in the free energy and the  $L_{2h}-L_{2d}$  transition is second order as a result of a weak coupling between the distortion and the chain tilt. In a recent diffraction study,<sup>13</sup> a peak associated with chain backbone order was found only in the CS and  $L_2''$  phases of heneicosanoic acid, which appears to rule out *long-range* herringbone order in the other monolayer phases and lends support to Sirota's view. Würger<sup>14</sup> has shown that distortion drives transitions between hexagonal, orthorhombic and herringbone ordered phases in a two-dimensional model in which the pair potentials are obtained from the rotational pair potential of alkane molecules. A coupling between distortion and strain also lies at the heart of the treatment of monolayers by Eckhardt and co-workers, who describe monolayers as disordered solids.<sup>15</sup>

In both the Kaganer and Sirota pictures, the distinctions between the two NNN mesophases should be the same as those between the equivalent NN phases. There can be no direct transition between the  $L_2'$  and  $Ov$  phases in monolayers of acids because they are separated by the intervening  $L_2$  phase, but they can be brought into contact in mixtures. While no phase boundary is evident in BAM studies of the merged  $L_2'$  and  $Ov$  phases in the mixtures, a subtle change might have been missed. If the boundary exists, it is likely to be close to the temperature at which the two fields have merged, which should be close to the  $L_{2h}-L_{2d}$  transition line. We have, therefore, undertaken a diffraction study of an acid-ester mixture in which the two NNN phases appear to have merged in order to examine how the structure changes along a path that passes through this transition region.

## EXPERIMENT

The Brewster-angle microscopy studies were carried out at UCLA and three separate sets of diffraction measurements were performed at the D41B beamline of the LURE-DCI storage ring in Orsay, France.

The compounds methyl octadecanoate and octadecanoic acid were obtained from Nu Chek Prep and are claimed to be 99+ % pure. Without further purification they were spread from chloroform (Fischer spectranalyzed) solutions onto pure water (Millipore Milli-Q at 18 MΩ) contained in custom-built Teflon Langmuir troughs. Solutions of the mixtures were prepared from solutions of the pure components. The first and third series of samples were prepared at UCLA while the second series of samples was prepared in a similar way at the CEA Saclay, Service de Physique de l'État Condensé.

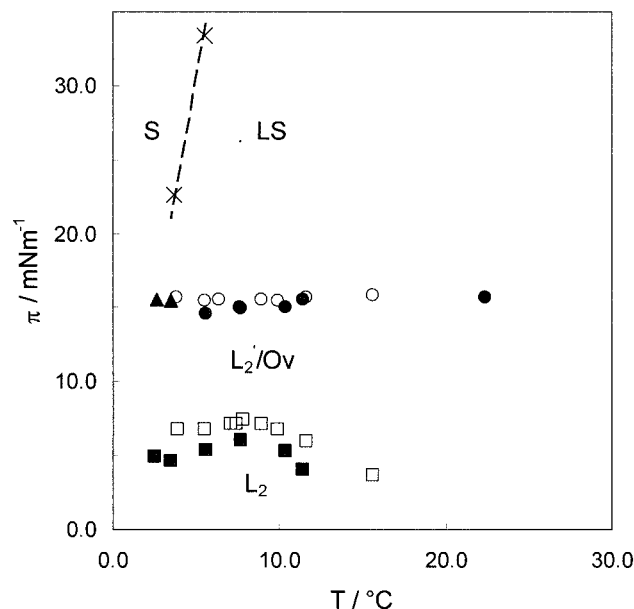


FIG. 2. Surface pressure-temperature phase diagram of a 49.7 mol % mixture of methyl octadecanoate in octadecanoic acid determined by BAM. Asterisks represent transitions between the *LS* and *S* phases; other symbols as in Fig. 1. Open and dark symbols indicate transitions observed in two different samples with nominally identical compositions.

Details of the BAM measurements at UCLA have been described previously.<sup>9</sup> The  $\text{Ar}^+$  laser was operated at 750 mW instead of 500 mW to increase signal contrast. The GID experiments utilized 0.1488 nm radiation, which was selected using a Ge (111) monochromator. A mirror was used to fix the grazing angle of incidence at 2.09 mrad, which was slightly below the critical angle for total external reflection. Slits limited the width and height of the incident beam and the diffracted radiation was selected using a Soler collimator (opening 0.5 mm/350 mm or 1.43 mrad, i.e.,  $0.06 \text{ nm}^{-1}$ ), and detected in a vertically mounted argon-filled position-sensitive detector. In order to reduce radiation damage to the monolayer, helium saturated with water vapor was flowed through the container housing the trough; a new monolayer was spread when any damage became apparent.

## RESULTS

Figure 2 shows the surface pressure-temperature phase diagram as determined by BAM for a 49.7 mol % mixture of the ester with the acid. At this concentration the  $L'_2$  and *Ov*

phases have just merged and there is a narrow continuous region of NNN phase just below the transition to the untilted phase. Variations in the phase boundaries between compressions and expansions did not exceed  $0.2 \text{ mNm}^{-1}$  and were generally  $0.1 \text{ mNm}^{-1}$ . Phase boundaries were marked by rearrangements of the mosaic-like texture of the monolayer as described previously.<sup>16</sup> The open and closed symbols in the figure represent two different samples that were nominally identical. The pressure of the NN-NNN boundary is very sensitive to the concentration in this range of compositions and the variation seen here is consistent with an uncertainty of a 0.2–0.3 mol %.

Although there is no transition evident on heating at constant pressure in the  $L'_2/\text{Ov}$  phase, different transitional rearrangement patterns were observed on the two sides of the maximum in the transition line between the NN and NNN phases. On the high-temperature or “*Ov* side” of the apex and at high compression rates, some domains developed thin parallel and perpendicular stripes that can be described as hash marks that quickly annealed away. This pattern occurred within a temperature range of a few degrees and always near the apex. On the low-temperature or “ $L'_2$  side” of the apex, the transition was detectable by sharp changes in the reflectivities of the domains.

The GID measurements were performed in the  $L'_2\text{--Ov}$  phase just below the tilted–untilted phase transition. Data were collected approximately every 0.5 K from 3 to 14 °C. The pressure was set by locating the discontinuity in the isotherm at the transition to the untilted phase and then expanding to a pressure  $1 \text{ mNm}^{-1}$  lower.

Representative data plots are shown in Fig. 3. At low temperatures there are two distinct  $q_{xy}$  peaks of different size. This is consistent with a distorted hexagonal unit cell, for which there should be two first-order peaks, one of which is doubly degenerate. Both peaks lie above  $q_z=0$ , consistent with a NNN phase. As the temperature is increased the peaks move together and their widths increase, with the position of the nondegenerate peak changing more rapidly than that of the degenerate peak. At high temperature there is one broad, slightly asymmetric peak.

## DISCUSSION

At temperatures below the maximum in the tilt–tilt transition line determined by BAM, the diffraction peaks are consistent with those of the  $L'_2$  phase of fatty acids<sup>1</sup> and the

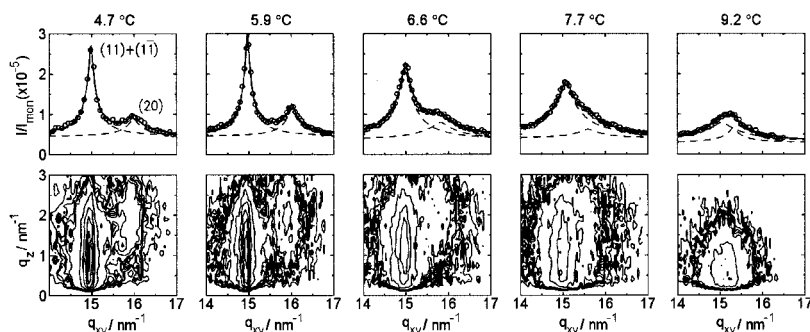


FIG. 3. Representative diffraction data for a 49.7 mol % mixture of methyl octadecanoate in octadecanoic acid as a function of the temperature. At each temperature the intensity as a function of  $q_{xy}$  is plotted above a  $q_{xy}\text{--}q_z$  contour diagram. The lines through the peaks are the result of a fit with two Lorentzians and a linear baseline.

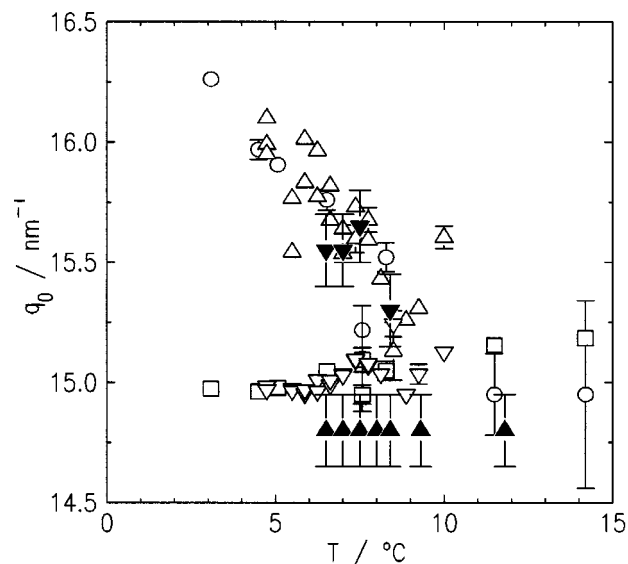


FIG. 4. Positions of peak maxima as a function of the temperature. The error bars represent the standard deviations determined from the fitting procedures. Data are shown for two synchrotron runs: Run 1,  $\square$  (11)+(1 $\bar{1}$ ),  $\circ$  (20); Run 2,  $\nabla$  (11)+(1 $\bar{1}$ ),  $\triangle$  (20). The filled triangles are the data of Foster *et al.* (Ref. 18) for methyl eicosanoate shifted downward by 13.5 K.

single broad peak at higher temperatures is similar to that observed in the  $Ov$  phase of nonadecanoic acid,<sup>17</sup> the only system for which a diffraction study in this phase has been reported. The positions of the in-plane peaks were determined by fitting the data with two Lorentzians and a linear baseline. Below about 7 °C, two peaks are clearly distinguishable in the data and the fitting allows a reasonable separation into two peaks up to 8 and 9 °C, but at higher temperatures the separation of the broad peak into two closely spaced components is problematic. The positions of the peaks are plotted against the temperature in Fig. 4. It is evident that the change between the two structures occurs most sharply at a temperature close to the maximum in the NNN–NN transition line so that in some sense there is a remnant of the phase boundary that existed between the two NNN phases. Within the limited precision of the data there is a continuous change and no evidence of a first-order transition.

The fitting at the highest temperatures shows the nondegenerate peak at a larger wave vector than the degenerate peak, which would imply a change in the direction of distortion of the unit cell. Such a change is known to occur at lower temperatures where there is a competition between distortion associated with herringbone order and that induced by tilt.<sup>1</sup> We would not expect herringbone order to be present beyond the transition region, so a crossover seems highly unlikely. The apparent switch is unlikely to be real and can be attributed to the large uncertainties in determining the peak positions.

The changes in the diffraction peaks with temperature are similar to those observed in measurements on pure methyl eicosanoate by Foster *et al.*<sup>18</sup> in which two distinct peaks were observed at temperatures below 22 °C and a single peak above 23 °C. Their measurements at a pressure about 4 mNm<sup>-1</sup> below the transition to the untilted phase,

have also been plotted in Fig. 4 with the temperature shifted downward by 13.5 K. Foster *et al.* assume that there are two distinct phases; the temperature intervals at which they made measurements are too large to decide the order of the transition. The similarity between the data for the pure ester and those for the mixture is further evidence that the mixtures can be employed to provide a continuous path between the phase diagrams of the acid and the ester.

In disagreement with Kaganer and Loginov<sup>11</sup> we do not find a first-order transition between the  $L'_2$  and  $Ov$  phases. Our data are more consistent with a continuous transition, which would lend support to the assumption that there is a second-order transition to one-dimensional backbone order and that the  $S$ – $LS$  transition is first order only because of fluctuations. However, nothing in our measurements gives direct evidence of the existence of herringbone order.

If the distinction between the  $S$ – $LS$  and  $L'_2$ – $Ov$  transitions is the result of fluctuations, however, one might expect the  $L'_2$ – $Ov$  transition to become first order in the neighborhood of the transition to an untilted phase, where the tilt angle is small. In contrast, if, as Sirota argues, the controlling factor is the coupling between tilt and distortion, a second-order transition should be observed at small tilt angles where the coupling term is small. At larger tilt angles, where the coupling would induce a weak but finite distortion in the  $Ov$  phase, the two NNN phases would be of the same symmetry and there could be either a first-order transition or no transition at all.

Our data are neither sufficiently precise nor extensive to resolve these questions. Additional diffraction studies of the tilted phases in both pure substances and mixtures might be helpful if they can be carried out with sufficient precision. An examination of the effects of the chain length on these transitions would be interesting if, as Sirota has suggested, the essential symmetry difference between the  $L'_2$  and  $Ov$  phases is destroyed by chain-end disorder. This effect would become less important as the chain length increases.

## ACKNOWLEDGMENTS

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