

# Discontinuities in the Tilt Angle of Octadecanol Langmuir Monolayers As Observed with Brewster Angle Autocorrelation Spectroscopy

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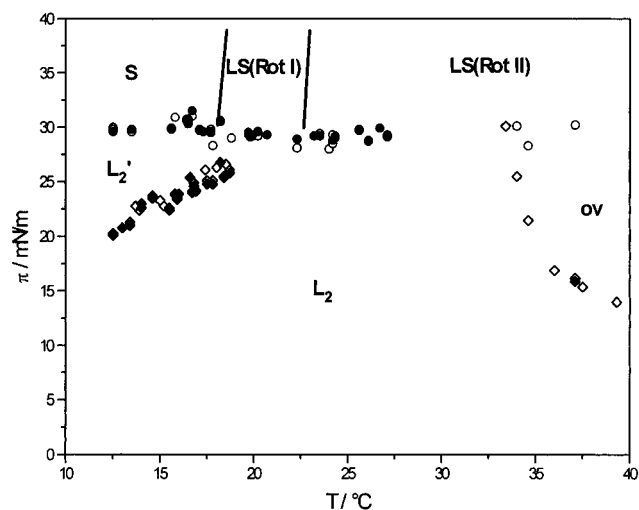
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We have studied the tilt angle of Langmuir monolayers of octadecanol ( $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$ ) using Brewster angle autocorrelation spectroscopy. Measurements were carried out at the triple point of the next nearest neighbor tilted  $\text{L}_2'$ , the untilted distorted hexagonal LS(Rot I), and the crystalline herringbone S phase and at the triple point of the next nearest neighbor tilted  $\text{L}_2'$ , the untilted distorted hexagonal LS(Rot I), and the hexagonal undistorted LS(Rot II) phase. We show that the transition from the tilted phase to the untilted phases as a function of temperature changes from second order ( $\text{L}_2'/\text{S}$ ) to first order ( $\text{L}_2'/\text{LS(Rot I)}$ ) to second order ( $\text{L}_2'/\text{LS(Rot II)}$ ) and that the S/LS(Rot I) and LS(Rot I)/LS(Rot II) phase transition lines at high pressure continue into the tilted  $\text{L}_2'$  phase. The  $\text{L}_2'$  phase actually consists of three different phases of different tilt angle with some similarity to the phase behavior of fatty acids. Strong superheating and supercooling effects prevent a direct observation of both phase transitions.

## Introduction

The existence of a general phase behavior of Langmuir monolayers of simple amphiphiles such as fatty acids, their esters, and alcohols has been shown employing classical surface pressure isotherm experiments,<sup>1–3</sup> neutron and X-ray diffraction,<sup>4–6</sup> X-ray reflection,<sup>7,8</sup> and optical methods, such as polarized fluorescence<sup>9–11</sup> and Brewster angle microscopy.<sup>12–15</sup> However, differences in the structure of monolayers of fatty acids and alcohols occur, affecting the distortion of the hexagonal packing and the tilt azimuth order<sup>16,17</sup> of the tilted hexatic phases.

In heneicosanoic acid (see Figure 1), for example, there is a transition from an untilted hexagonal distorted phase LS(Rot I) (low temperature) to an untilted hexagonal undistorted phase LS(Rot II) (high temperature), which changes to a transition from a distorted phase with the tilt azimuth in the direction of the next nearest neighbors  $\text{L}_2'$  (low temperature) to another distorted phase with the tilt azimuth pointing toward the nearest neighbors  $\text{L}_2$  (high temperature) when expanding into the tilted phases. The continuity of the phase transition line suggests that the distortion and the tilt azimuth order are coupled. However in long-chain alcohols the LS(Rot I) to LS(Rot II) transition occurs as well, but the continuity of the phase transition line into the tilted phase (see Figure 2) could not be observed either by X-ray diffraction<sup>6</sup> or by Brewster angle microscopy.<sup>15</sup> There is only a next nearest neighbor distorted hexagonal phase  $\text{L}_2'$ , and no discontinuity in the tilt azimuth angle nor in the amount of distortion within the  $\text{L}_2'$  phase has been reported. Fischer et al.<sup>18</sup> have carried out optical measurements on acid alcohol mixtures, revealing that the  $\text{L}_2/\text{L}_2'$  transition and the  $\text{L}_2/\text{OV}$  (OV = Overbeck) transition of the pure acid both join at acid/alcohol concentrations of 22:78 and are disconnected from the tilted/untilted transition and the S/LS(Rot II) and LS(Rot I)/LS(Rot II) transitions at higher alcohol concentrations. Teer et al.<sup>19</sup> have associated the  $\text{L}_2/\text{L}_2'$  transition with the interaction of the hydrated headgroups. Shih et al.<sup>20</sup> gave a similar explanation for the  $\text{L}_2/\text{L}_2'$  transition and associated the LS(Rot I)/LS(Rot II) transition with the tail–tail interaction of the molecules. The arguments are convincing because the phase behavior of the alcohols and acids is the same in the untilted phase, while the

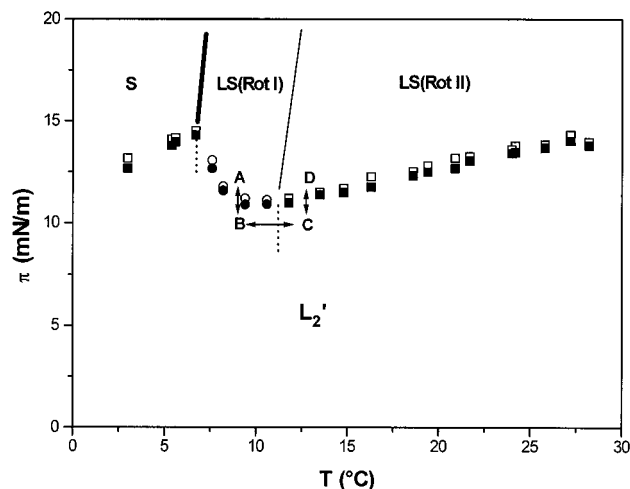


**Figure 1.** Phase diagram of heneicosanoic acid (from ref 18) showing the three untilted phases (S, LS(Rot I) and LS(Rot II)) as well as the  $\text{L}_2/\text{L}_2'$  transition which merges with the LS(Rot I)/LS(Rot II) transition.

different headgroups lead to a different phase behavior in the tilted phases.

Overbeck et al.<sup>15</sup> have carried out optical investigations of eicosanol at the tilted/untilted transition using Brewster angle microscopy. They reported differences in the contrast and texture of the monolayer when crossing the tilted/untilted phase transition line at different temperatures. However, no description of the contrast in the vicinity of both triple points has been given, and no extension of the S/LS(Rot I) and LS(Rot I)/LS(Rot II) into the tilted  $\text{L}_2'$  phase has been found. Using Brewster angle autocorrelation spectroscopy Lautz et al.<sup>21</sup> have shown in octadecanol that in the  $\text{L}_2'$  phase of octadecanol close to the triple point of the next nearest neighbor tilted  $\text{L}_2'$  phase, the untilted distorted hexagonal LS(Rot I) phase, and the hexagonal LS(Rot II) phase a discontinuity in the tilt angle occurs and that indeed the LS(Rot I)/LS(Rot II) phase transition line extends into the tilted phase. In this paper we extend the studies of the tilt angle of octadecanol to the triple point of the next nearest neighbor tilted  $\text{L}_2'$ , the untilted distorted hexagonal LS(Rot I), and the crystalline herringbone S phase. We show that there is a discontinuity of the tilt angle within the  $\text{L}_2'$  phase

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**Figure 2.** Phase diagram of octadecanol (from ref 21). The same three untilted phases (S, LS(Rot I), and LS(Rot II)) as in the acids occur. The dashed lines within the tilted  $L_2'$  phase indicate first-order phase transitions as observed with Brewster angle autocorrelation spectroscopy and discussed within this paper.

in the vicinity of both triple points and that the transitions between the phases of different tilt angle exhibit strong hysteresis effects.

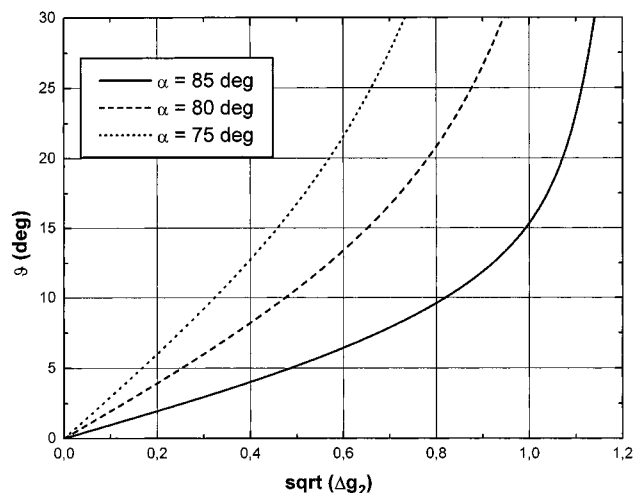
### Experimental Section

Brewster angle autocorrelation spectroscopy is a method for determination of the tilt angle of Langmuir monolayers. The experimental setup of the Brewster angle autocorrelation spectroscope and the film balance was described previously.<sup>21</sup> For further increase of the signal intensity of the reflected light hitting the photon counter an Argon ion laser (ILA 120, LES GmbH Jena) with a maximum power of 1.5 W at 514 nm was used. Autocorrelation functions with a sufficient signal-to-noise ratio could be obtained in sample times shorter than 3 min.

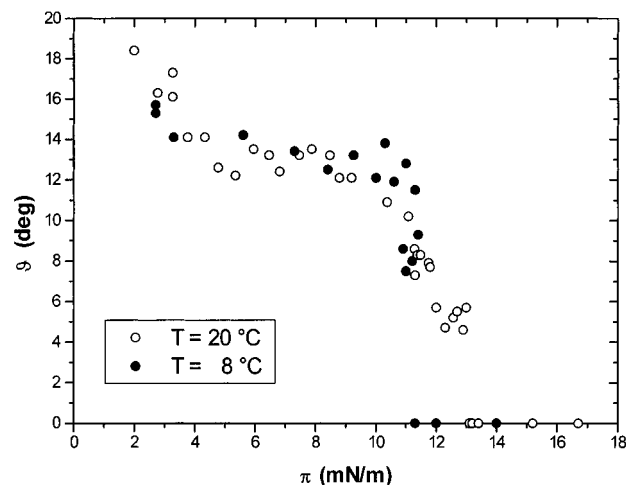
A monolayer with domains smaller than the autocorrelation spot (about 20  $\mu\text{m}$ ) and dust on the surface alter the values of the tilt angle. All measurements were done with simultaneous observation of the monolayer on the TV screen during the whole measurement, and only correlation functions from domains bigger than 100  $\mu\text{m}$  in diameter and without dust were taken for further evaluations.

The octadecanol used was obtained from Sigma and Aldrich and claimed to be 99+% pure. Without further purification it was spread from chloroform (p.a. Merck) onto pure water (Millipore Milli-Q at 18  $\text{M}\Omega\text{ cm}$ ) contained in a home-built Teflon trough.

The measurement of the tilt angle with Brewster angle autocorrelation spectroscopy is based on the correlation of intensity fluctuations because of the different reflectivities of the single domains in the monolayer when it flows under the correlation spot. This leads to a plateau in the autocorrelation function, the height of which ( $\Delta g_2$ ) is proportional to the contrast of the domains. The contrast of the different domains depends on the tilt angle of the aliphatic chain in the Langmuir monolayer. The analytical evaluation was presented elsewhere.<sup>21</sup> It could be shown that the decay height  $\Delta g_2$  depends only on the tilt angle, the Brewster angle, the analyzer angle  $\alpha$ , and the refractive index along and perpendicular to the aliphatic chain. All parameters entering the relation can be determined from the experiment or are known from the literature.<sup>22</sup> The plateau height does not depend on any fit parameters nor on the monolayer thickness. Figure 3 shows the relation between  $\sqrt{\Delta g_2}$  and tilt angle  $\vartheta$  for octadecanol for different analyzer



**Figure 3.** Relation between the square root of the plateau height of the autocorrelation function, measured with Brewster angle autocorrelation spectroscopy and the tilt angle for different analyzer angles. The values of the refractive index of the monolayer were taken from the literature,<sup>22</sup> e.g.  $n_{||} = 1.54$  and  $n_{\perp} = 1.48$ , the Brewster angle is 53.1°. All experiments were performed with analyzer angles of either 80° or 85°.



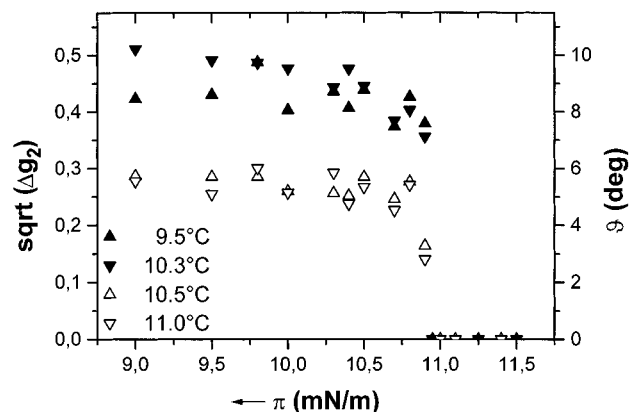
**Figure 4.** Tilt angles in octadecanol for  $T = 8\text{ }^{\circ}\text{C}$  (solid circles) and  $T = 20\text{ }^{\circ}\text{C}$  (open circles), obtained on isothermal compression. The phase transition from the tilted phase to the untilted phase is first order at  $T = 8\text{ }^{\circ}\text{C}$  and second order at  $T = 20\text{ }^{\circ}\text{C}$ .

angles. As can be deduced from these curves, it is possible to measure the tilt angle once the analyzer angle is measured with a precision of at least 1°.

### Results

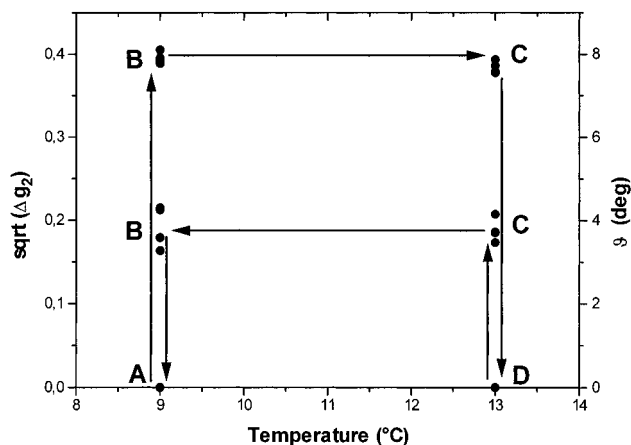
The phase diagram of octadecanol is shown in Figure 2. It has been determined for the first time by Harkins et al.<sup>1</sup> and Shih et al.<sup>6</sup> using X-ray diffraction. The phase transition from the tilted  $L_2'$  phase to the untilted S and LS(Rot II) phase is of second order, while the transition from the  $L_2'$  to the LS(Rot I) phase is of first order.

The behavior of the tilt angle on increasing surface pressure is shown in Figure 4 at  $T = 8.0\text{ }^{\circ}\text{C}$  ( $L_2'/\text{LS(Rot I)}$  transition) and  $T = 20.0\text{ }^{\circ}\text{C}$  ( $L_2'/\text{LS(Rot II)}$  transition). The difference in order of the tilt/untilt transition can be clearly seen. At 8.0  $^{\circ}\text{C}$  there is an abrupt change in tilt angle from about 8° at 11.1 mN/m to zero tilt at 11.2 mN/m, while the decrease within the tilted phase from zero pressure to 11.1 mN/m is only about 40% (from 15° to 8°). At  $T = 20.0\text{ }^{\circ}\text{C}$  the tilt angle changes continuously from 18° at zero pressure to 4° at 12.4 mN/m and



**Figure 5.** Tilt angles of octadecanol in the vicinity of the triple point  $L_2'/LS(Rot\ I)/LS(Rot\ II)$  as a function of surface pressure for different temperatures  $T = 9.5, 10.3, 10.5$ , and  $11.0\ ^\circ\text{C}$ . As one can see, there is a distinct discontinuity in the tilt angle between  $10.3$  and  $10.5\ ^\circ\text{C}$ .

zero at  $12.5\ \text{mN/m}$ . As one can see from this data, the tilt angle slightly below the tilt/untilt pressure has quite different values at  $T = 8.0\ ^\circ\text{C}$  and  $T = 20.0\ ^\circ\text{C}$ . The change from low tilt at high temperature to high tilt at low temperature is shown in Figure 5, when approaching and crossing the triple point ( $L_2'/LS(Rot\ I)/LS(Rot\ II)$ ), where the order of the tilt/untilt transition changes. In contrast to the measurements in Figure 4 the values of  $\vartheta$  are obtained by leaving the  $LS(Rot\ I)$  and  $LS(Rot\ II)$  phase, respectively, and entering the  $L_2'$  phase by isothermal expansion. In the case of the second-order phase transition between the  $LS(Rot\ II)$  and the  $L_2'$  phase, we waited approximately 10 min before starting the autocorrelation measurements. This ensured that the domains could heal so that they were larger than the spot on the monolayer detected by the photon counter. The data in Figure 5 reveal that the tilt angle obtained below the untitled/tilted transition stays at approximately  $7.5^\circ$  even at  $10.3\ ^\circ\text{C}$ , slightly below the temperature of the triple point, and stays low at  $10.5\ ^\circ\text{C}$ , slightly above the triple-point temperature. There is a jump in tilt angle from  $8^\circ$  to  $3^\circ$  within a temperature interval of  $0.2\ ^\circ\text{C}$  in the  $L_2'$  phase. This indicates that there is a first-order transition from one tilted  $L_2'$  phase to a  $L_2'$  phase of different tilt angle. As in acids the transition line  $LS(Rot\ I)/LS(Rot\ II)$  continues into the tilted phase now separating two tilted phases with different tilt angle. On isobaric heating or cooling across  $10.4\ ^\circ\text{C}$  one would expect to see a change in contrast of the Brewster angle microscopy images. We measured the tilt angle near the triple point, following the path shown in the phase diagram in Figure 2. We started in the untitled  $LS(Rot\ I)$  phase at point A ( $T = 9\ ^\circ\text{C}$ ,  $\pi = 13\ \text{mN/m}$ ) following along an isotherm to point B in the high tilted  $L_2'$  phase, heating to point C along an isobar, and then isothermally compressing to the untitled  $LS(Rot\ II)$  phase. The same experiment was performed in the opposite direction. The result of this experiment is shown in Figure 6. The tilt angle obtained at point B when expanding from point A is consistent with those presented in Figure 5. If we now heat up to point C, the tilt angle does not change and stays at approximately  $7.5^\circ$ . On compressing into the  $LS(Rot\ II)$  phase, the tilt angle vanishes at point D. Expanding back to C now gives a tilt angle of  $3^\circ$ , in accordance with the values obtained in Figure 5. Cooling to B does not change this tilt angle. On compression to A, the tilt again vanishes. As one can see from Figure 6, no first-order phase transition happened, neither on isobaric heating nor on isobaric cooling. The original tilted phase obtained on isothermal expansion is maintained instead. The domain structure and the tilt angle at any point of the  $L_2'$  phase near the triple point depend on the path in the phase



**Figure 6.** Hysteresis effect observed in the tilt angle, when compressing (expanding) and cooling (heating) along the path ABCD in Figure 2 and reverse.

diagram taken to reach these points (memory effect). This memory effect is no longer visible far away from the triple point, i.e. at lower surface pressure, e.g.  $5\ \text{mN/m}$ .

The clear differences in tilt angle behavior in the  $L_2'$  phase in a small temperature region between  $10.3$  and  $10.5\ ^\circ\text{C}$  indicate a first-order phase transition. However, this transition can be induced neither on isobaric heating nor on cooling due to strong supercooling and superheating effects.

These experiments reveal that, like in the fatty acid monolayers, the phase transition boundary line between the distorted hexagonal phase  $LS(Rot\ I)$  and the undistorted hexagonal phase ( $Rot\ II$ ) extends into the tilted phase  $L_2'$ . However, in the acids this phase boundary is additionally associated with a change in tilt azimuth order, e.g. a transition from  $L_2$  to  $L_2'$ .

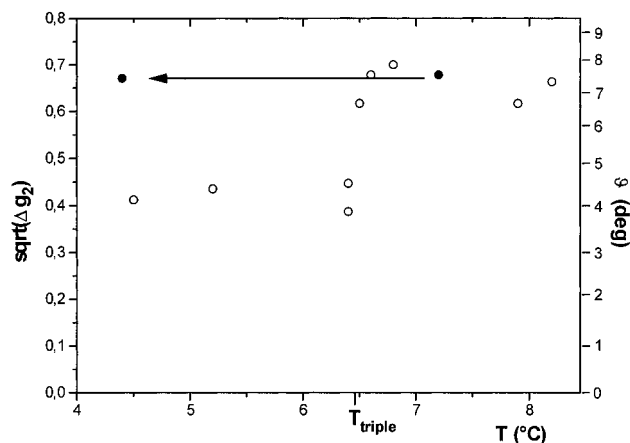
There is a second triple point in octadecanol separating the next nearest neighbor tilted  $L_2'$ , the untitled distorted hexagonal  $LS(Rot\ I)$ , and the crystalline herringbone S phase. One might ask the question whether similar behavior is observed in the  $L_2'$  phase near this triple point. As at the triple point discussed before, the phase transition boundary line between the two untitled phases separates two phases of different symmetry, e.g. long-range periodic positional order in the S phase from short-range positional order in the  $LS(Rot\ I)$  phase. Does this phase boundary stop at the untitled/tilt transition or extend to the tilted phase?

We studied the tilt angle in the  $L_2'$  phase also in the vicinity of this triple point. It is plotted in Figure 7 versus temperature for the surface pressure below the transition  $L_2'$  to the untitled phase. The tilt angles (open circles) were obtained on heating to the desired temperature within the untitled phase followed by an isothermal expansion from the untitled phase to the tilted phase. Again there is a distinct jump in tilt angle from  $4^\circ$  to  $7.5^\circ$  between  $6.4$  and  $6.5\ ^\circ\text{C}$ , indicating an extension of the  $S/LS(Rot\ I)$  phase boundary into the  $L_2'$  phase.

The behavior of the tilt angle on isobaric cooling at  $\pi = 12.8\ \text{mN/m}$  ( $0.5\ \text{mN/m}$  below the triple point) from  $T = 7\ ^\circ\text{C}$  to  $T = 4.4\ ^\circ\text{C}$  is shown in Figure 7 (solid circles). Again no change in tilt angle could be induced because supercooling effects prevent the occurrence of the transition. The tilt angle stayed at  $7.5^\circ$  during the whole process. It was not possible to do the experiment in the reverse direction because of the slope of the  $L_2'/LS(Rot\ I)$  boundary near the triple point (see Figure 2).

## Conclusion

The behavior of the tilt angle in octadecanol has been investigated using Brewster angle autocorrelation spectroscopy.



**Figure 7.** Tilt angles of octadecanol in the vicinity of the triple point  $L_2'/LS(Rot\ I)/S$ , as obtained by isothermal expansion from the untilted phase to surface pressures 0.1 mN/m below the tilt/untilt transition (open circles) and on isobaric cooling from 7 to 4.4 °C at  $\pi = 12.8$  mN/m (solid circles). There is a discontinuity between 6.4 and 6.5 °C on the isothermal expansion measurements, while the higher tilted phase is supercooled on isobaric cooling.

Clear differences in the autocorrelation measurements between first- and second-order phase transitions allowed us to investigate the tilt angle behavior of two triple points  $L_2'/S/LS(Rot\ I)$  and  $L_2'/LS(Rot\ I)/LS(Rot\ II)$ . We found discontinuities of the tilt angle in the  $L_2'$  phase near both triple points, indicating two first-order phase transitions between phases of different tilt angle. Both transitions are associated with hysteresis effects which prevent a direct observation of the transition. The phase behavior of the alcohols therefore is more similar to that of the fatty acids than expected before. Like in the acids the phase boundary  $LS(Rot\ I)/LS(Rot\ II)$  extends into the tilted phase, but it is not associated with changes in the tilt azimuth order of the monolayer.

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## References and Notes

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