The Chain-Length Compatibility and Molecular Area in Mixed Alcohol Monolayers

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The average area per molecule in mixed monolayers of alkyl alcohols depends on the chain-length compatibility of the surfactant molecules. The minimum area/molecule was observed when both components possessed the same chain length. The results were interpreted in terms of the thermal motion of surfactant molecules in the monolayer. There was no significant effect of film compression rate on surface pressure–area curves of pure component films, but for mixed monolayers an increased compression rate caused significant expansion (excess area molecule). The thermal motion of additional methylene groups in higher molecular weight alkyl alcohols increases the intermolecular spacing by 0.12 A at 20 dynes/cm. This suggests that such small changes in the intermolecular spacing affect the properties of systems containing mixed surfactants.

The chain-length compatibility strikingly influences the properties of systems containing mixed surfactants or a surfactant and a paraffinic oil. Schick and Fowkes (*1*) showed that the maximum lowering of CMC (critical micelle concentration) and maximum foam stability occurred when both the anionic and nonionic surfactants had the same chain length. Lawrence (*2*) reported that the maximum emulsion stability and maximum surface viscosity of mixed monolayers occurred when both the ionic and nonionic surfactants had the same chain length. Fort (*3*) reported that the coefficient of friction between polymeric surfaces decreased strikingly as the chain length of paraffinic oils approached that of
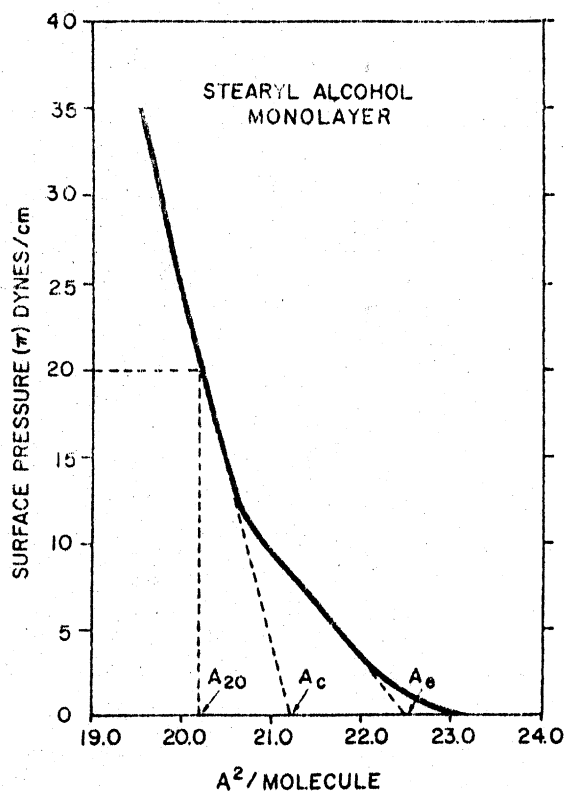
Figure 1.   Surface pressure–area curve of stearyl alcohol monolayer at pH 2.0, 25°C. Compression rate: 6.5 A²/molecule/min.

stearic acid which was used as a lubricant additive. Cameron and Crouch (4) studied the effect of chain length of fatty acids on lubrication by measuring scuff load. The maximum scuff load was observed when the fatty acid had the same chain length as that of the hydrocarbon oil. Askwith *et al.* (5) studied the viscosity of very thin layers (3.5×10^{-4} inch thickness) of oil containing fatty acids of various chain length. Here also, the maximum viscosity of the thin layers was observed when fatty acid and oil had the same chain length. Similar effects of chain-length compatibility on rust prevention and dielectric absorption were reported by others (6, 7). However, no explanation based on molecular properties has been offered to explain the chain-length compatibility effect in these systems.

The present study was designed to obtain a better understanding of the chain-length compatibility effect in terms of molecular areas of sur-

factants. Although several systems, used in the chain-length compatibility studies mentioned previously (1–7), were mixtures of ionic and nonionic surfactants, we have used the surfactants with the same polar group in our mixed monolayer studies to attribute any change in the molecular area to the chain-length compatibility. In the mixed monolayers reported here, the chain length of one component was kept constant, and that of the other component was varied from C_{16} to C_{22}.

Materials and Methods

The experiments on mixed monolayers were carried out using alkyl alcohols (C_{16}, C_{18}, C_{20}, C_{22}). These surfactants were obtained from Supelco, Inc. (Bellefonte, Pa.) with purity greater than 99+%. The C_{22} alcohol was purchased from the Applied Science Laboratories, Inc. (State College, Pa.). The solutions of all pure alkyl alcohols were prepared (concentration 0.004 M) in a mixture of chloroform, methanol, and
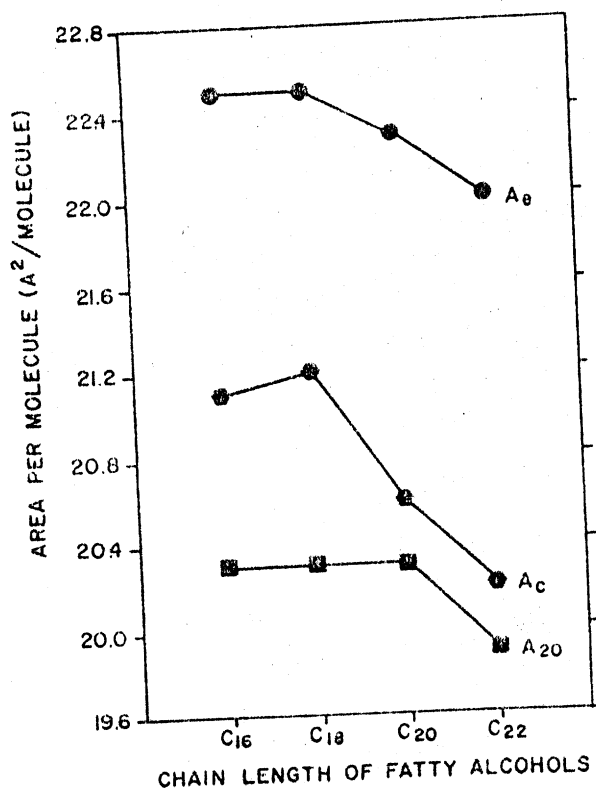
Figure 2. *Average area per molecule (A_t, A_c, and A_{20}) of various alkyl alcohols*

n-hexane (1:1:3 v/v/v). First, the single component films of alkyl alcohols were studied on the subsolution of 0.01M HCl. Next, the mixed monolayers of alkyl alcohols were studied on the subsolution of 0.01M HCl. Reagent grade chemicals and double-distilled water were used in all experiments.

The Wilhelmy plate connected to a Honeywell transducer was used to measure the surface tension which was fed directly to Y axis of an X–Y recorder. The monolayer tray was made from Plexiglass with dimensions of 25 × 12 × 1.5 cm. The temperature of the subsolution was controlled by pumping the water from a thermostated water bath through a glass coil which was immersed in the subsolution. The temperature was controlled at 25° ± 0.1°C. The subsolution was poured in the trough about 2 to 3 mm above the rim of the trough. The surface of the subsolution was cleaned by moving a wax coated glass slide from one side of the trough to the other and then sucking the impurities by a capillary con-
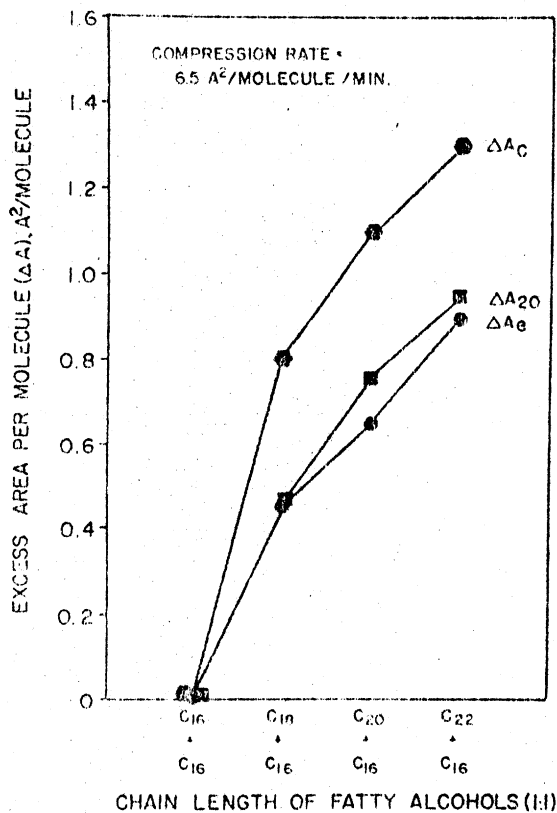

Figure 3.   Excess area per molecule of A_c, A_c, and A_{2c} vs. various alkyl alcohol mixtures (1:1 molar ratio) with C_{16} alcohol as the common component at pH 2.0, 25°C
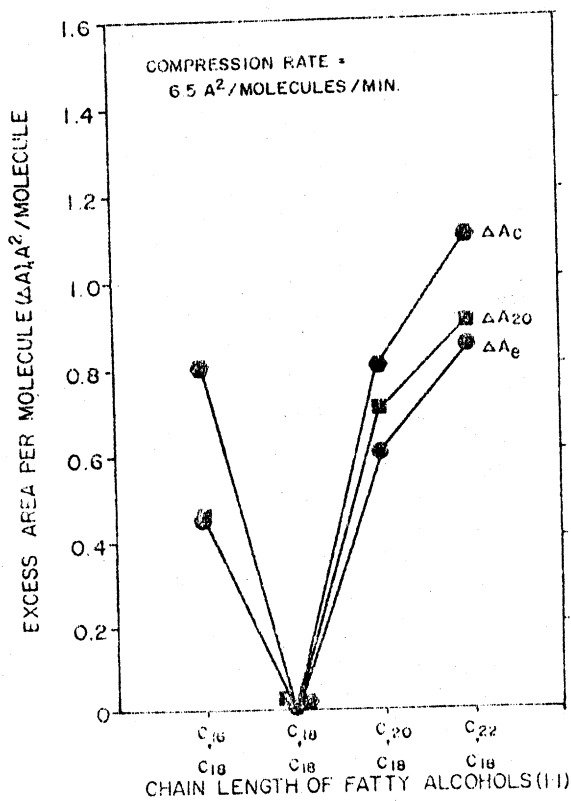
Figure 4. Excess area per molecule of A_c, A_e, and A_{20} vs. various alkyl alcohol mixtures (1:1 molar ratio) with C_{18} alcohol as the common component at pH 2.0, 25°C

nected to a vacuum pump. This was done several times to make sure no impurities remained on the surface. The monolayers were spread evenly on the surface by using an Agla microsyringe. The spreading volume of the solution was 0.025 ml for each experiment. A time interval of 5 minutes was allowed for spreading solvents to evaporate or diffuse in the subsolution from the monolayers. The monolayer was compressed at 6.5, 2.7, and 1.0 A^2/molecule/min. The motor driving the compression bar was connected to a 10-turn potentiometer which provided the potential difference proportional to the movement of the compression bar. This was connected to the X axis of the X–Y recorder. In this way, the surface pressure–area curve for a monolayer was automatically plotted on the X–Y recorder for each surfactant mixture. Three to five monolayers of each mixture were studied, and the results reported are average values. Because of the standardization of the experimental procedure such as the method of spreading, the evaporation time of solvents, and the rate of compression, the standard error of the surface pressure–area curves is ±0.15 A^2/molecule.
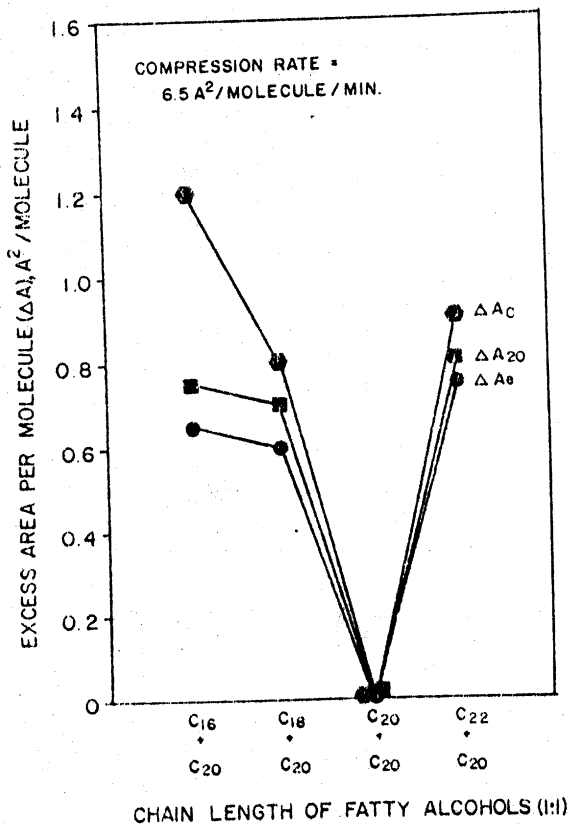
Figure 5. *Excess area per molecule of* A_c, A_8 *and* A_{20} *vs. various alkyl alcohol mixtures (1:1 molar ratio) with* C_{20} *alcohol as the common component at pH 2.0, 25°C*

Theory

If at a surface pressure, π, the average area per molecule of two surfactants in their individual monolayers is A_1 and A_2, then in the mixed monolayer (1:1 molar ratio) of these two surfactants, the average area per molecule should be $(A_1 + A_2)/2$ at the same surface pressure provided the surfactant molecules occupy the same area in the mixed monolayer as they do in their individual monolayers (8, 9). However, in many cases, the average area per molecule in a mixed monolayer is greater or smaller than that expected from the simple additivity rule (10, 11, 12). A reduction in the average area/molecule in a mixed monolayer can be attributed to the molecular attraction between the surfactants or to the "intermolecular cavity effect" (9, 13). An expansion in the average area/

molecule in a mixed monolayer can be attributed to molecular repulsion or to greater disorder in the mixed monolayer. In the present study, we have calculated excess molecular area for mixed monolayers using the following expression:

$$\text{Excess molecular area} = \left(\frac{\text{av. area}}{\text{molecule}}\right) \text{Expt.} - \left(\frac{\text{av. area}}{\text{molecule}}\right) \text{Ideal}$$

$$= (A_m)_\pi - \left(\frac{A_1 + A_2}{2}\right)_\pi$$

where A_m, is the area/molecule in the mixed monolayer and A_1, A_2 are
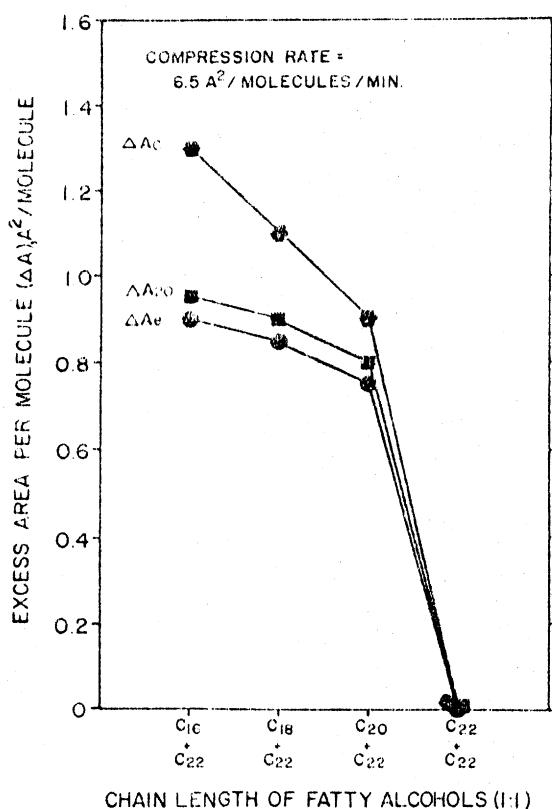

Figure 6.   *Excess area per molecule of* A_c, A_e, *and* A_m *vs. various alkyl alcohol mixtures (1:1 molar ratio) with* C_{22} *alcohol as the common component at pH 2.0, 25°C*
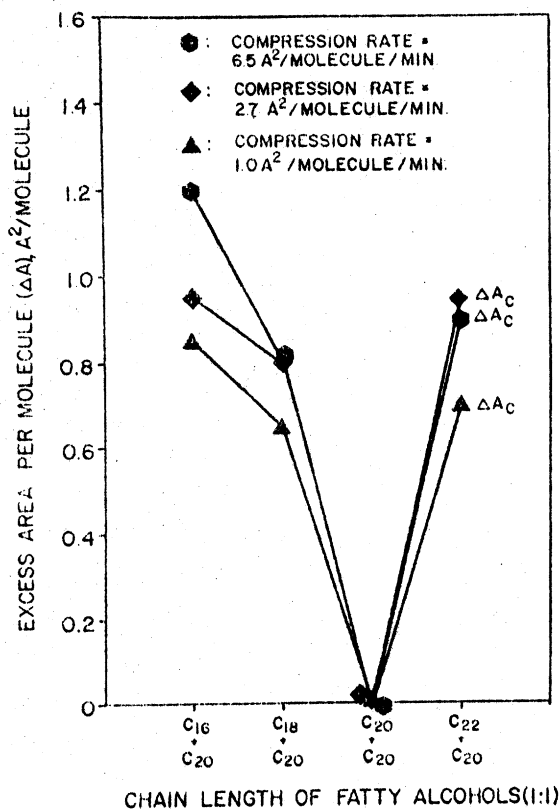
Figure 7. *Effect of the rate of compression on the excess area/molecule of A_e for various alkyl alcohol mixtures with C_{20} alcohol as a common component at pH 2.0, 25°C*

the area/molecule of the components in their individual monolayers at a specific surface pressure π.

Results

Figure 1 shows the surface pressure–area curve of stearyl alcohol monolayer at pH 2.0 and 25°C, where A_o is the area/molecule in the expanded state at zero surface pressure, A_c is the area/molecule in the condensed state at zero surface pressure, and A_{20} is the area/molecule at surface pressure of 20 dynes/cm. Figure 2 shows the values of A_o, A_c, and A_{20} for various alkyl alcohols. From this diagram the average area per molecule in mixed monolayers was calculated using simple additivity rule. Figure 3 shows the excess molecular area when C_{16} alkyl alcohol

was mixed with alkyl alcohols of various chain lengths. This result indicates that there is an expansion of the mixed monolayers compared with the molecular area calculated using the simple additivity rule. It is also evident that the greater the difference between the chain length of the components, the greater is the excess molecular area in the mixed monolayers. It is also evident that A_e is most strikingly influenced by the differences in chain length. Figures 4, 5, and 6 show the results on the excess molecular area when the common components in the mixed monolayers were C_{18}, C_{20}, and C_{22} alkyl alcohols, respectively. Note that the extremely small values of excess area/molecule shown in Figures 3 to 6 were not measured directly. The area/molecule values in the mixed monolayers were measured experimentally and showed considerable expansion when compared with the surface pressure–area curves of pure components. The excess area/molecule is the difference between the experimentally obtained area/molecule in the mixed monolayers and that expected from the simple additivity rule.

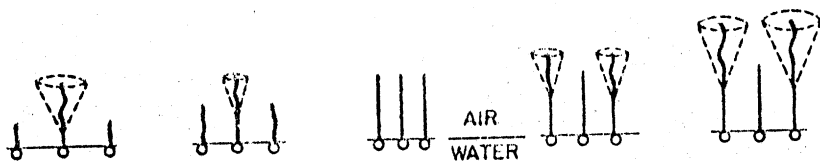----- SPACE OCCUPIED BY THE THERMAL MOTION OF CHAINS

Figure 8. Schematic of the thermal motion of the upper segments of hydrocarbon chains at the air–water interface. The cones shown by broken lines represent the time-average space occupied by the thermal motion of the segments.

Figure 7 shows the effect of the rate of compression on the excess area/molecule in A_e for various alkyl alcohol mixtures with C_{20} as a common component. There seems to be a small increase in excess area/molecule at a faster rate of compression. Similar rate-of-compression effects were observed also with the mixed monolayers containing C_{16}, C_{18}, or C_{22} alcohol as common component. The area/molecule of pure components did not exhibit any significant dependence on the compression rates used in this present study. The area/molecule values of pure components at various compression rates were within experimental error (± 0.15 Å^2/molecule) at any given surface pressure.

Discussion

The results on the surface pressure–area curve of stearyl alcohol monolayer shown in Figure 1 and the area/molecule of other alkyl alco-

hols shown in Figure 2 agree with the results reported for some of these alkyl alcohols by others (*14, 15*). Figure 3 shows that the values for the excess molecular area of A_e are 1.3, 1.1, and 0.8 A^2 per molecule for the difference of six, four, and two methylene groups between the common component and the longer alkyl alcohols.

In the previous studies on the chain-length compatibility (*1–7*), the only explanation suggested for the observed effects was the term "the best fit" of surfactant molecules. Our explanation for these chain-length compatibility effects is shown schematically in Figure 8 based upon the monolayer studies. When the chain lengths of the two components are equal, the mixed film will be very condensed. However, when the chain length is different, the portion of molecules above the height of the adjacent molecules will exhibit thermal motion (vibrational, oscillational, and rotational modes). If this thermal disturbance were limited to the portion above the height of the adjacent molecules, it would not change the average area per molecule. However, this disturbance presumably propagates along the chain at a considerable length towards the polar group of the molecule. Therefore, the mixed monolayers will be more expanded and hence exhibit a greater average area per molecule. As the difference in the chain length increases, the corresponding thermal disturbance and expansion will also increase because the length of the segment undergoing rotation, vibration, and oscillation increases. Figure 8 schematically shows the thermal motion of these segments and its effect propagating considerably below the height of the adjacent molecules. The time–average space occupied by this segment of methylene groups is shown by a cone with dashed lines. The concept of thermal motion of hydrocarbon chains at the interface was advanced by N. K. Adam (*16*) in his classical book on the physics and chemistry of surfaces. We have also used this concept to propose the existence of intermolecular cavities in mixed monolayers which may be responsible for an apparent condensation in lecithin–cholesterol monolayers (*8, 9, 10, 13*). A similar concept was also used by Bruun (*17*) to explain his results on mixed monolayers of isodextropimaric acid and straight chain fatty acids.

Philips *et al.* (*18*) reported that in mixed monolayers of dioleoyllecithin–distearoyllecithin, the area/molecule showed expansion from the additivity rule because the unsaturated fatty acid chains increased the kinetic motion of saturated chains. However, in contrast to the studies here on $C_{16} + C_{18}$ alcohols, they found no expansion in the mixed monolayers of dipalmitoyllecithin–distearoyllecithin.

It is interesting that the rate of compression did not influence significantly the area/molecule in the monolayers of pure components. However, for mixed monolayers, there was a small but significant increase in

the excess area/molecule with increase in the rate of compression (Figure 7). This suggests that perhaps the disordered segments of hydrocarbon chains may begin to orientate themselves in a more ordered state, resulting in smaller excess area/molecule as one decreases the rate of compression.

We have shown (10, 19, 20) that a change of 0.3 to 1.5 A in the intermolecular spacing between lipid molecules in the monolayer strikingly influences the interaction of metal ions and enzymic hydrolysis in monolayers. One can calculate the intermolecular spacing in monolayers by assuming the average area per molecule to be a circle and then calculating the radius R. The distance $2R$ will be the intermolecular spacing in the monolayer which is the distance between the centers of the adjacent molecules. For example, in mixed monolayers of $C_{16} + C_{22}$ alkyl alcohols, (Figures 3 and 6) where an excess molecular area of 0.95 A^2 was observed at 20 dynes/cm, we can calculate the increase in the intermolecular spacing caused by mixing. For the mixed monolayers of $C_{16} + C_{22}$ alkyl alcohols, the average area per molecule based upon simple additivity rule at a surface pressure of 20 dynes/cm is 20.10 A^2 per molecule. The experimentally observed area per molecule is 21.05 A^2 per molecule. The corresponding radii for the circles of these areas are calculated to be 2.53 and 2.59 A respectively. Hence, the intermolecular spacing ($2R$) for these two molecular areas would be 5.06 and 5.18 A. Therefore, the difference between these two intermolecular spacings represents the expansion in the intermolecular spacing caused by the excess molecular area which is induced by the thermal motion of chain segments in the mixed monolayer. The increase in the intermolecular spacing caused by expansion of the monolayer would be 0.12 A (5.18 − 5.06 = 0.12 A). These calculations suggest that a change in the intermolecular spacing of the order of 0.12 A must be of significant importance in determining the properties of mixed surfactant systems and phenomena such as foams, emulsions, as well as lubricants, and dielectric absorption by paraffins.

Summary

The excess area per molecule in the mixed monolayers of alkyl alcohols of dissimilar chain length is a minimum when the two components have the same chain length. The expansion of mixed monolayers arising from unequal chain length is presumably caused by the thermal motion of the hydrocarbon chains. The thermal motion increases the intermolecular spacing in the monlayer by about 0.12 A at a surface pressure of 20 dynes/cm. In view of the observed effects of chain-length compatibility in foams, emulsions, and lubrication it is proposed that such small changes in intermolecular spacing are important in determining the properties of the above systems.

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