Optical measurements of the phase diagrams of Langmuir monolayers of fatty acid, ester, and alcohol mixtures by Brewster-angle microscopy

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Surface pressure–temperature phase diagrams have been determined by Brewster-angle microscopy for Langmuir monolayers of heneicosanoic acid with the esters methyl and ethyl heneicosanoate and octadecanoic acid with methyl, ethyl, and propyl octadecanoate. The behavior is similar to that found previously in mixtures of an acid and an alcohol. In each case with increasing ester concentration the L_2/L_2' phase boundary moves toward lower pressure and higher temperature while the L_2/Ov boundary moves toward lower pressure and lower temperature. The L_2' and Ov phases eventually merge and the boundary with the L_2 phase moves to zero pressure. The phase diagram of eicosyl acetate is similar to that of the fatty acids. We attribute the variations in the diagrams to the extent of hydrogen bonding between the head group and the subphase. © *1997 American Institute of Physics.* [S0021-9606(97)52405-6]

I. INTRODUCTION

There is an increasingly rich body of literature describing the phase behavior of insoluble monolayers of simple amphiphilic molecules at the air/water interface. The phase diagrams of such Langmuir monolayers of fatty acids, alcohols, and esters have been examined by a variety of methods, starting with the classical studies of surface pressure-area isotherms and determinations of the surface potential and now including x-ray diffraction and reflectometry, fluorescence microscopy, and Brewster-angle microscopy (BAM).

The *n*-alkanoic acids have been the most extensively studied and the phase diagram shown in Fig. 1 is generally applicable to them. The diagram is in most respects that determined by Stenhagen[1,2] from isotherms. X-ray studies[3] provide a precise microscopic description of the phases. The phases CS, S, and LS are untilted, i.e., they are phases in which the chain axes are normal to the water surface. There are four "tilted phases" L_2, L_2', and L_2'', and Ov. (There is no signature of the Ov phase in the isotherms and it was only recently discovered in microscopic studies.[4]) In the L_2 and L_2'' phases the tilt is toward nearest neighbors (NN) and in L_2' and Ov it is towards next-nearest neighbors (NNN). Further distinctions between the phases can be made in terms of the degree of translational order, distortion of the unit cell and the ways in which the chains pack.[3]

The phase diagram in Fig. 1 does not apply to the fatty alcohols. An x-ray diffraction study of heneicosanol[5] revealed that the high-temperature low-pressure phase has NNN tilt and was identified as L_2', rather than L_2, as it is in the acids. BAM measurements of eicosanol[6] showed no evidence of an L_2/L_2' transition. Similarly, this transition was not observed in isotherm measurements of octadecanol[7] but evidence was found for a division of the L_2' phase into two regions, L_2^* and S^*.[8]

Shih *et al.*[9] examined the relation between the acid and alcohol phase diagrams by carrying out experiments in which they studied the way in which the isotherms evolved as heneicosanoic acid was mixed with heneicosanol. (An examination of the diffraction from the mixtures showed that the acid and alcohol were miscible.) They found that with increasing alcohol the L_2/L_2' phase boundary moved to lower pressure and at a concentration in excess of 30 mol % the L_2 phase could no longer be found. Subsequent measurements of the phase diagrams of the mixtures by BAM (Ref. 10) revealed that the L_2/Ov phase boundary moved to lower temperature and lower pressure with dilution of the acid by the alcohol and that the L_2' and Ov fields merged at a concentration of about 25 mol %. With further increase in the alcohol concentration the combined L_2'–Ov phase moved to lower pressure, eventually forcing the L_2 phase out of the diagram. Shih *et al.* were unaware of the involvement of the Ov phase because the L_2/Ov transition is not seen in the isotherms.

The heneicosanol phase diagram is consistent with the diagrams that Lundquist determined for the $C_{18}-C_{23}$ ethyl esters from isotherm measurements.[11] There are two tilted phases in these diagrams, which she identified as L_2'' and L_2'. However, Stenhagen[2] believed that the high-temperature tilted phase in ethyl docosonoate was L_2 while Bibo *et al.*,[7] who carried out isotherm measurements on mixtures of ethyl eicosanoate with docosanoic acid, concluded that the L_2'/L_2 phase transition could be observed in the pure ester. These results have been called into question by recent diffraction experiments on methyl eicosanoate,[12] in which the L_2 phase was not observed. Lundquist also carried out extensive isotherm studies of *n*-alkyl acetates[13] and found phase diagrams similar to those for the acids; there are three tilted phases, L_2, L_2', and L_2''.

To resolve the uncertainty about the phase diagrams of the esters we have carried out BAM studies of the phase diagrams in a number of binary acid/ester mixtures. By ex-
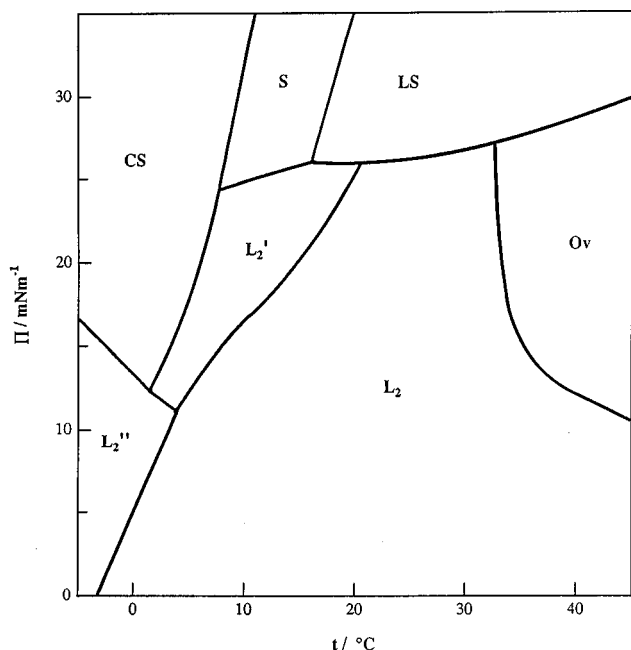
FIG. 1. Surface pressure–temperature phase diagram for heneicosanoic acid. The diagram has been adapted from Fig. 1 in Ref. 15. Phase diagrams for other *n*-alkanoic acids can be obtained by shifting the temperature axis by 6 K per methylene group. These boundaries have been determined by direct observation. There is evidence (Ref. 4) that additional phase boundaries exist within the L_2', L_2, and LS fields.

amining the ways in which the diagrams evolve with composition from the well-established diagram for the acids, we can determine the nature of the phases and at the same time examine the relation between the existence of tilted phases and the nature of the head group.

II. EXPERIMENT

The experiments were performed in two laboratories, at UCLA and at the University of Leipzig. In both groups optical transitions were studied by BAM. In the UCLA experiments, heneicosanoic acid, methyl heneicosanoate, ethyl heneicosanoate, octadecanoic acid, ethyl octadecanoate, propyl octadecanoate, octadecyl acetate, and heneicosal acetate were obtained from Nu Chek Prep and claimed to be 99+% pure (see Table I). Without further purification they were spread from chloroform (Fischer spectranalyzed) solutions

onto pure water (Millipore Milli-Q, 18 MΩ) contained in a custom-built Teflon trough. Solutions of the mixtures were prepared from solutions of the pure components. Details of the BAM measurements at UCLA have been described previously.[15] The Ar$^+$ laser was operated at 750 mW instead of 500 mW to increase signal contrast. The observations were generally begun 1 h after the monolayer was spread, which allowed the mosaic textures to develop into larger, more regular shapes that allowed the transitions to be more easily seen. Development of the texture was slower for longer chain lengths and observations were begun two hours after spreading.

In the Leipzig experiments, octadecanoic acid, methyl octadecanoate, and octadecanol were obtained from Sigma Aldrich and claimed to be 99+% pure. Without further purification they were spread from chloroform (p.a. Merck) onto pure water (Millipore Milli-Q, 18 MΩ) contained in a Teflon trough. The BAM was comprised of an Ar$^+$ laser (Carl Zeiss Jena, #ILA 120) emitting 200 mW at 514 nm, a Glan-Thompson Polarizer and Analyzer (Bernhard Halle Nachfl.) with extinction coefficients of 10^{-8} and 10^{-6}, respectively; a focusing lens (Nikon, #CF SLWD20x) with a numerical aperture of 0.35 and a working distance of 20.50 mm; and a CCD camera (Hamamatsu, #C 3077-01) with a minimum sensitivity of 0.5 lux.

III. RESULTS

Figures 2 and 3 show the surface pressure–temperature phase diagrams of octadecanoic acid and heneicosanoic acid mixed with varying amounts of a corresponding ester. Methyl, ethyl, and propyl octadecanoate were mixed with octadecanoic acid while methyl and ethyl heneicosanoate were mixed with heneicosanoic acid. Hysteresis did not exceed 0.2 mN m^{-1} and was generally 0.1 mN m^{-1} between compressions and expansions (not shown).

We saw no evidence of hydrolysis of the esters. This is in accord with the measurements of Alexander and Schulman.[16] They found that rate constants for the acid/base catalyzed hydrolysis decreased markedly with increasing compression of the monolayers. For ethyl hexadecanoate and ethyl octadecanoate in the liquid-condensed phase the pseudo-first-order rate constant at 21 °C was 0.005 min^{-1} and for methyl octadecanoate it was 0.021 min^{-1} on a sub-

TABLE I. A summary of compounds.

| Name	Formula	L_2 Phase?
Octadecanoic Acid	$CH_3(CH_2)_{16}COO\,H$	Yes
Octadecanol	$CH_3(CH_2)_{17}OH$	No
Methyl Octadecanoate	$CH_3(CH_2)_{16}COO\,CH_3$	No
Ethyl Octadecanoate	$CH_3(CH_2)_{16}COO\,CH_2CH_3$	No
Propyl Octadecanoate	$CH_3(CH_2)_{16}COO\,CH_2CH_2CH_3$	No
Octadecyl Acetate (Octadecyl Ethanoate)	$CH_3(CH_2)_{17}OOC\,CH_3$	Yes
Eicosyl Acetate (Eicosyl Ethanoate)	$CH_3(CH_2)_{19}OOC\,CH_3$	Yes
Heneicosanoic Acid	$CH_3(CH_2)_{19}COO\,H$	Yes
Methyl Heneicosanoate	$CH_3(CH_2)_{19}COO\,CH_3$	No
Ethyl Heneicosanoate	$CH_3(CH_2)_{19}COO\,CH_2CH_3$	No
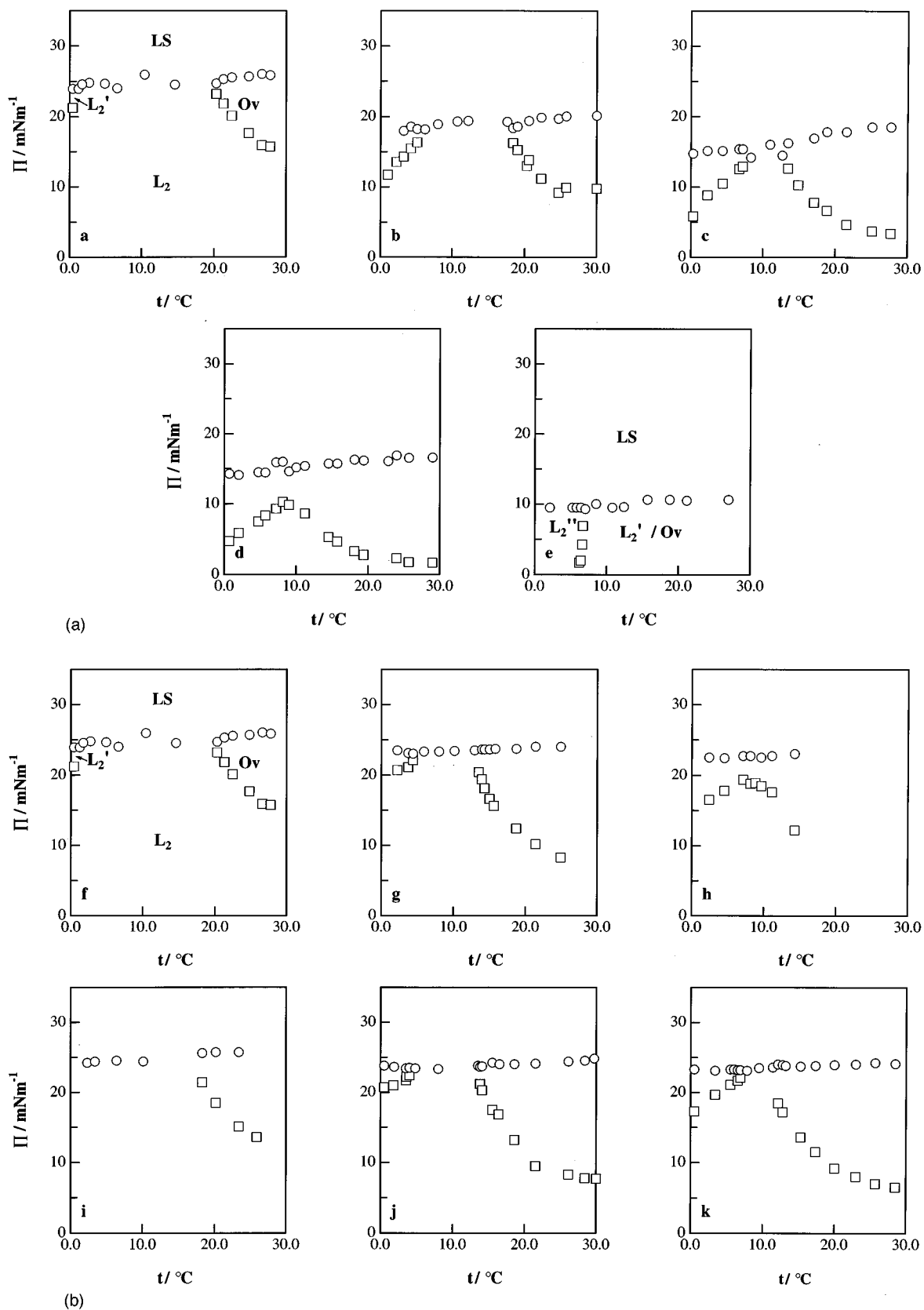
FIG. 2. A series of pressure–temperature phase diagrams with an increasing concentration of methyl (a–e), ethyl (f–h), or propyl (i–k) octadecanoate in octadecanoic acid. Squares represent NN to NNN transitions while circles are tilted to LS transitions. The phase boundaries were observed by BAM during isothermal compression. Concentrations in mol %: (a) 0; (b) 30.0; (c) 40.0; (d) 50.0; (e) 100; (f) 0; (g) 14.8; (h) 18.0; (i) 5.60; (j) 11.4; (k) 13.4.
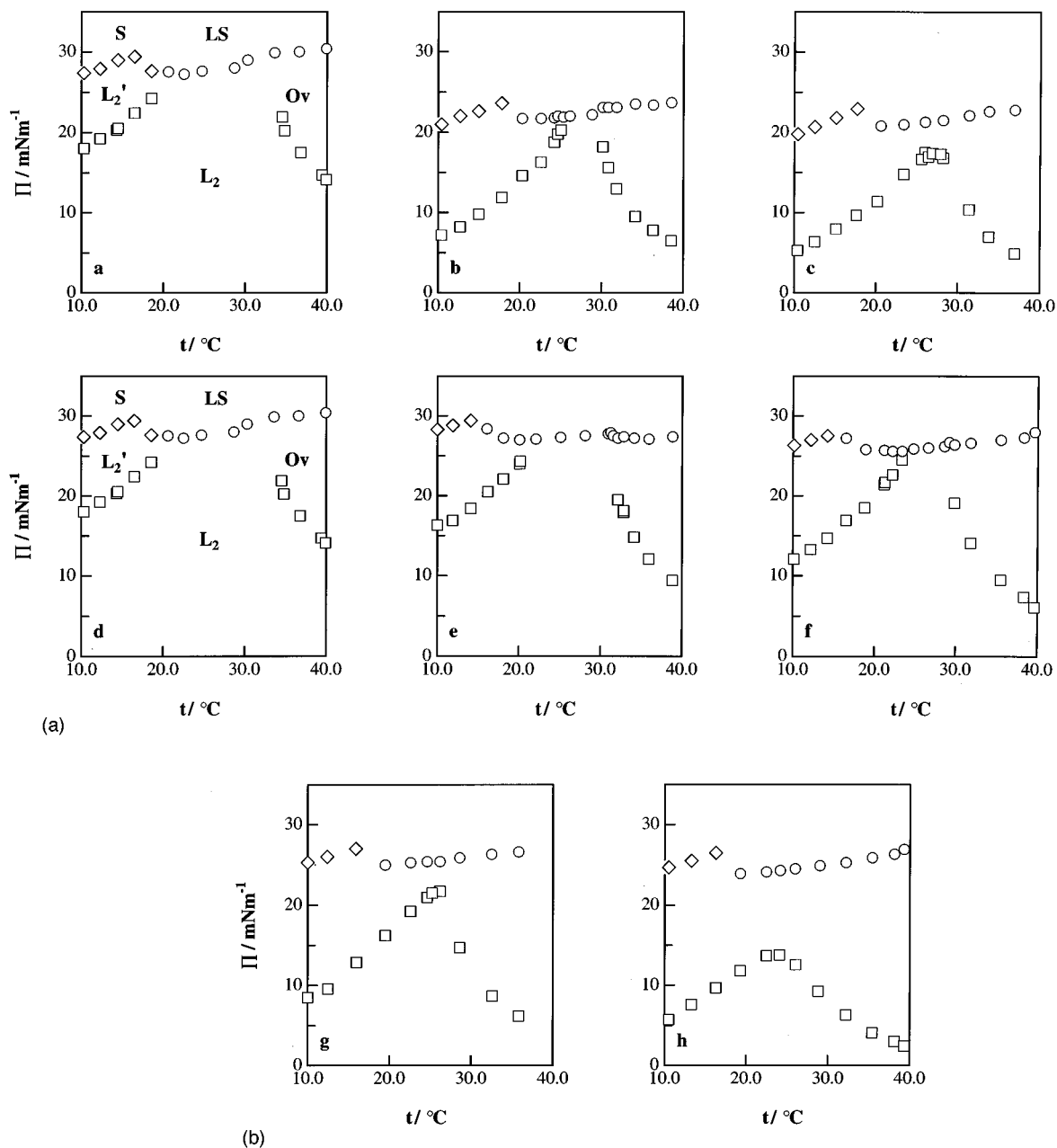
FIG. 3. A series of pressure–temperature phase diagrams with an increasing concentration of methyl (a–c) or ethyl (d–h) heneicosanoate in heneicosanoic acid. Squares represent NN to NNN transitions, circles are tilted to LS transitions, while diamonds mark tilted to S transitions. Concentrations in mol %: (a) 0; (b) 27.2 (c) 32.0; (d) 0; (e) 6.73; (f) 12.1; (g) 15.8; (b) 18.9.

phase at pH 2. At pH 5.5 the rate constants would be smaller by roughly a factor of 10^4, so that during the 5–6 h period of a measurement there would be a negligibly small amount of hydrolysis.

The phase boundaries were marked by rearrangements of the mosaic-like texture of the monolayer. Transitions to the LS phase, which are indicated by circles, were accompanied by a complete loss of contrast. The L_2/L_2' and L_2/Ov transitions (squares) were accompanied by a rearrangement of domains to different constrasts. At the L_2/L_2' transition all the domains underwent rearrangements, but only some of the domains changed at the L_2/Ov transition. At the transition to

the Ov phase in the C_{21} mixtures some domains developed thin parallel and perpendicular stripes that can be described as hash marks. This texture was also observed at very fast compression rates in the C_{18} mixtures but it would soon anneal away. The L_2'/S transition, which is denoted by diamonds, was accompanied by a general loss of contrast and rearrangement to a two-tone mosaic pattern. Transitions near the intersections of coexistence lines were difficult to determine. The image was often blurred or lacked contrast. As noted in the study of the phase diagram of the acids,[15] the mosaic patterns are recovered after a compression–expansion cycle through a transition. This ''memory'' of the
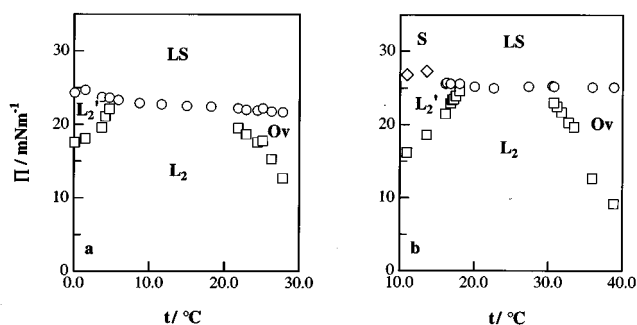
FIG. 4. Pressure–temperature phase diagrams of (a) octadecyl acetate and (b) eicosyl acetate. Squares represent NN to NNN transitions, circles are tilted to LS transitions, while diamonds mark tilted to S transitions.

texture was not observed in transitions involving the LS phase.

The changes in the topology of the phase diagram with increasing ester concentration parallel those found in acid/alcohol mixtures.[10] The L_2/L_2' phase boundary moves towards lower pressure and higher temperature with increasing ester concentration while the L_2/Ov boundary moves more rapidly towards lower pressure and lower temperature. The L_2' and Ov fields eventually merge and displace the L_2 phase as they move toward zero pressure.

In several isobaric studies we carefully searched for an

L_2'/Ov transition within the merged phase but were unable to find one. However, the changes in the textures observed on the transition from the L_2 phase to the merged L_2'/Ov phase do show a dependence on temperature. The hashmark texture is found at high temperature while at low temperature the transition is often observed as a front that moves across the field of view. Thus we cannot preclude the existence of a continuous transition from an L_2' to an Ov phase. We see no evidence of a transition within the L_2 phase between L_{2h} and L_{2d} phases as required by the Landau theory developed by Kaganer[3,17] and for which there is evidence in a recent diffraction study.[3] We have also not seen the transition in methyl octadecanoate found by Foster *et al.*[12] between the L_2 phase and a phase that they have designated τ. In addition, there are no changes in the images that could be attributed to a separation of the L_2' phase into L_2^* and S^* regions.[3,8]

The pressure–temperature phase diagrams for octadecyl acetate and heneicosyl acetate are shown in Fig. 4. In agreement with Lundquist's isotherm studies,[14] we find that the diagram closely resembles that of the acids. The similarity includes the presence of an Ov phase, which Lundquist would not have been able to detect. To round out the series of phase diagrams studied we have investigated some mixtures of octadecanol and methyl octadecanoate; the results are shown in Fig. 5. The principal effect of adding the alco-
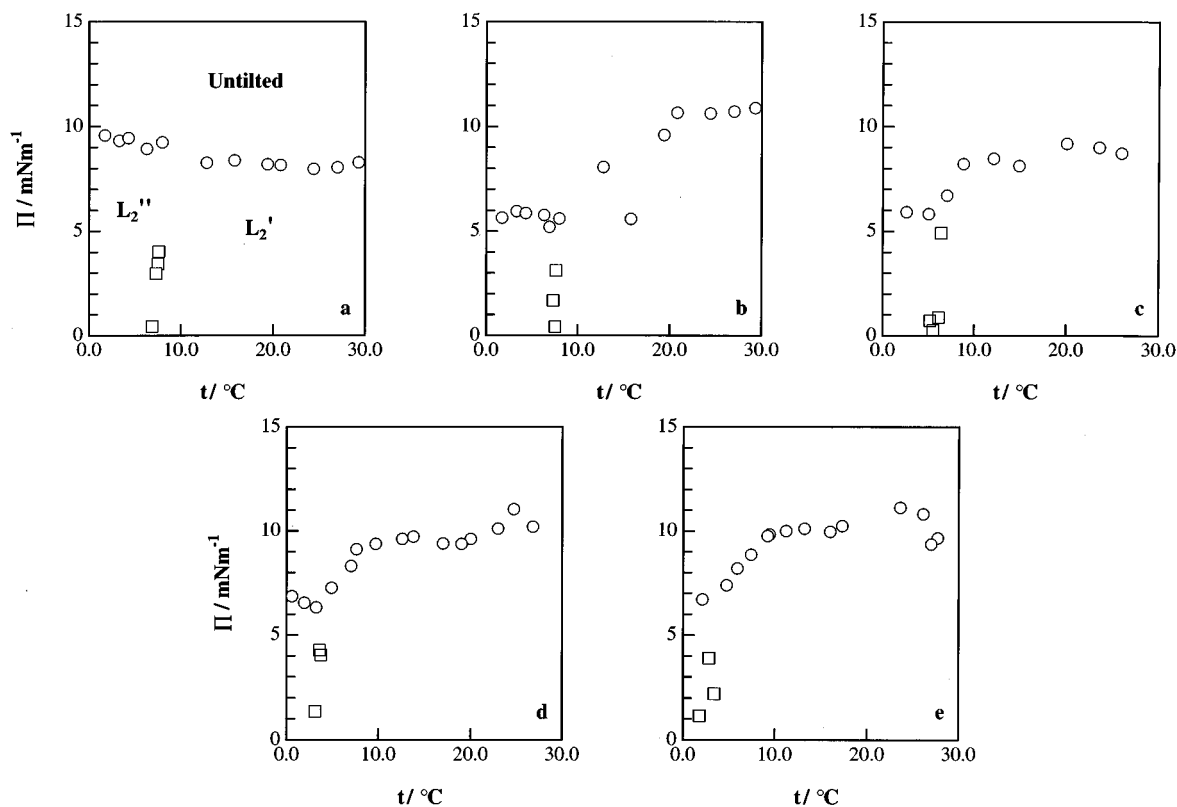

FIG. 5. A series of pressure–temperature phase diagrams with an increasing concentration of octadecanol in methyl octadecanoate. Squares and triangles represent NN to NNN transitions while circles are tilted to untilted transitions. Concentrations in mol %: (a) 0.50; (b) 1.00; (c) 2.00; (d) 3.50; (e) 5.00. The L_2/L_2'' boundary in the 5 mol % mixture was determined by scanning the temperature.
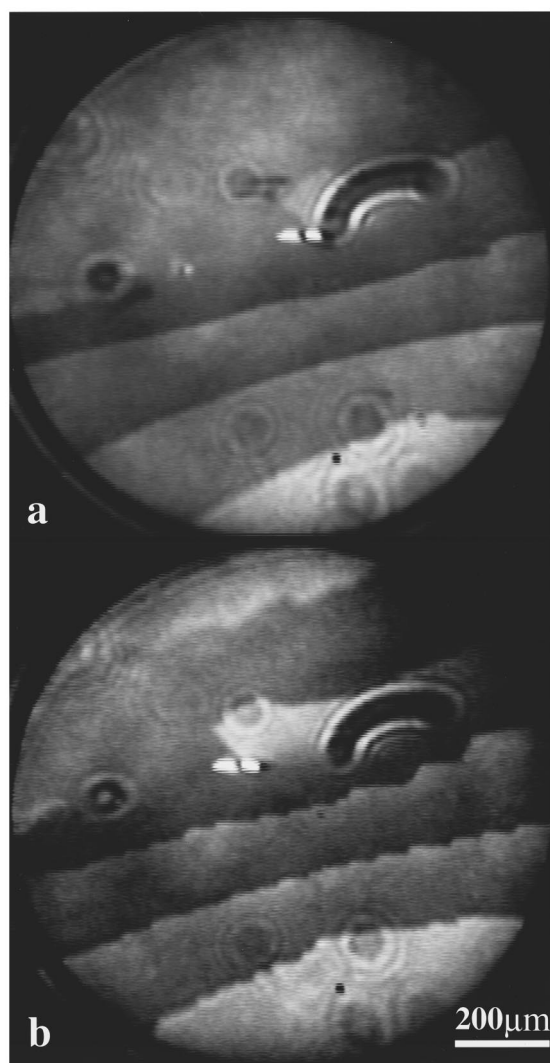
FIG. 6. The formation of zig–zags at the L_2/Ov transition. Shown here is the transition in a 5.6 mol % mixture of propyl octadecanoate in octadecanoic acid at 25.9 °C. (a) $\Pi=13.6$ mN m^{-1}; (b) $\Pi=13.7$ mN m^{-1}. The zig–zags disappear immediately when the pressure is lowered. The worm-like feature at center right is the result of an imperfection in the polarizer.

hol to the ester is a shift of the L_2''/L_2' boundary to lower temperature.

In several of the acid/ester mixtures we found that long, wide stripes, Fig. 6(a), reminiscent of those found in several acids[19,20] formed in the L_2 and Ov phases after repeated cycling of the monolayer into the LS phase. The edges of the stripes are smooth in the L_2 phase but they immediately develop a zig–zag form when the L_2/Ov boundary is crossed, Fig. 6(b). The zig–zag relaxes rapidly as the pressure is dropped and the phase boundary is recrossed. Schwartz *et al.*[20] had observed a similar zig–zag transition in stripes of pentadecanoic acid but did not understand its origins. If one adjusts the temperature for the difference in chain length it is apparent that the transition in pentadecanoic acid also occurred at the L_2/Ov boundary. We speculate that the stripes form only when the range of the hexatic order is sufficiently

long and that this order is promoted by annealing in the LS phase.

IV. DISCUSSION

It is evident from the way in which the phase diagrams evolve with increasing ester concentration that Lundquist's identification of the phases in the ethyl esters is correct—the L_2 phase is not observed. The analysis of subtle changes in the isotherms of ethyl eicosanoate with docosanoic acid by Bibo *et al.* was therefore in error as was Stenhagen's assignment of the phases in ethyl docosanoate.

We can now address the question of how changes in the head group affect the phase behavior of these simple amphiphiles. Diffraction studies on fatty acids show that the tilt angle increases with decreasing pressure[3] and that the L_2'/L_2 transition occurs when the tilt angle is roughly 20°. The Ov/L_2 transition, which has been examined by diffraction only in nonadecanoic acid,[21] occurs at a similar tilt angle. The x-ray experiments on heneicosanoic acid–heneicosanol mixtures[9] show that the effect of adding the alcohol to the acid is to decrease the head-group lattice spacings, which also decreases the molecular tilt angle because the chains adopt the tilt angle that allows them to be close packed. This dependence of tilt on head-group spacing has also been shown in a molecular model for tilting phase transitions in monolayers.[22] Thus, the angles at which the NNN to NN transitions occur move to lower pressures with increasing alcohol concentration, eventually reaching zero pressure and the transition is no longer observed.[23] We conclude, therefore, that the loss of the L_2 phase should be associated with a decrease in the effective head-group size, which decreases the zero-pressure tilt angle.

The phase diagrams of the pure components fall into two classes. In that of the acids and the acetates there is a NN phase that is stable at low pressure and high temperature. It can undergo a transition to NNN phases upon compression. The alcohols, methyl, ethyl, and propyl esters belong to the other class in which there is only a NNN phase. Why are the esters of fatty acids like the fatty alcohols and why are the acetates similar to the acids? The answer can be found in the work of Alexander and Schulman,[16] who, on the basis of measurements of the surface potential and rate of hydrolysis, argued that on compression the ester head group underwent a conformational change from the Z to the E form as shown in the following diagram:
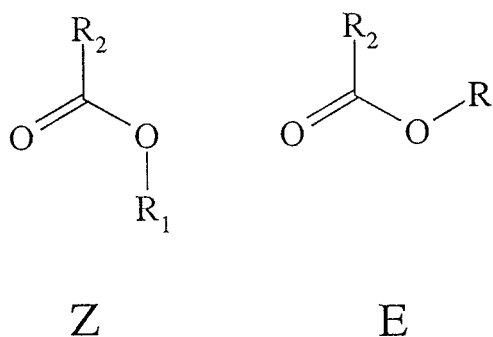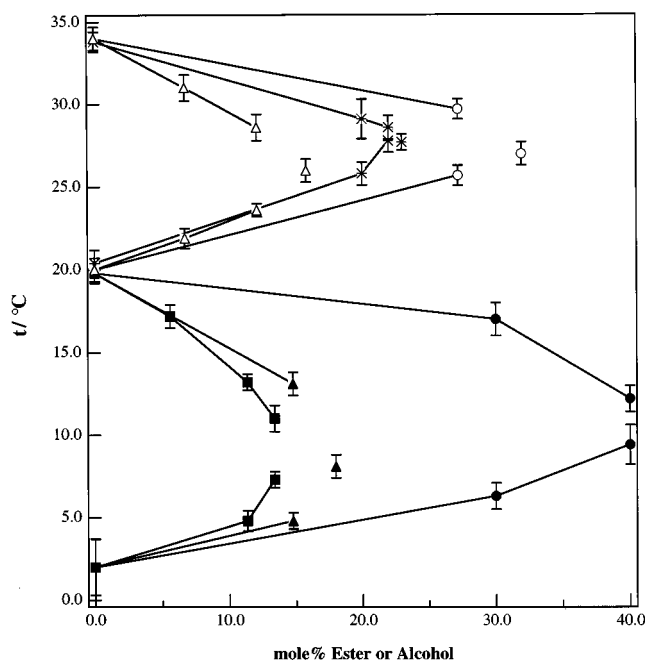
FIG. 7. Summary of C_{18} data from Fig. 2 (closed symbols), C_{21} data from Fig. 3 (open symbols), and previous work (Ref. 10) on heneicosanol (asterisks) that shows the persistence of the L_2 phase with concentration of ester or alcohol. Propyl, ethyl, and methyl ester mixtures are represented by squares, triangles, and circles, respectively. The two points at each concentration represent the temperatures at which the $L_2/L_{2'}$ and L_2/Ov coexistence lines intersect the tilted/untilted coexistence line. The last unconnected point in some sets represents the lowest measured concentration at which the merged L_2-Ov phase is observed and the temperature is that of the maximum in the $(L_{2'}$-Ov)-L_2 phase boundary. Thus the junction of the two phases lies at a lower concentration.

The surface potential is lower in the Z form because the C=O and O−R bond dipoles are partially opposed and the rate of hydrolysis is lower because the terminal R group sterically hinders attack at the carbonyl. Recent infrared studies of monolayers of fatty acids and esters are in accord with this interpretation.[24] Moreover, they show that hydrogen bonding with the subphase is markedly reduced when the esters are in the Z form, which leads to a denser packing of the head groups. The spectra of acetate monolayers have not been studied but it is obvious from their structures that the terminal methyl group cannot interfere with hydrogen bonding to the carbonyl so the head-group packing is similar to that in the acids and, as a result, there is a NN phase. This is consistent with the hydrolysis measurements,[15] which show that octadecyl acetate reacts seven times faster than methyl octadecanoate.

The extent to which the L_2 phase persists with increasing concentration is also consistent with the extent of hydrogen bonding. This is shown in Fig. 7 in which the temperatures at which the L_2'/L_2 and Ov/L_2 boundaries intersect the untilted phase are plotted against the ester concentration for each set of data from Figs. 2 and 3. The intersections were determined by extrapolation of the data points to the untilted coexistence line. Data from the previous study of heneicosanol and heneicosanoic acid[10] have also been included.

The NN phase persists to the highest concentration with the methyl esters. This is consistent with the observation by Alexander and Schulman[16] that the rate of the hydrolysis for monolayers of methyl octadecanoate is four times faster than that for ethyl octadecanoate. The smaller steric hindrance at the carbonyl in the methyl ester allows for more hydrogen bonding and therefore leads to a greater head-group spacing. Gericke and Hühnerfuss' measurements of the IR spectra of monolayers[24] also show that the degree of protonation of the carbonyl in the methyl esters is higher than that for those with a longer alcohol residue and that both the ethyl and propyl esters are completely unprotonated in compressed monolayers, which is in accord with the small difference between them seen in the figure.

V. CONCLUSION

A consistent picture of the phase behavior of monolayers of the fatty-acid esters and the fatty-alcohol acetates has now been established and the influence of hydrogen bonding with the subphase on the phase diagrams has been demonstrated. With the exception of the Ov phase, which leaves no signature in the isotherms, the phase diagrams are those determined over 25 years ago by Lundquist, but the visual observation of the phase boundaries removes the uncertainties associated with the interpretation of subtleties in isotherms. The presence of other transitions, such as those between L_{2h} and L_{2d} phases, cannot be ruled out by our measurements because the changes in texture may be slight or continuous.

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