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Phase transitions in Langmuir films of fatty acids: L_2-L_2'-L_2'' triple point and order of the transitions

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Using Brewster angle microscopy we have studied the low-temperature region of the phase diagram of Langmuir monolayers of long-chain fatty acids. We have shown that the transitions between the three tilted phases, L_2, L_2', and L_2'' are first order, and have located the triple point precisely. We have observed a radical change of the tilt-azimuth texture at the L_2-L_2'' phase transition, even though the tilt direction with respect to the lattice is the same in the two phases. The transition between the tilted phase L_2'' and the crystalline untilted phase CS is also studied. Its character possibly changes from second order below the L_2-L_2'-L_2'' triple point to first order above. [S1063-651X(96)08808-3]

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The phase diagram of Langmuir films of fatty acids appears to become more and more complicated as our knowledge of it increases [1,2]. The large number of different phases, first revealed by surface pressure versus area measurements [3–6], was later confirmed by x-ray scattering experiments [7–11]. This technique has provided important information about the microscopic structure of the phases, and has shown that even small changes in isotherms can correspond to real phase transitions. In addition to the two-dimensional gaseous, liquid (L_1), and crystalline (CS) phases, a variety of mesophases (hexatic phases) has been found. From x-ray scattering experiments, it was concluded that the structure of these mesophases is as follows: their lattice is locally hexagonal or distorted hexagonal (centered rectangular); the orientational order of the bonds between the molecules is long range but the translational order of the molecules is only short range. An analogy between monolayers of amphiphilic molecules and the different phases found in thin films of smectic liquid crystals has thus been established [1]. Optical techniques such as polarized fluorescence microscopy [12] and Brewster angle microscopy [13], which allow for a direct observation of the texture of the different phases on a macroscopic scale ($>1\,\mu$m), have recently provided important information about the different phases in Langmuir monolayers of long-chain fatty acids. In this way, a new tilted phase (''Overbeck'') has been discovered [14], and the changes in the film texture at the transitions between tilted phases or between tilted and untilted phases have been visualized [2,15]. Also, a very weak optical anisotropy due to the anisotropic shape of the unit cell has been detected in two untilted phases (S and CS) [16,2], and information about the order of the phase transitions have been obtained [2].

In this paper, we focus on the low-temperature region (between 5 °C and 12 °C of the phase diagram of behenic (C20) acid. This part of the phase diagram has received relatively little attention and several points still need to be clarified. Brewster angle microscopy is used to locate the different phase boundaries precisely, to allow for observations of the changes in texture occurring at the phase transitions and to obtain information on the order of the transitions. From isotherm measurements, it was concluded that (at least) four condensed phases exist in this temperature range: three tilted phases, L_2, L_2', and L_2'', and an untilted crystalline phase, CS. The CS phase displays all the characteristics of a two-dimensional (2D) crystal: a very low compressibility and long-range positional order. In this phase, the chains of the molecules are vertical and the lattice is centered rectangular with herringbone order. In the L_2 and L_2' phases, the molecules are tilted away from the surface normal, towards a nearest neighbor in L_2, and a next-nearest neighbor in L_2'; their unit cell is centered rectangular. The L_2' phase is probably a rotator phase [17], i.e., the chains of the molecules are free to rotate around their long axis, because the cross-sectional area normal to the molecular axis is sufficiently large. Recent x-ray scattering experiments [17,18] seem to indicate that the L_2 phase is, in fact, subdivided into two distinct phases by a vertical line in the pressure versus temperature phase diagram, L_{2d} and L_{2h}: the high-temperature phase L_{2d} would be a rotator phase, whereas the low-temperature L_{2h} is not, and would be characterized by a herringbonelike positional order. Such a transition was first predicted using Landau theory [19,20]. The L_2'' phase has been observed in isotherm measurements, and more recently an x-ray diffraction study of this phase has been performed in heneicosanoic acid [8] (the phase was labeled B). This phase was found to be a 2D crystal, only differing from the CS phase in that the molecules are tilted towards a nearest neighbor. Considering these x-ray diffraction results, one may wonder how the L_2-L_2'' transition manifests itself on a macroscopic scale, since the two phases seem to differ from each other just in the positional order of the molecules.

Microscopy at the Brewster angle [13], using the properties of reflectivity of an interface illuminated at the Brewster angle with light polarized in the plane of incidence, allows for a direct observation of monolayers or multilayers at the

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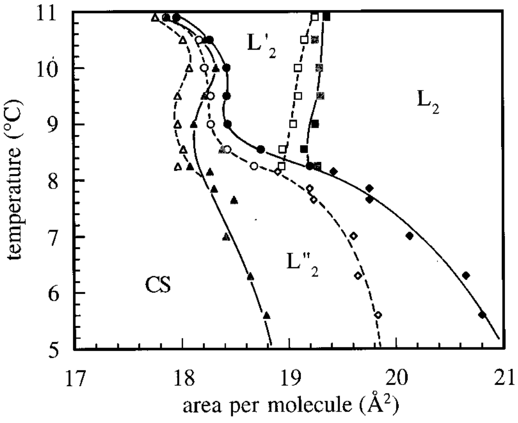

FIG. 1. Temperature versus area per molecule phase diagram for a monolayer of behenic acid on water at *p*H 2. The boundaries between phases were obtained by Brewster angle microscopy observations of changes in the monolayer texture. Experiments were made at constant temperature and varying area per molecule. The open symbols mark measurements on compression, the filled ones measurements on expansion (whenever a difference was noticed between compression and expansion). The temperature is controlled to within ±0.2 °C.

air-water interface. First-order phase transitions, i.e., coexistence between two phases, have been studied in this way. For instance, coexistence between domains of the L_2 phase and either the gaseous phase [21] or the liquid expanded phase L_1 [22] has been visualized. In order to obtain information on the optical anisotropy of the films, an analyzer can be placed in the path of the reflected light. This allows us to visualize anisotropies that are due either to the tilt of the molecules [21,22,2] or to the anisotropy of the unit cell in untilted phases [16,2]. In the tilted phases, all the molecules have the same tilt angle with respect to the surface normal, and the polarization of the reflected light depends on the tilt-azimuthal angle: each shade of gray on a Brewster angle microscope image corresponds to a different tilt-azimuthal orientation of the molecules. For the untilted phases, each shade of gray on the images corresponds to a different orientation of the unit cell.

Behenic acid, $CH_3(CH_2)_{20}COOH$ (Sigma 99% grade), was used without further purification and spread onto a subphase of ultrapure water (MilliRO-MilliQ system) at *p*H 2, in a Teflon trough. Chloroform (Merck, Pro Analysis grade) was used as spreading solvent. The experiments were, in general, carried out at a fixed temperature (between 5 °C and 12 °C) and the phase transitions were observed varying the surface pressure, i.e., the area per molecule in the monolayer, with a Teflon barrier driven by a motor.

Figure 1 shows the phase boundaries, in the temperature versus area per molecule plane, obtained from Brewster angle microscopy observations in the low-temperature region. As expected, three different tilted phases are observed, L_2, L_2', and L_2''; the triple point between these phases is found to be located at about 8.2 °C. Upon increasing the surface pressure at constant temperature, the phase sequence observed is L_2-L_2'' for temperatures below 8.2 °C, and L_2-L_2'-L_2'' for temperatures between 8.2 °C and 12.5 °C. The L_2-L_2'-L_2'' sequence is thus shown to exist over a temperature range much wider than the range (from about 10 °C to 12 °C for behenic acid) found in the phase diagram of Bibo *et al.*, which is generally believed to be universal [1,2].

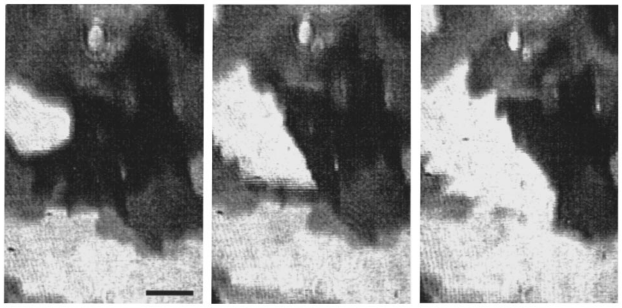

FIG. 2. Brewster angle microscope images of the L_2-L_2' transition in behenic acid at about 9.5 °C. The bar represents 50 μm. A propagation of the transition front through the film can be observed. The delay between two successive images is 0.4 s.

When observed with analyzer, the phases appear to be divided into uniform regions of different tilt-azimuthal orientations by straight or curved defect lines, as described in Ref. [2]. For the L_2 and L_2' phases, the size of such regions generally ranges from 100 to 5000 μm^2 whereas in the L_2'' phase, the regions are smaller and more elongated. The three transitions, L_2-L_2', L_2'-L_2'', and L_2-L_2'', manifest themselves as a sudden and drastic change in the arrangement of the different tilt-azimuthal regions: both the positions of the defect lines and the orientation of the molecules change. The change in the structure and the anisotropy of the different regions is fast (about 1 s). However, the regions can sometimes be observed growing, and a propagation of the transition front can be observed on subsequent images, indicating that these transitions are first order (see Fig. 2). This is also confirmed by the small reproducible hysteresis observed for the transitions, as shown in Fig. 1, and by a hydrodynamic movement of the film during the transition, indicating an abrupt change in the area per molecule. A very striking observation is that, in spite of the radical change in the morphology of the film, the texture of the phases is almost reversible through several compression-expansion cycles [2]. However, this is less evident for a transition towards or from the L_2'' phase than for the L_2-L_2' phase transition: at each compression towards the L_2'' phase, some small changes in the arrangement of the uniformly tilted regions can often be observed from the image, especially at the L_2-L_2'' transition (see Fig. 3). For the L_2-L_2' and L_2'-L_2'' transitions, as the chains of the molecules rotate through an angle of $+30°$ or $-30°$ with respect to the molecular lattice, this reversibility means that most of the molecules rotate in the opposite direction through the same angle when the phase boundary is crossed in the opposite sense: the molecules return towards the same neighbor.

The observation of a radical change in the texture may seem a bit surprising at the L_2-L_2'' transition, since the molecules are supposed to be tilted towards a nearest neighbor both in the L_2 and in the L_2'' phases; thus we do not expect a rotation of the chains at this transition. However, since the L_2-L_2'' transition is first order, the lattice direction is not necessarily the same in the two phases. Nevertheless, the lattice directions in the two phases seem to be related somehow to

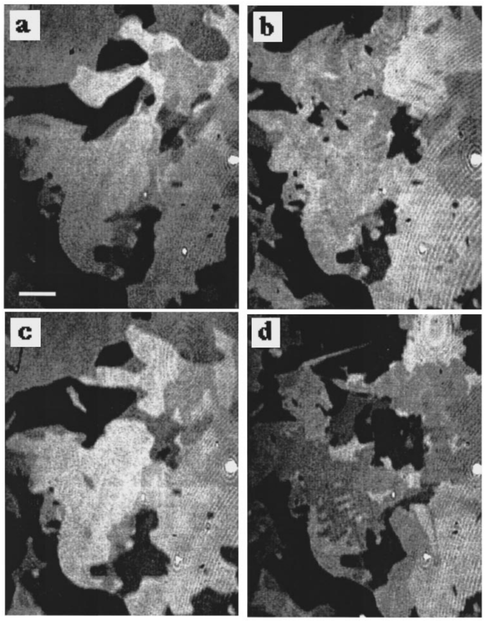

FIG. 3. Brewster angle microscope images of a L_2-L_2'' compression-expansion cycle in behenic acid at about 9.5 °C. The bar represents 50 μm: (a) L_2 phase; (b) after compression into the L_2'' phase; (c) after reexpansion into the L_2 phase, most of the texture is recovered, but some domains have changed in size; (d) after recompression in the L_2'' phase the mosaic of (b) is partly but not entirely recovered.

each other since the same direction of the lattice is retrieved for the largest part of the film after a compression-expansion cycle. The reversibility is probably related to the presence of many defect lines, with preferred directions with respect either to the lattice, or to the tilt-azimuth direction [2,15]. The texture changes at the transition, but the same defect lines and the same molecular orientations are retrieved after each cycle; this observation shows that the preferred orientations of the defect lines with respect to the molecular orientation are different in the two phases. The difference between the two phases is probably related to different values of the elastic constant, which determine the energetically favorable orientations of the defect lines [24].

Over the whole temperature range studied (5 °C–12.5 °C), the L_2''-CS transition could be observed upon increasing the surface pressure. This transition was previously studied in Ref. [2] for temperatures between 8.5 °C and 12.5 °C. The CS phase is slightly anisotropic, because of the rectangular shape of the unit cell. Several shades of gray can be distinguished on the images (see Fig. 4), each corresponding to a different orientation of the rectangular lattice in the plane. At the L_2''-CS phase transition, many of the domains retain the same shape, although some neighboring L_2'' regions form a single domain in the CS phase: some defect lines disappear; the other ones remain at the same position. The texture is completely reversible upon cycling (see Fig. 4): the regions display exactly the same arrangement and anisotropy after each compression-decompression cycle. This perfect reversibility of the transition can be explained in terms of the presence of a large number of defect lines with energetically favorable directions: as, according to x-ray diffraction experiments [8,23], the L_2''-CS phase transition is of second (or weakly first) order, it can be assumed that the orientation of the lattice does not change at the transition, and that the defect lines we do not observe any longer in CS could still exist, but cannot be observed because the contrast is too weak. Then, if in the L_2'' phase the energy of the defect lines is minimal for a given angle between the defect lines and the molecular orientation, the molecules tilt back to this azimuthal direction when entering the L_2'' phase from CS, and the same texture is retrieved. When compressing again to the CS phase, the lattice orientation does not change, so that the texture of the film is the same as in the first compression. This reasoning supposes that the anchorage conditions of the CS lattice on the defect lines are negligible, or are the same as in the L_2'' phase, or that the CS phase is too rigid to be able to relax constraints.

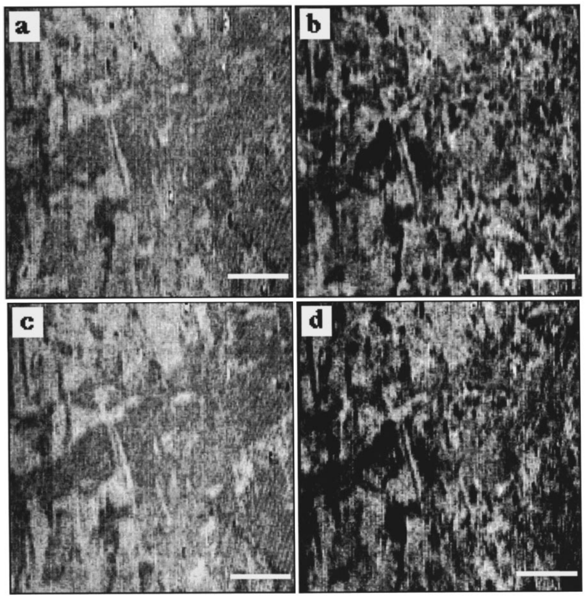

FIG. 4. Brewster angle microscope images of the L_2''-CS transition in behenic acid at about 7 °C. The bars represent 50 μm. (a) CS phase, the different gray levels correspond to different lattice orientations; (b) after expansion into the L_2'' phase, the different gray levels correspond to different tilt-azimuthal directions, the contrast is better than in (a), and many new defect lines have appeared; (c) after recompression in the CS phase, the texture of image (a) is recovered; (d) after reexpansion into the L_2'' phase, the texture of image (b) is recovered.

The study of the L_2''-CS phase transition over a wider range of temperatures than in Ref. [2] has revealed a striking observation. Above 8.2 °C, the tilt angle passes from a finite value to zero at the transition; moreover, the transition exhibits a hysteresis (see Fig. 1) and is accompanied by an abrupt flow in the monolayer, indicating an abrupt variation of the area per molecule. All these observations are indicative of a first-order phase transition. On the contrary, for temperatures below 8.2 °C, the tilt angle of the molecules appears to decrease continuously when compressing the L_2'' phase, to reach zero in the CS phase. Furthermore, no hysteresis, and no flow in the film at the phase transition can be observed, indicating that probably the area per molecule has no discontinuity. All these observations are indicative of a second-order (continuous) phase transition below 8.2 °C.

Our observations thus seem to indicate a change in the order of the L_2''-CS transition from second order below 8.2 °C to first order at higher temperatures. We considered the possibility that this could be related to a change in the nature of the L_2'' phase: it could be separated in two distinct phases, a crystalline phase below 8.2 °C and a mesophase above 8.2 °C. We looked for a transition between such phases by heating up the monolayer at fixed area per molecule, within the L_2'' phase, but we did not find any evidence for such a transition: neither a change in the tilt-azimuthal texture nor a flow of the film were observed. Moreover, very recently x-ray experiments were carried out for a wide region of the L_2'' phase of behenic acid [23], from which it was concluded that this phase is crystalline.

The L_2''-CS transition, which is thus a solid-solid transition, can be either of first or of second order. It is in general believed to be of second order (see, e.g., Ref. [18]). However, little experimental attention has been paid to this transition. On some of the published isotherms one can observe what could be a short CS-L_2'' plateau. For instance, in Ref. [7], Fig. 1, the 7.6 °C isotherm for behenic acid, or in Ref. [8], Fig. 1, the 3.5 °C isotherm for heneicosanoic acid (i.e., above the triple-point temperature, which is at about 3 °C). Moreover, in recent x-ray experiments [23] a very small change in the area per molecule was observed at the L_2''-CS transition. This change is very small, and this is probably why it is hardly visible in the isotherms.

In conclusion, we have studied in detail the low-temperature part of the phase diagram of behenic acid on water. We have observed the transition sequence L_2-L_2'-L_2'' over a wide range of temperatures (from 8.2 °C to 12.5 °C), a much larger range than would be expected from the commonly admitted phase diagram. We have located precisely the L_2-L_2'-L_2'' triple point (8.2 °C, 18 Å^2/molecule). We have also observed a probable change in the order of the L_2''-CS transition, from second order at low temperatures (below the triple point) to first order at higher temperatures.

[1] A. M. Bibo, C. M. Knobler, and I. R. Peterson, J. Phys. Chem. **95**, 5591 (1991).

[2] S. Rivière, S. Hénon, J. Meunier, D. K. Schwartz, M.-W. Tsao, and C. M. Knobler, J. Chem. Phys. **101**, 10 045 (1994).

[3] S. Ställberg-Stenhagen and E. Stenhagen, Nature **156**, 239 (1945).

[4] E. Stenhagen, in *Determination of Organic Structures by Physical Methods*, edited by E. A. Braude and F. C. Nachod (Academic, New York, 1955), Chap. 8.

[5] M. Lundquist, Chem. Scr. **1**, 5 (1971).

[6] M. Lundquist, Chem. Scr. **1**, 197 (1971).

[7] R. M. Kenn, C. Böhm, A. M. Bibo, I. R. Peterson, H. Möhwald, J. Als-Nielsen, and K. Kjaer, J. Phys. Chem. **95**, 2092 (1991).

[8] B. Lin, M. C. Shih, T. M. Bohanon, G. E. Ice, and P. Dutta, Phys. Rev. Lett. **65**, 191 (1990).

[9] M. K. Durbin, A. Malik, R. Ghaskadvi, M. C. Shih, P. Zschack, and P. Dutta, J. Phys. Chem. **98**, 1753 (1994).

[10] M. L. Schlossman, D. K. Schwartz, P. S. Pershan, E. H. Kawamoto, G. J. Kellogg, and S. Lee, Phys. Rev. Lett. **66**, 1599 (1991).

[11] M. C. Shih, T. M. Bohanon, J. M. Mikrut, P. Zschack, and P. Dutta, Phys. Rev. A **45**, 5734 (1992).

[12] V. T. Moy, D. J. Keller, H. E. Gaub, and H. M. McConnel, J. Phys. Chem. **90**, 3198 (1986).

[13] S. Hénon and J. Meunier, Rev. Sci. Instrum. **62**, 936 (1991); D. Hönig and D. Möbius, J. Phys. Chem. **95**, 4590 (1991).

[14] G. A. Overbeck and D. Möbius, J. Phys. Chem. **97**, 7999 (1993).

[15] B. Fischer, M.-W. Tsao, T. Fischer, D. K. Schwartz, and C. M. Knobler, J. Phys. Chem. **98**, 7430 (1994).

[16] G. A. Overbeck, D. Hönig, L. Wolthaus, M. Gnad, and D. Möbius, Thin Solid Films **242**, 26 (1994).

[17] I. R. Peterson, R. M. Kenn, A. Goudot, P. Fontaine, F. Rondelez, W. G. Bouwman, and K. Kjaer, Phys. Rev. E **53**, 667 (1996).

[18] V. M. Kaganer, I. R. Peterson, R. M. Kenn, M. C. Shih, M. Durbin, and P. Dutta, J. Chem. Phys. **102**, 9412 (1995).

[19] V. M. Kaganer and V. L. Indenbom, J. Phys. II (France) **3**, 813 (1993).

[20] V. M. Kaganer and E. B. Loginov, Phys. Rev. E **51**, 2237 (1995).

[21] S. Hénon and J. Meunier, J. Chem. Phys. **98**, 9148 (1993).

[22] S. Rivière, S. Hénon, and J. Meunier, Phys. Rev. E **49**, 1375 (1994).

[23] G. M. Bommarito, W. J. Foster, P. S. Pershan, and M. L. Schlossman, J. Chem. Phys. (to be published).

[24] T. M. Fischer, R. F. Bruinsma, and C. M. Knobler, Phys. Rev. E **50**, 413 (1994).