

# Interfacial Rheology and Structure of Straight-Chain and Branched Hexadecanol Mixtures

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Langmuir monolayers of mixtures of straight-chain and branched forms of hexadecanol were studied using surface pressure–area isotherms, Brewster angle microscopy, and interfacial rheology measurements. For mixtures containing less than 30% branched molecules, the isotherms show only a lateral shift to a lower area that is proportional to the percentage of straight chains. Above this fraction, the isotherms are qualitatively different. The surface viscosities of both straight and mixed monolayers show a maximum in the condensed untilted phase near  $\Pi = 20$  mN/m. The addition of branched molecules results in a non-monotonic increase in surface viscosity, with the maximum occurring near 12% branched molecules. Visualization of these immiscible monolayers using Brewster angle microscopy in the liquid condensed phase reveals the formation of discrete domains that first increase in number density and then decrease as surface pressure is increased.

## 1. Introduction

Fatty alcohols and fatty acids display remarkable phase behavior and can adopt a wide range of phases at the air/water interface. Reference 1 provides a detailed summary of classical measurements on these systems. Their rich polymorphism is a result of their ability to self-assemble at the interface with the hydrophilic head groups arranged in regular lattices and with their aliphatic tails in tilted configurations. X-ray diffraction studies<sup>2,3</sup> have been used to reveal the structure of these lattices as a function of surface pressure and temperature. This powerful tool has been combined more recently with a number of optical methods, such as polarized fluorescence microscopy<sup>4</sup> and Brewster angle microscopy,<sup>5,6</sup> to assist in mapping out the rich phase diagrams associated with these materials. A review of the findings using this array of experimental tools can be found in ref 7.

Many past studies have monitored the presence of fatty alcohols spread at the air/water interface at their equilibrium spreading pressures. This procedure involves depositing droplets or particles of the material of interest at the interface, and monolayers consisting of condensed phases emanate from these excess reservoirs of the sample. Alternatively, these materials can be spread using volatile, insoluble solvents onto water contained in Langmuir troughs and subsequently compressed from expanded to condensed phases. Either technique can generate monolayers that are available for study using the structural measurements mentioned above as well as classical measurements of surface pressure.

Measurements of the surface pressure as a function of temperature reveal a discontinuous slope,  $d\Pi/dT$ , at a transition temperature,  $T_f$ , that identifies a first-order phase transition. X-ray diffraction measurements<sup>2</sup> demonstrate that this is a transition between tilted and untilted configurations. However, unlike analogous fatty acids, which show transitions between nearest neighbor (NN) and next-nearest neighbor (NNN) tilting directions, fatty alcohols appear to lack NN tilted phases.

Viscoelastic measurements using a variety of methods have also been employed to study the dynamics of fatty acid monolayers. Surface quasi-elastic light scattering and electrocapillary wave methods<sup>8</sup> have been used to probe dilational viscoelasticity. A surprising result reported on dodecanol ( $C_{12}H_{25}OH$ ) from these approaches is a negative sign on the dilational viscosity. This unusual behavior is largely unexplained, although it is thought to arise from a coupling of dilational modes of deformation to phase transitions. Measurements of the surface shear viscosity and moduli of eicosanol ( $C_{20}H_{41}OH$ ) have been reported using an interfacial stress rheometer.<sup>9</sup> As reported in earlier studies,<sup>1</sup> a maximum was found in the surface viscosity as a function of surface pressure. The origin of this maximum, however, has not been satisfactorily explained.

Mixtures involving fatty acids and fatty alcohols have also been investigated in the past. Many mixtures are immiscible, but there are exceptions. This topic is discussed at some length in chapter 6 of ref 1 and in ref 7. In the 1950s, Ries and Cook<sup>10</sup> reported on mixtures of stearic acid with isostearic acid. Although isostearic acid only differs from stearic acid by a single methyl side chain, it has a much larger cross-sectional area and a lower collapse pressure. This work only presents isotherm measurements on an equimolar mixture, and the data suggest few cooperative interactions between these two molecules. Both the extrapolated area per molecule and the collapse pressure are simple averages of the individual components.

Monolayers formed from mixtures of fatty acids and fatty alcohols have also been studied using a variety of methods.<sup>11–13</sup> This particular combination allows a direct examination of the influence of head groups on the polymorphism of these materials. As mentioned above, fatty acids display a phase transition between NN and NNN tilt transitions, whereas this is absent in fatty alcohols. By systematically studying mixtures of heneicosanoic acid and heneicosanol, the appearance and disappearance of this tilt transition was mapped out in detail.

The object of the present study is 1-hexadecanol (cetyl alcohol), which consists of an aliphatic tail of 16 carbon atoms attached to a hydroxyl head group. This molecule has been the subject of extensive past research, and a good deal is known about its phase behavior, structure, and transport properties at the air/water interface. This paper describes the consequences

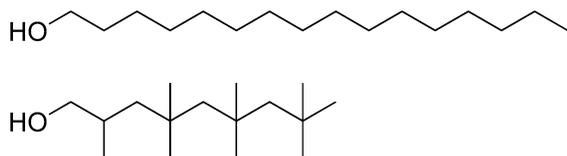
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**Figure 1.** Schematic diagram of 1-hexadecanol (top) and its branched form (bottom).

of mixing the straight-chain form of this alcohol with its branched form, 2,4,4,6,6,8,8-heptamethylnonan-1-ol. Schematics of the molecular structure of these two molecules are shown in Figure 1. Such mixtures offer the possibility of creating new microstructures at the interface with distinct interfacial rheological behavior. Although these two forms of the alcohol may mix at very low surface pressures, it is expected that they will phase separate as a mixed monolayer is compressed and the straight chains begin to crystallize. The details of this separation, however, are expected to depend on the composition of the mixture, and since both components will remain associated with the monolayer, it is difficult to predict the surface viscoelastic response as either component is “squeezed out”.

## 2. Experimental Section

**2.1. Materials.** The straight-chain 1-hexadecanol used in these experiments was acquired from Aldrich and used as received. The purity of these samples was confirmed by comparison of measured  $\Pi$ - $A$  isotherms to those reported elsewhere.<sup>1</sup> The branched hexadecanol was synthesized by BASF.

Chloroform, used as the spreading solvent for these experiments, was manufactured by Mallinckrodt Chemicals and certified to be 100.0% pure by gel chromatography.

All water used in this work was purified to a resistivity of 18.2  $M\Omega \cdot \text{cm}$  using a Millipore Milli-Q system.

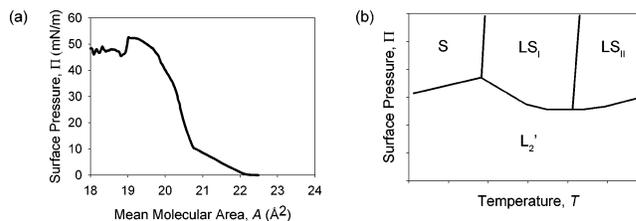
**2.2. Isotherm, Surface Rheology, and Brewster Angle Microscopy Measurements.** Measurements of both  $\Pi$ - $A$  isotherms and surface rheological properties were carried out at room temperature ( $T = 22.5 \pm 0.5$  °C) in Teflon Langmuir troughs with movable Delrin barriers, all supplied by KSV Instruments (Finland). Surface pressure measurements used a platinum Wilhelmy plate connected to a balance with a reported resolution of 4  $\mu\text{N/m}$ .

To form monolayers, hexadecanol solutions were prepared in chloroform and gently added dropwise to the air/water interface using a glass syringe. The solvent was allowed to evaporate for approximately 30 min after deposition. To manipulate the surface concentration, the barriers were moved at a rate of 1 mm/min, corresponding to a surface area change of 150  $\text{mm}^2/\text{min}$ .

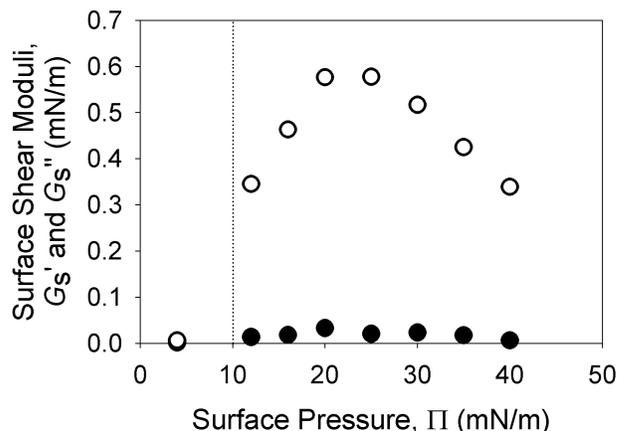
Surface viscoelasticity measurements were performed using the oscillating-rod interfacial stress rheometer (ISR) developed by Brooks *et al.*<sup>9</sup> In short, a magnetic rod is held at the interface of interest by surface tension, and the position of the rod is controlled by applying a magnetic field gradient with Helmholtz coils. As the rod moves, it shears the interface, and the rheological properties can be determined from the stress-strain relationship the rod displays.

Measurements made using the ISR were performed at constant surface pressure, and the amplitude of the rod’s motion was kept small enough to ensure that the system remained in the linear viscoelastic regime. The maximum shear strain reached was approximately 2%.

A homemade Brewster angle microscope (BAM) was used to visualize the hexadecanol monolayers. The apparatus uses a



**Figure 2.** (a) Surface pressure–molecular area isotherm for straight-chain 1-hexadecanol at room temperature. (b) Schematic of the phase diagram of hexadecanol adapted from ref 2.



**Figure 3.** Straight-chain hexadecanol rheology as a function of surface pressure: (●) elastic modulus,  $G_s'$ ; (○) viscous modulus,  $G_s''$ . The dotted line marks the isotherm phase transition.

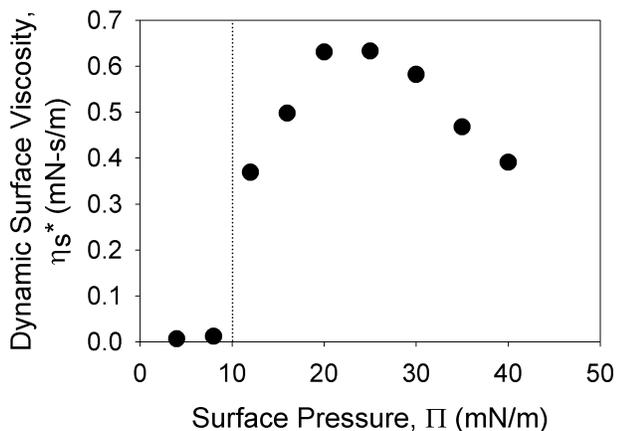
10 mW HeNe laser (Uniphase,  $\lambda = 632.8$  nm) as the light source and a CCD camera (Hamamatsu C2400) as the detector.

## 3. Results and Discussion

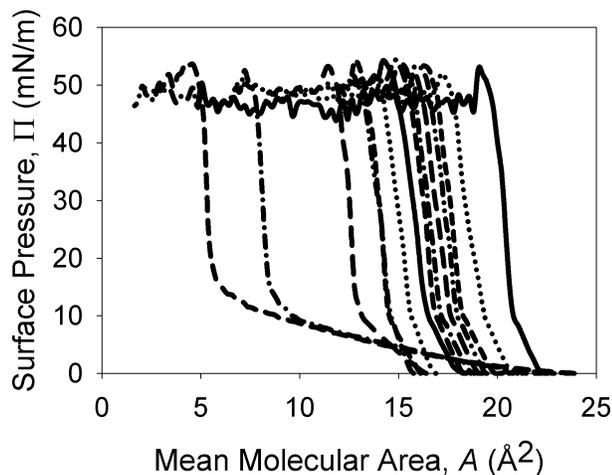
**3.1. Pure Linear-Chain Monolayers.** The pressure–area isotherm at room temperature for the straight-chain hexadecanol sample is shown in Figure 2a. Figure 2b is a schematic showing the phase diagram for this molecule as determined using X-ray diffraction studies. The isotherm shows several transitions that are well-documented in the literature. At an area per molecule of 22  $\text{\AA}^2$ , the  $L_2'$  phase is formed with the head groups in a hexagonal lattice and the aliphatic tails tilted toward their next-nearest neighbors. This value of the molecular cross section of hexadecanol estimated from the  $\Pi$ - $A$  isotherm is in good agreement with previously reported values in the neighborhood of 22  $\text{\AA}^2$  (ref 1). At a surface pressure of 10 mN/m, a distinct kink in the isotherm signals the onset of a transition to the untilted  $LS$  phase where the tilt angle has been reduced to zero. Ultimately, the monolayer collapses at a surface pressure of approximately 50 mN/m.

The interfacial rheology of the straight chain is shown in Figure 3, where the elastic and viscous moduli are shown plotted as functions of surface pressure. These measurements were performed at a frequency of  $\omega = 0.9205$  rad/s. These data show that the viscous modulus is significantly larger than the elastic modulus, indicating that these layers are very fluid. In Figure 4, these moduli are converted to the complex surface viscosity using the relationship,  $\eta^*(\omega) = G^*/i\omega$ .

The complex surface viscosity shows a non-monotonic response to the surface pressure with a maximum at approximately  $\Pi = 22$  mN/m. This surface pressure is in the vicinity of the location of a slight shoulder in the isotherm shown in Figure 2, but the microstructural basis for this maximum is not clear. It is interesting to note that the surface viscosity



**Figure 4.** Complex surface viscosity as a function of surface pressure. The dotted line marks the isotherm phase transition.

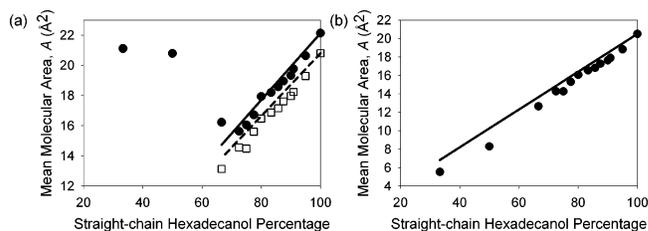


**Figure 5.** Pressure–area isotherms of mixtures of straight and branched hexadecanol. From right to left, the straight-chain percentages are 100, 95, 90.9, 90, 87.5, 85.7, 83, 80, 77.5, 75, 72.5, 66.7, 50, and 33.3.

maximum occurs in the  $LS$  phase, where the molecules are believed to be oriented vertically. This is in contrast to previous studies of a slightly longer fatty alcohol, eicosanol, by Brooks *et al.*,<sup>9</sup> where a surface viscosity maximum is observed in the  $L'_2$  phase.

**3.2. Mixed Monolayers.** Isotherms at room temperature for spread monolayers of mixtures of straight and branched hexadecanol are shown in Figure 5. An isotherm for a pure branched hexadecanol monolayer is not included since this material did not appear to form a layer that could be compressed. Indeed, the surface pressure for the pure branched material was not stable for any compressed surface areas. This suggests that although the branched chains have the same number of carbon atoms as the straight chains, it is the overall length of the aliphatic tail that is important in forming a stable Langmuir film. In ref 1, it is suggested that a backbone of at least 12 carbons in length is necessary to produce a stable monolayer.

The stable mixtures producing the isotherms pictured in Figure 5 can be broadly classified into two categories: those that produce isotherms that have the same shape as pure straight hexadecanol with only a lateral shift difference and those whose isotherms are qualitatively different. The former category includes mixtures with branched-chain concentrations up to 30 wt %, while the latter group comprises those mixtures with higher branched-chain fractions. In the former category, the isotherms indicate a first transition to a NNN tilted phase at an



**Figure 6.** (a) Average areas per molecule at the first (●) and second (□) transitions. Straight lines indicate predicted values based only on the contribution of straight-chain hexadecanol. The solid line corresponds to the solid circles; the dashed line corresponds to the open squares. (b) Average area per molecule at  $\Pi = 20$  mN/m. Again, the straight line indicates the predicted values based only on the straight-chain contribution.

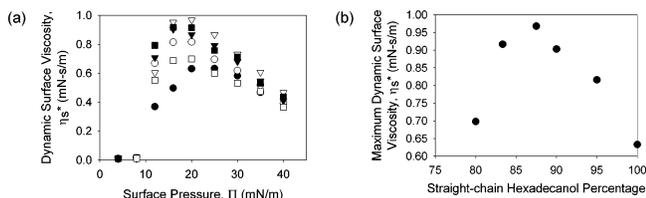
area per molecule that progressively decreases with the concentration of branched chains. Indeed, the area at which this transition occurs decreases linearly with concentration, as shown in Figure 6. This linear progression in the surface area is observed until the concentration of linear chains decreases below 70%, which marks the beginning of the second concentration regime. Here, the area marking the transition to the tilted phase increases with increasing branched-chain fraction.

For those mixtures in the former category in the tilted phase, the surface pressure increases with a compressibility that is roughly independent of composition until the transition to the untilted state. This occurs at a surface pressure that is insensitive to composition and approximately equal to 10 mN/m. The average area per molecule at this second transition is also linear with composition as shown in Figure 6a. In the untilted phase, the slopes of the isotherms are also largely invariant with respect to the branched component concentration. Finally, the collapse pressure of the mixtures is in the range of 50–55 mN/m and is independent of composition.

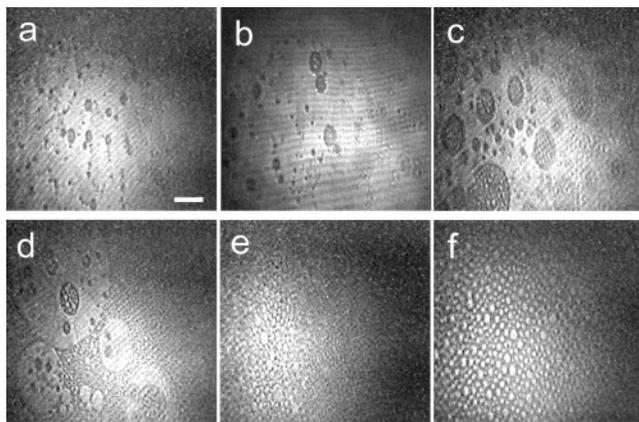
These trends highlight the extent of the immiscibility between the straight and branched chains. For branched-chain compositions less than 30%, it seems clear that the branched molecules are simply expelled from the straight-chain monolayer as soon as surface pressure begins to develop. This results in the linear shift in the liftoff area and an isotherm shape that is invariant with respect to composition. At higher branched-chain fractions, while some branched chains do remain integrated at the onset of surface pressure generation, as the system is compressed, the branched chains are again expelled from the monolayer. Figure 6b presents the mean molecular area as a function of composition when  $\Pi = 20$  mN/m. In contrast to Figure 6a, which addresses liftoff area, at higher surface pressures, the linear dependence of area on straight-chain percentage holds for all compositions studied. Additionally, the fact that the collapse pressure for all mixtures studied is independent of composition confirms the immiscibility of the two components. If the substances were miscible, the collapse pressure would be expected to vary with composition.<sup>1</sup>

The dynamic surface viscosities for various mixtures of straight and branched chains are shown in Figure 7a plotted as functions of surface pressure. As in the case of the pure straight chains, the mixtures show a pronounced maximum in the surface viscosity as a function of surface pressure. However, as branched chains are mixed with the straight chains, the maximum in the viscosity moves to smaller surface pressures and increases in magnitude. However, as seen in Figure 7b, the pressure maxima in surface viscosity also go through a maximum as a function of concentration at approximately 12.5% branched chains. The dynamic surface viscosities for hexadecanol mixtures have the same order of magnitude up to a concentration of 50% branched chains.

## D



**Figure 7.** (a) Dynamic surface viscosity of straight/branched hexadecanol mixtures as a function of surface pressure for straight-chain hexadecanol percentages of 100 (●), 95 (○), 90 (▼), 87.5 (▽), 83.3 (■), and 80 (□). (b) Maxima in the dynamic viscosities from part a as a function of mixture composition.



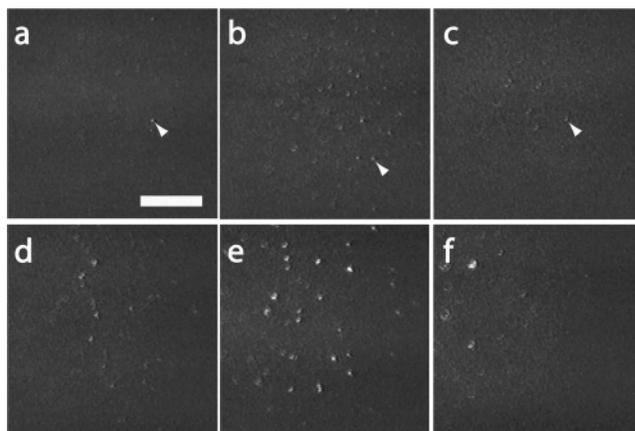
**Figure 8.** Brewster angle microscopy images of monolayers of straight/branched hexadecanol mixtures at the liftoff area. For branched chain compositions of 0% (a) and 2.5% (b), there is a light background with dark domains. For 10% branched systems, BAM imaging shows both dark domains on a light background (c) and the inverse case (d). At 25% (e) and 50% (f) branched chains, the background is dark and the round domains are light. The scale bar in part a indicates a length of 125  $\mu\text{m}$ .

Brewster angle microscopy images for a range of compositions just prior to isotherm liftoff are shown in Figure 8. For mixtures up to 5% branched hexadecanol, the images reveal a light background with many small, dark domains. At intermediate concentrations, from 10 to 15% branched chains, the same film may appear as a light background with dark domains and as a dark background with light domains in different regions. For concentrations greater than 16.7%, only a dark background with light domains are seen. The solid, round, light domains seen for 25–50% branched chains are qualitatively similar, while the solid, round, light domains for 66.7% branched chains are approximately twice as large and fewer in number density.

BAM images during compression of two straight/branched mixtures are shown in Figure 9. These images are all at pressures above the transition to the untilted phase. Once the monolayer crosses into this state, small, bright domains appear in the images and increase in number density until surface pressures between 40 and 45 mN/m are reached. Above a surface pressure of 45 mN/m, these domains diminish in number and ultimately disappear from view just prior to collapse of the monolayer at a surface pressure of 50–55 mN/m. While these domains are most visible for mixed straight/branched monolayers, films of straight hexadecanol also show these bright domains over the same surface pressure range.

## 4. Discussion and Conclusions

The principal findings of the measurements reported above are as follows: (1) for compositions below a concentration of



**Figure 9.** Brewster angle microscopy images of monolayers of straight/branched hexadecanol mixtures during their compression in the untilted phase. Images a–c are for a 10:1 straight/branched mixture, and d–f are for a 5:1 straight/branched mixture. Surface pressures: (a and d) 14 mN/m; (b and e) 30 mN/m; (c and f) 45 mN/m. The scale bar in image a indicates a length of 125  $\mu\text{m}$ .

30% branched chains, the isotherms remain similar in shape to that of the pure straight chains but are shifted in area by an amount proportional to the component composition; (2) the surface viscosity in the untilted phase initially rises with surface pressure prior to showing a maximum and then decreases as the pressure is increased toward a collapse of the layer; (3) this non-monotonic behavior in the surface viscosity is observed for the pure straight-chain system as well as the mixtures; (4) the addition of branched chains causes a non-monotonic increase in the surface viscosity as the concentration of the branched chains is increased with a maximum surface viscosity at a branched-chain concentration of about 12%; (5) BAM imaging of the monolayer mixtures reveals a population of small, discrete domains that first increase in number density before passing through a maximum in concentration as a function of surface pressure.

One interpretation of the physical processes that are occurring within these monolayer mixtures is that, for mixtures with less than 30% branched chains, the branched hexadecanol chains are easily displaced by the more efficiently packed straight chains. Although the branched hexadecanol chains contain the same number of carbon atoms, they are effectively only nine carbons long and are more easily lifted off the surface. Indeed, it is evident that all of the branched chains are forced to leave the air/water surface at the transition from the gaseous phase into the tilted phase. This effectively leaves a monolayer of pure straight chains. The light background in the BAM image for 0% branched chains is most likely due to the straight chains, while the dark spots correspond to the bare water surface. Similarly, the light background for the 2.5–5% branched chains corresponds to the straight chains, while the dark domains are filled with white spots, revealing the effect of a small fraction of branched chains on the structure. For higher concentrations of branched chains, from 10 to 15% branched chains, regions showing both a light background with dark domains and a dark background with light domains are seen. In each case, the domains are well-structured, unfilled, and generally round in shape. The images with a dark background and light domains are most likely due to islands of branched chains expelled from the monolayer. At a branched chain concentration greater than 15%, only a dark background is seen along with light domains. The light domains probably represent branched chains, which have been expelled from the monolayer into a second layer. In this case, the dark background represents the

monolayer of pure straight chains. The presence of light and dark domains in the observed BAM images confirms the immiscibility of straight and branched hexadecanol molecules in Langmuir films.

For all the hexadecanol systems studied here, we observe the formation of small, bright spots in the BAM images for surface pressures from 15 to 45 mN/m. These spots are apparent for the pure straight-chain film, although they are significantly more evident for mixed straight/branched systems. The domains grow in number density as the layer is compressed; however, this number density passes through a maximum before tending toward zero just prior to collapse of the film. Although the BAM available in our laboratory was not able to detect a microstructure for the neat straight chains in the untilted phase, it is possible that the domains formed from the branched chains are *decorating* a microstructure that exists within the straight-chain layer which nucleates the coalescence of the branched chains. The maximum that is observed in the surface viscosity of the layers in the untilted phase adds additional support to this interpretation, since the mechanical response of the Langmuir films is expected to be sensitive to such a microstructure.

Mixtures containing greater than 30% branched chains behave in a way that is qualitatively different. Evidently, the preponderance of branched chains in such mixtures ultimately forces the liftoff area to shift to a size approaching that of a branched chain. This size can be estimated by using the straight-chain cross-sectional area as a starting point. By replacing the hydrogen atoms on alternating carbons in the straight chains with the CH<sub>3</sub> groups of the branched chains, the cross-sectional area will increase, but in a manner that depends on the mobility of the structure. If the chains are unable to rotate about their axes, we estimate the area per molecule to be about 30 Å<sup>2</sup>. However, if the molecules are mobile and able to sweep out a circular area, the cross-sectional area could be as large as 50–70 Å<sup>2</sup>. As seen in Figure 5, the area per molecule rapidly increases but does not reach these estimates before the concentration of branched chains becomes too large and stable films cannot be produced. While systems in this regime behave differently at low surface pressures, as  $\Pi$  is increased, the branched chains are eventually expelled from the straight-chain film, as is the case for mixtures containing less than 30% branched chains.

## Acknowledgment

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