

# Phase diagrams for monolayers of long-chain thioacetates

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In honor of Dietmar Möbius on his 60th birthday.

## Abstract

Brewster-angle microscopy has been employed to determine the phase diagrams of Langmuir monolayers of several long-chain thioacetates: S-hexadecyl acetate, S-octadecyl acetate, S-eicosyl acetate and S-docosyl acetate. The phases in S-octadecyl acetate were identified by carrying out a dilution study with octadecyl acetate. A composite thioacetate diagram could be established by superimposing the diagrams for the individual thioacetates with suitable shifts to account for the differences in chain length. Infrared reflection-absorption spectroscopic studies of monolayers of octadecyl acetate and S-octadecyl acetate show that the differences between their phase diagrams can be attributed, at least in part, to the extent of hydrogen bonding of the carbonyl group. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Although some of the early pressure-area isotherm measurements on Langmuir monolayers of simple amphiphiles such as fatty acids and their esters [1,2] revealed that there were many monolayer phases, the complexity of the phase diagrams was not widely recognized until more modern techniques such as grazing-incidence dif-

fraction, fluorescence microscopy and Brewster-angle microscopy [3] were employed to determine the microscopic structures of the phases and to locate phase boundaries. The diagrams include high-surface-pressure phases in which the molecules are untilted (U), i.e. they are normal to the water surface. As the pressure is lowered there are transitions to tilted phases in which the molecules are inclined with respect to the surface normal. The tilted phases can be classified by the direction of the molecular tilt azimuth. Phases are found in which the molecules tilt toward their nearest neighbors (NN), toward their next-nearest neighbors (NNN) or in an intermediate direction.

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In the saturated fatty acids the progression of phases with decreasing pressure is typically  $U \rightarrow NNN \rightarrow NN$  [4,5] but in alcohols of similar chain length it is  $U \rightarrow NNN$ , with the next-nearest-neighbor tilt persisting to zero pressure [6]. This difference in phase behavior is related to the extent of molecular tilt, which is controlled by the head-group spacing. Tilted phases arise when the head-group spacing is larger than the chain diameter, in which case the chains tilt to maximize the chain–chain interaction. Grazing-incidence diffraction studies show [4] that the molecular tilt angle  $\theta$  and the molecular area  $A_x$  are related by

$$A_0/A_x = \cos \theta$$

where  $A_0$  is the molecular area at close packing. The tilt angle increases as the head-group area increases, as when the pressure is lowered. It is found that the transition from NNN to NN tilt occurs only at large tilt angles. Although the mechanism is not well understood such a relationship is found in model systems [7]. If the head group is small, the tilt angle does not become large enough to trigger the transition, even at zero pressure.

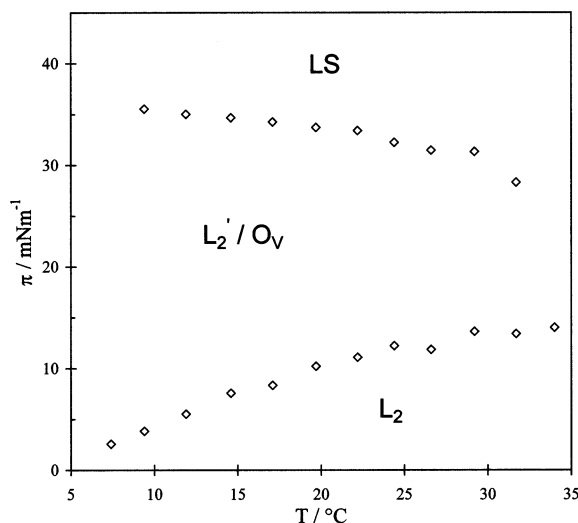


Fig. 1. Surface pressure–temperature diagram for S-octadecyl acetate obtained from Brewster-angle microscope (BAM) measurements. The identification of the phases follows from the dilution experiments shown in Fig. 2.

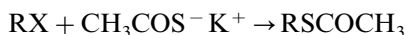
By preparing mixtures of an acid and an alcohol of identical chain length it was in effect possible to vary the size of the head group continuously and to follow the way in which the NN phase was lost [8,9]. (Diffraction measurements showed that the mixtures remained homogeneous [8].) A similar set of studies was carried out in which acids were mixed with methyl, ethyl and propyl esters of long-chain acids and with acetate esters of long-chain alcohols [10]. From these experiments it appeared that there are essentially two types of phase diagrams for these simple amphiphiles: one in which there are both NN and NNN phases, which is typical of the acids and acetates, and the other in which the NN phase is absent, which is found for alcohols, methyl, ethyl and propyl esters. The fact that the esters and alcohols had similar phase diagrams showed that the geometric size of the head group alone was not the determining factor and it was argued that hydrogen bonding also played a significant role.

The regularity of phase behavior for these simple amphiphiles suggests that it might be possible to determine the molecular features that control the stability of the phases, eventually making it possible to control phase behavior by molecular design. Systematic studies of the effects of head-group structure on phase behavior have therefore been undertaken. In this paper we report studies of the effect of sulfur substitution in esters and acetates.

## 2. Experimental

### 2.1. Synthesis of thioacetates (RSAc)

Esters of ethanethioic acid were prepared according to the reaction



In the procedure, 2 mmol of potassium thioacetate (Aldrich) and 2 mmol of the *n*-bromoalkane (Sigma) were dissolved in 10 ml dry tetrahydrofuran under nitrogen gas purge in a round-bottom flask and stirred overnight with a magnetic stirrer. The reaction mixture was orange–brown in color and had a white precipitate. It was then placed

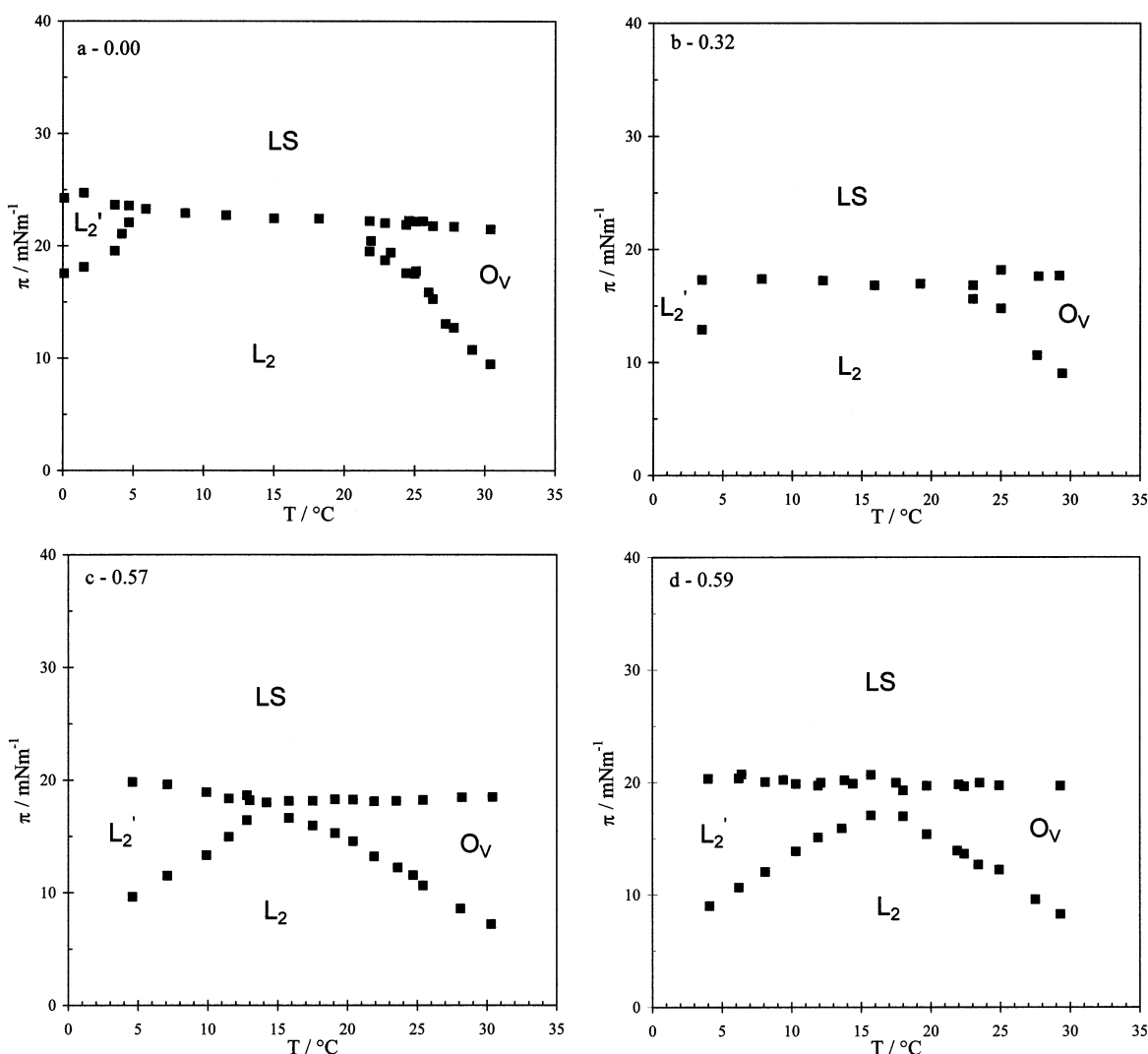


Fig. 2. Surface pressure–temperature diagrams for octadecyl acetate and mixtures of octadecyl acetate and S-octadecyl acetate. Mole fraction of thioacetate: a, 0; b, 0.32; c, 0.57; d, 0.59; e, 0.67.

into a separatory funnel containing 10 ml each of ethyl acetate and ice water and shaken. The aqueous layer was extracted two more times with 5-ml aliquots of ethyl acetate. The combined organic portion was washed with 1 M sodium bicarbonate and 3 M sodium chloride and then dried over magnesium sulfate. The solvent was then removed with a roto-evaporator and the product was dried under nitrogen gas. The product was

purified by silica-gel column chromatography. The identities of the products were confirmed by proton NMR and mass spectroscopy. Analyses by thin-layer chromatography showed only a single spot for each compound. Sample purities were estimated by measuring peak heights on gas chromatograms. The hexadecyl, octadecyl and eicosyl esters were 99% pure and the purity of the docosyl ester was 98%.

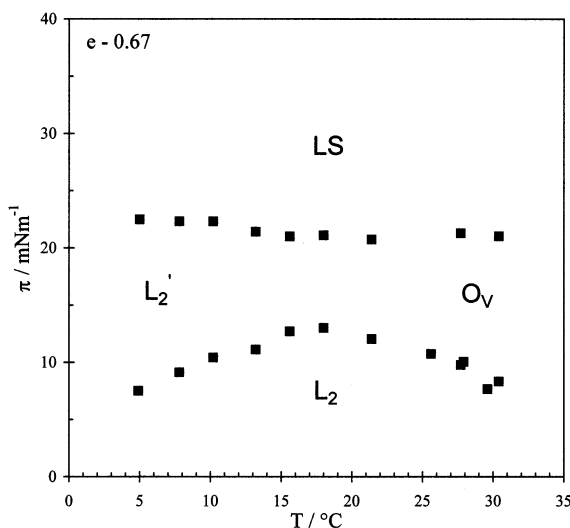


Fig. 2. (Continued)

### 2.2. Brewster-angle microscope (BAM) measurements

BAM measurements of the phase diagrams were carried out with a home-made instrument that has already been described in detail [11]. The trough is constructed of Teflon and has an area of about 100 cm<sup>2</sup>. Water from a thermostatic bath circulates through the base and the temperature was measured with a thermocouple in the sub-phase. The surface pressure was measured with an R&G transducer fitted with a filter-paper Wilhelmy plate.

Solutions of the thioacetates in chloroform (Fisher Scientific, spectranalyzed) were deposited on Milli Q purified water from a glass microliter syringe. As shown in previous studies [5], transitions between tilted phases are marked by sharp changes in the optical texture of the monolayer, which include changes in contrast and the rearrangement of boundaries. At a transition from a tilted to an untilted phase there is a loss of contrast.

### 2.3. FTIR measurements

Infrared reflection-absorption spectroscopy measurements [12] were performed with a Bio-Rad

(Digilab) FTS 60A spectrometer equipped with an MCT detector. The IR beam is focused by a BaF<sub>2</sub> lens (100 mm focal length) and directed to the water surface by a plane mirror; the angle of incidence was 30°. The monolayer was spread in a home-made thermostatted Langmuir trough (8 × 20 cm<sup>2</sup>) that is mounted on a shuttle device with another trough containing only water. This allows

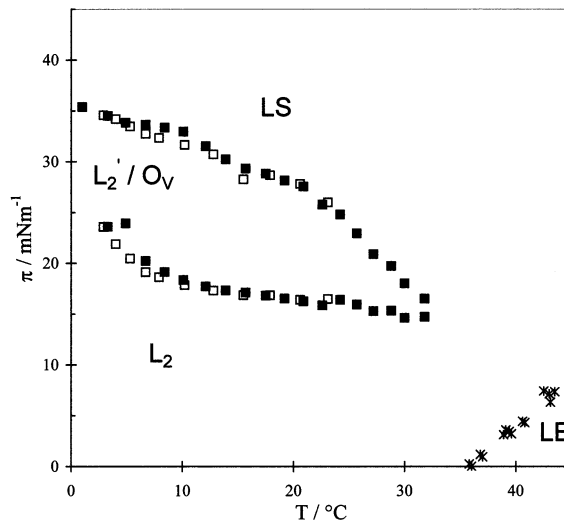


Fig. 3. Surface pressure–temperature diagram for S-hexadecyl acetate. Open and full symbols distinguish different measurement sets.

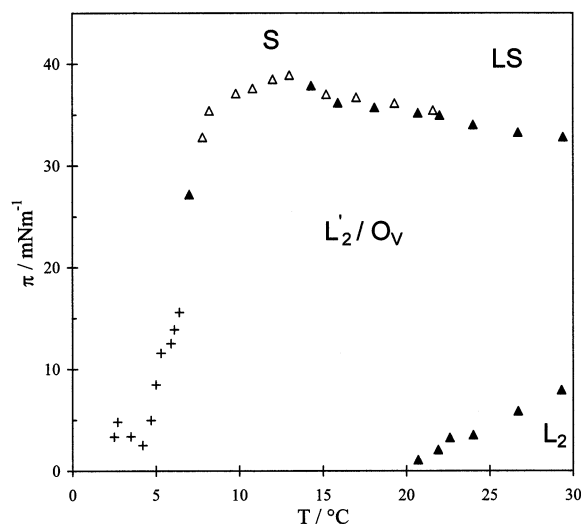


Fig. 4. Surface pressure–temperature diagram for S-eicosyl acetate. Symbols indicate different measurement sets. The existence of the S phase is inferred by the observation of texture in the untilted phase at temperatures below 13°C.

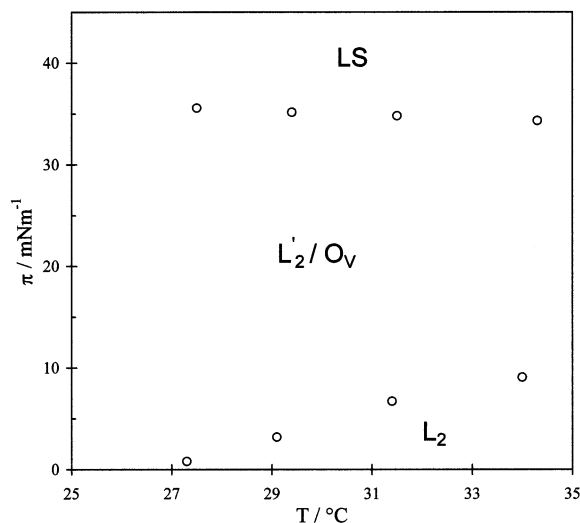


Fig. 5. Surface pressure–temperature diagram for S-docosyl acetate.

the IR beam to be switched between the sample and a reference area [13]. Spectra were acquired by coaddition of 1024 scans with a resolution of 8  $\text{cm}^{-1}$ , apodized with a triangular function and Fourier-transformed with one level of zero-filling.

When necessary, residual water-vapor bands were removed by the use of an appropriate reference spectrum.

### 3. Results

The surface pressure–temperature phase diagram for S-octadecyl acetate is shown in Fig. 1. Two phase boundaries are evident, one at low pressure between tilted phases and another at high pressure to an untilted phase. It was not possible to distinguish the slight changes in texture in the untilted regions that are associated with transitions between untilted phases with different degrees of backbone order [4]. This diagram is similar in topology to that observed for acid/alcohol [9] or acid/ester [10] mixtures in that there is a boundary between tilted phases that does not intersect the tilted–untilted transition line.

In order to identify the phases, we followed the evolution of the phase diagram as S-octadecyl acetate was added to octadecyl acetate. Measurements were carried out at 12 compositions and representative data from these experiments are shown in Fig. 2. As shown in Fig. 2a, there are

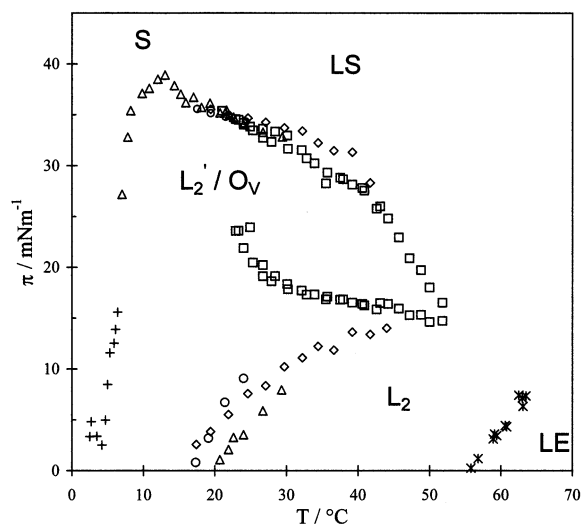


Fig. 6. Combined phase diagram for the S-alkyl acetates. The temperature scale is appropriate for S-eicosyl acetate. The data for the other compounds have been offset using a shift of 5 K per methylene. Symbols: C16 ( $\square$ ); C18 ( $\diamond$ ); C20 ( $\triangle$ ,  $+$ ); C22 ( $\circ$ ).

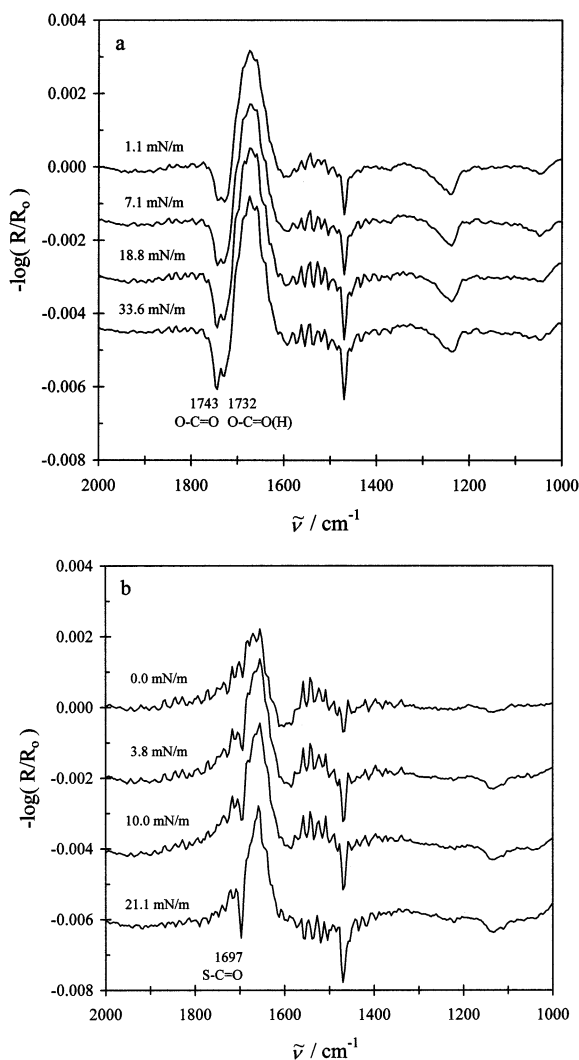


Fig. 7. Infrared reflection-absorption spectra for (a) octadecyl acetate. For clarity, successive spectra have been shifted downward by 0.0015. (b) S-octadecyl acetate. Successive spectra have been shifted by 0.0020. The features associated with the carbonyl stretch are indicated in the diagrams.

three distinct tilted phases in octadecyl acetate, a NN phase,  $L_2$ , and two NNN phases,  $L'_2$  and Ov. This identification of phases is supported by the extensive isotherm studies of acetates by Lundquist [14]. The evolution of the phase diagram with increasing concentration of the S-octadecyl ester is similar to that observed in acid/alcohol or acid/ester mixtures. The  $L_2/L'_2$  transition moves to lower pressure and higher

temperature and the  $L_2$ /Ov boundary moves to lower pressure and lower temperature, Fig. 2b,c. The  $L'_2$  and Ov phase regions then merge at a mole fraction of about 0.57 and the boundary of the combined phase continues to move to lower pressures with increasing concentration, Fig. 2d,e. But, unlike the diagrams for the alcohols and esters, the  $L_2$  phase is not completely suppressed and persists at the pure S-octadecyl acetate. The tilted/untitled boundary also changes with composition, initially dropping with addition of the S-acetate and then rising.

At temperatures above about 30°C, monolayers of S-octadecyl acetate begin to collapse quickly as the pressure approaches the tilted/untitled transition and the collapse pressure moves toward lower pressure with increasing temperature. The tilted/untitled transition can still be located in rapid compressions. No transition to the liquid expanded phase is observed below 45°C, the highest temperature that was examined. In contrast, monolayers of octadecyl acetate are stable up to the tilted/untitled transition at least as high as 33°C, and the liquid expanded phase (not shown in Fig. 2a) appears at about 28°C [2].

BAM studies of the S-hexadecyl, S-eicosyl and S-docosyl acetates yield the phase diagrams shown in Figs. 3–5. There is a single tilted/tilted boundary in the hexadecyl compound, Fig. 3, and

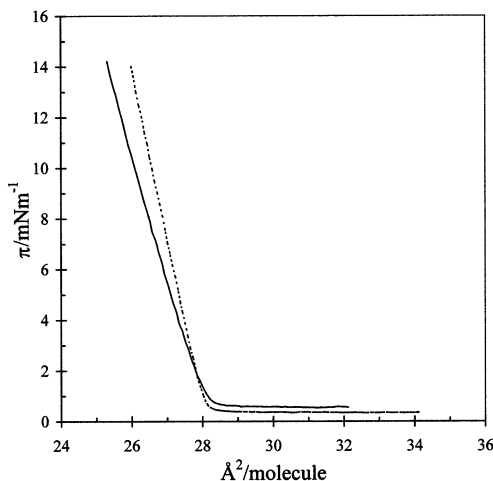


Fig. 8. Surface pressure-area isotherms at 22°C for octadecyl acetate (full line) and S-octadecylacetate (dashed line).

a tilted/untilted transition; the coexistence line with the liquid expanded phase is also observed. Several transition lines appear in the diagram for the eicosyl compound, Fig. 4. A transition between tilted phases rises from zero pressure at about 20°C and there is a nearly vertical tilted/tilted line at 5°C. The tilted/untilted boundary has the ‘Dutch clog’ shape first discussed by Peterson [18,19] and a faint texture in the untilted phase similar to that observed in the S phase of the acids [5] appears below 13°C. The LS/S transition line was not determined, however, because the film collapses rapidly at high pressure. There is evidence of another transition at about 4 mN/m between tilted phases at the lowest temperatures studied. Only two phase boundaries can be observed in S-docosyl acetate, Fig. 5. There is a transition between tilted phases that first becomes apparent at about 26°C and a transition to an untilted phase at high pressure. The measurements could not be performed at lower temperatures because the very stiff films responded very sluggishly and fractured upon decompression.

Dilution studies with these compounds have not been carried out but it seems plausible that the effect of the change in chain length is simply to shift the temperature scale as it does for fatty acids. The tilted/untilted transition lines in the diagrams can be brought into register by assuming a shift of 5 K for each methylene group. Such a composite diagram is shown in Fig. 6 in which there is no offset in temperature for S-eicosyl acetate. The tilt–tilt boundaries in the C22, C20 and C18 acetates agree reasonably well with each other but in the C16 compound that boundary moves upward with decreasing temperature rather than falling to zero pressure.

#### 4. Discussion

If one accepts that the changes in the phase diagrams as observed in the acid/alcohol and acid/ester dilution studies reflect a continuous variation in behavior with head-group size then it is not surprising to find pure substances whose phase diagram lies intermediate between those of acids or acetates and those of alcohols or esters.

Teer et al. [10] argued that in determining head-group size it was necessary to include the effects of hydrogen bonding with the subphase and cited evidence from infrared absorption-reflection measurements on the esters [15,16] that the hydrogen bonding with the carbonyl oxygen seen in the acids was diminished in the methyl esters and absent in the ethyl or propyl esters.

In the spectrum of octadecyl acetate, Fig. 7a, there is a splitting of the carbonyl stretch that is indicative of hydrogen bonding. The peak at 1743  $\text{cm}^{-1}$  is associated with the unprotonated C=O while that at 1732  $\text{cm}^{-1}$  is assigned to the singly protonated carbonyl. It decreases relative to the unprotonated peak as the pressure increases. In the S-octadecyl acetate, Fig. 7b, the unprotonated carbonyl stretch is shifted to 1697  $\text{cm}^{-1}$ ; the protonated peak is not evident (although it could possibly be obscured by the large positive peak at 1659  $\text{cm}^{-1}$ ).

The thioacetate diagrams lie part way between those of the acetates (and acids) and the esters (and alcohols) in that their topologies are similar to those found in mixtures of these two classes of compounds. This is consistent with a smaller effective head-group size at low pressure than that of the acetates because of decreased hydrogen bonding. As shown by the spectra, hydrogen bonding in the acetates diminishes with increasing pressure, which can account for the fact that the transition to the untilted phase occurs at lower pressure in the acetates than it does in thioacetates. In the absence of hydrogen bonding, the head-group size is determined by steric interactions and the presence of the sulfur makes the thioacetates larger than the acetates. A comparison of the isotherms for octadecyl acetate and S-octadecyl acetate, Fig. 8, shows that the thioacetate is less compressible, consistent with this argument.

The phase diagram of the S-hexadecyl acetate is qualitatively different from those of its longer-chain homologues. Recent diffraction studies of ethyl hexadecanoate [17] show the presence of a NN phase while none is present in the longer-chain ethyl esters [10]. Thus a dependence of the phase diagram on chain length other than a shift in temperature appears to arise for shorter chains.

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