Molecular Interactions in Monolayers: Molecular Association and Foam Stability of Fatty Acids and Alcohols[1]

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Abstract

Surface pressures and potentials of monolayers of stearic acid and of mixed monolayers of stearic acid-stearyl alcohol (1:1 and 1:3 molar ratios) were measured on buffered subsolutions at various pH values. The molecular area-pH plot for these monolayers at a surface pressure of 10 dynes/cm showed a maximum at pH 9.0. The average area per molecule in the mixed monolayers decreased at pH 9, as the per cent of stearyl alcohol was increased. The foam characteristics of decanoic acid, and 1:1 and 1:3 mixtures of decanoic acid-decanol solutions were studied at various pH values. At pH 9.0, foams of decanoic acid and of 1:1 mixture of decanoic acid-decanol had least stability. In contrast, the foam of the 1:3 mixture had maximum stability at pH 9.0. The results suggest that a stoichiometric association between a fatty acid and an alcohol strikingly influences the foam stability.

Introduction

Interactions in mixed monolayers have been of great interest in relation to molecular aspects of foam stability, emulsion formation, retardation of evaporation by films and reactions occurring at the cell surface. Various investigators have studied the mixed monolayers of fatty acids and alcohols using surface pressure, potential and viscosity measurements (1–3).

We have shown (4,5) previously that on subsolutions of tris buffer + NaCl at pH 8.8, stearic acid and stearyl alcohol form a stoichiometric association in a 1:3 molar ratio, which gives a minimum area per molecule. We have extended these studies further to correlate the monolayer characteristics of fatty acids and alcohols with the foam stability of their solutions at various pH values.

In the present paper the monolayers of stearic acid and the mixed monolayers of stearic acid-stearyl alcohol in molar ratios 1:1 and 1:3 were investigated over the pH range 2 to 13 by using surface pressure and potential measurements. Foam stability of solutions of decanoic acid, and of corresponding mixtures of decanoic acid-decanol were also studied at various pH values. The objective of the present study was first to investigate the influence of pH, and therefore, of ionization of carboxyl groups, and secondly of the presence of alcohols on monolayer and foam characteristics of fatty acids.

Experimental Procedures

Materials

Highly purified (>99%) stearic acid and stearyl alcohol were purchased from Applied Science Laboratories, Inc., (State College, Pa.). 1-Decanoic acid and 1-decanol of similar purity were purchased respectively from K & K Laboratories, Inc. (Plainview, N.Y.) and Humphrey Chemical Co. (North Haven, Conn.). For spreading monolayers, lipid solutions of 0.8 to 1.0 mg/ml concentration were prepared in methanol-chloroform-hexane (1:1:3) mixture. All solvents were of spectroscopic grade. Inorganic chemicals of reagent grade, and distilled-deionized water were used in all experiments. For pH close to 2, solutions of 0.05 M HCl were used; for pH 3 to 6, buffer solutions of citric acid-sodium citrate were used; for pH 7 to 9, buffer solutions of tris-HCl were used; for pH 10 to 11, buffer solutions of glycine-NaOH were used; for pH 12 to 13, solutions of 0.05 M and 0.1 M NaOH were used, respectively. All buffer solutions were of ionic strength 0.05 and were prepared according to the Biochemists' Handbook (6).

Methods

The surface pressure was measured by a modified Wilhelmy plate method, and the surface potential was determined by using a radioactive electrode as described previously (7).

One milliliter (≈0.9 g) of decanoic acid or decanoic acid-decanol (1:1 or 1:3) mixture was added to 20 ml of various buffer solutions in 100 ml glass-stoppered cylinders, and the solutions were shaken vigorously for 1 min. The foam height was then recorded at various time intervals. All measurements were carried out at 22 C and the results were not altered significantly by fluctuations in temperature of ±2 C.

Results and Discussion

Monolayer Studies

Figure 1 shows the average area per molecule plotted against pH of the subsolutions for stearic acid and stearic acid-stearyl alcohol monolayers at a surface pressure of 10 dynes/cm. The maximum area per molecule of stearic acid at pH 9 is presumably due to maximum repulsion or to the penetration of buffer ions in the monolayer at this pH. There is also considerable repulsion between molecules in stearic acid monolayers at pH 13. However, when the surface concentration of stearic acid is diluted by the addition of stearyl alcohol, as in the case of 1:1 and 1:3 mixed monolayers of stearic acid-stearyl alcohol, the average area per molecule decreases at pH 9 and 13. At pH 10.8, the average area per molecule for stearic acid monolayers is 16.5 A^2, which is less than that expected for a hydrocarbon chain (≈18 A^2). This may be due to slight solubility or structural rearrangement of ionized stearic acid molecules in the monolayer at this pH.

Figure 2 shows surface potential values of these monolayers at 20 A^2 per molecule. It is evident that the decrease in surface potential by increasing pH depends upon the fraction of stearic acid present in the monolayer.

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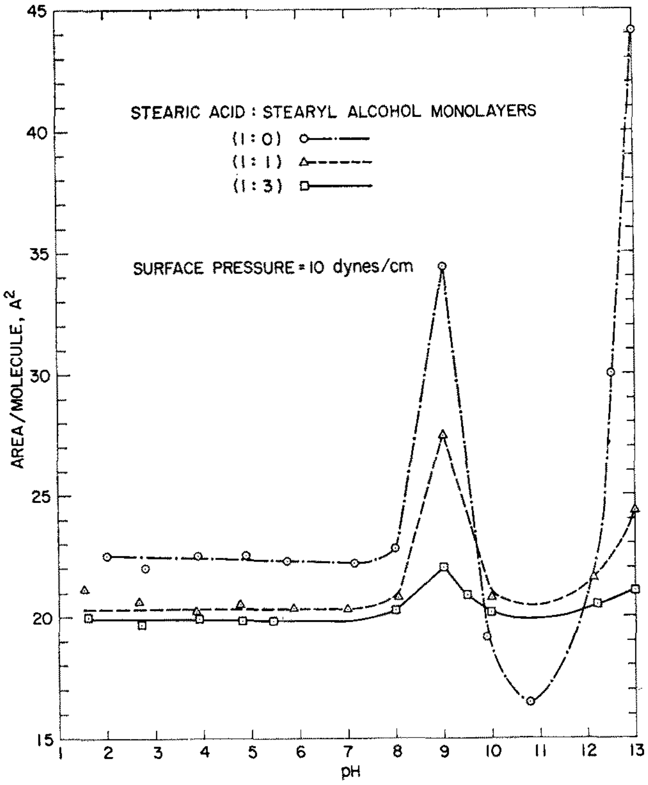

FIG. 1. Average area per molecule for monolayers of stearic acid and mixed monolayers of stearic acid-stearyl alcohol in 1:1 and 1:3 molar ratios on buffered subsolutions at various pH values at a surface pressure of 10 dynes/cm, 22 C.

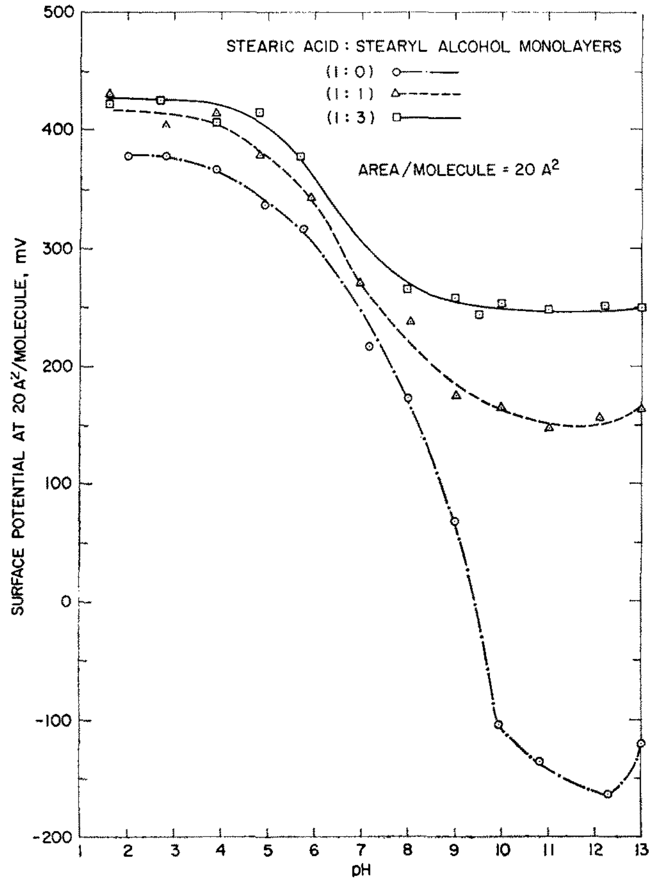

FIG. 2. Maximum surface potentials of monolayers of stearic acid and of mixed monolayers of stearic acid-stearyl alcohol in 1:1 and 1:3 molar ratios on buffered subsolutions at various pH values.

Figure 3, which is derived from the data in Figure 2, shows the values of $\frac{-\delta(\Delta V)}{\delta \, pH}$ plotted against the pH of various subsolutions. The term $\frac{-\delta(\Delta V)}{\delta \, pH}$ represents a change in surface potential caused by a small change in the pH of the subsolutions. It is clear from Figure 3 that the maximum rate of change in the surface potential occurs at pH 9.5, 6.9 and 6.7 respectively for monolayers of stearic acid, and for mixed monolayers of stearic acid-stearyl alcohol in 1:1 and 1:3 molar ratios.

It has been shown by Mattson and Volpenhein (8), and Benzonana and Desnuelle (9) from their titration studies of oleic acid that 50% ionization occurs at pH 8.8. Rosano and Feinstein (10) have reported from their studies on titration of micellar solutions of potassium laurate that buffering action occurs near pH 9.3. Bagg et al. (11) have analyzed skimmed monolayers of stearic and behenic acids from sodium containing subsolutions. They have reported that the pK value of the fatty acid monolayers is close to 8.9. Christodoulou and Rosano (12) have also reported that the pK value of stearic acid and behenic acid is close to 9.3 from surface potential measurements. From these results as well as from the monolayer and foam studies presented in this paper, it is concluded that at pH 9, where about 50% of fatty acid molecules are ionized (i.e., pK $\approx$ 9), *maximum separation exists between the fatty acid molecules in the presence of tris buffer* (since the area per molecule is maximum at pH 9).

If we consider the pK in monolayers as the pH value at which maximum change in surface potential occurs, then the pK values of carboxyl groups in monolayers of stearic acid, and 1:1 and 1:3 mixed monolayers of stearic acid-stearyl alcohol are 9.5, 6.9 and 6.7 (Fig. 3). The change in pK values can be explained as follows. If fatty acid molecules are packed closely in a monolayer, the carboxyl groups are no longer independent of one another, as they are in molecularly dispersed solutions such as is the case in a solution of acetic acid. This causes a cooperative phenomenon in the monolayer surface in which removal of a hydrogen ion involves work not

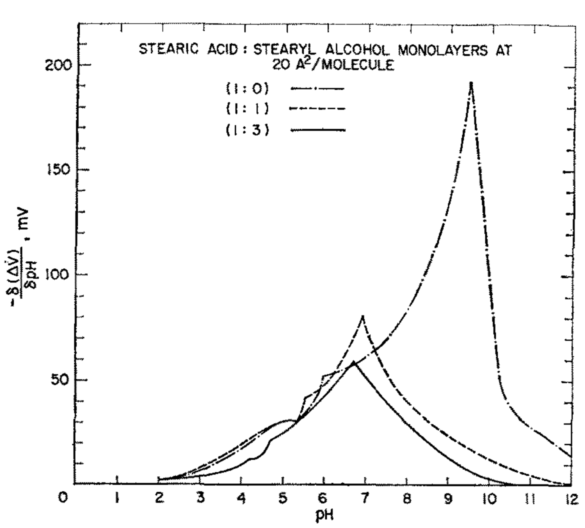

FIG. 3. $\frac{-\delta(\Delta V)}{\delta pH}$ —pH plots for monolayers of stearic acid and mixed monolayers of stearic acid-stearyl alcohol in 1:1 and 1:3 molar ratios on buffered subsolutions at various pH values.

against a single carboxyl group, but against all carboxyl groups in the vicinity of this hydrogen. Therefore, the pK of stearic acid in monolayers is as high as 9.5 compared to 4.8 for acetic acid in solution. However, when carboxyl groups are spaced apart by stearyl alcohol in mixed monolayers, there is less interaction between carboxyl groups, therefore the pK is 6.9 and 6.7 for 1:1 and 1:3 mixed monolayers of stearic acid-stearyl alcohol. Consequently, in general the closer the carboxyl groups the higher the pK. It should be noted that the presence of divalent cations (13,14) or of monovalent cations in high concentrations decreases the pK of fatty acids by 2 or 3 units (i.e., pK $\approx$ 6.0).

Figure 3 also shows a small hump at pH 4.5 or 5.0, which is presumably due to initial ionization of carboxyl groups; subsequent ion-dipole interaction results in the hump in the $\frac{-\delta(\Delta V)}{\delta \, \mathrm{pH}}$ −pH plot. The observation that binding of Ca^{++} to stearic acid monolayers begins to occur at pH 5 also supports this conclusion (13,14).

Foam Studies

Figure 4 shows foam characteristics of decanoic acid in various buffer solutions which were the same as those used in the monolayer studies, 5 min, 5 hr and 16 hr after foam formation. Two major conclusions which are evident from this figure are: first, decanoic acid does not produce foam below pH 7.0; and second, at pH 9 the foam has the least stability. The solution remaining under the foam at pH 9 is transparent, whereas at other pH values it is opaque. The characteristics of foam at pH 9 can be explained as follows. Since fatty acid molecules have the maximum area per molecule at pH 9.0, the intermolecular spacing is greatest in the monolayer and presumably in the foam lamellae. This reduces the surface viscosity in the lamellae and consequently gives the largest amount of foam. However, the separation between molecules in the lamellae causes a rapid rate of thinning and the foam collapses within 2 hr at pH 9. The solution at pH 9 is transparent, suggesting that the decanoic acid is molecularly dispersed in the solution and that they do not form aggregates of a size large enough to give the solution the opaque appearance observed at other pH values.

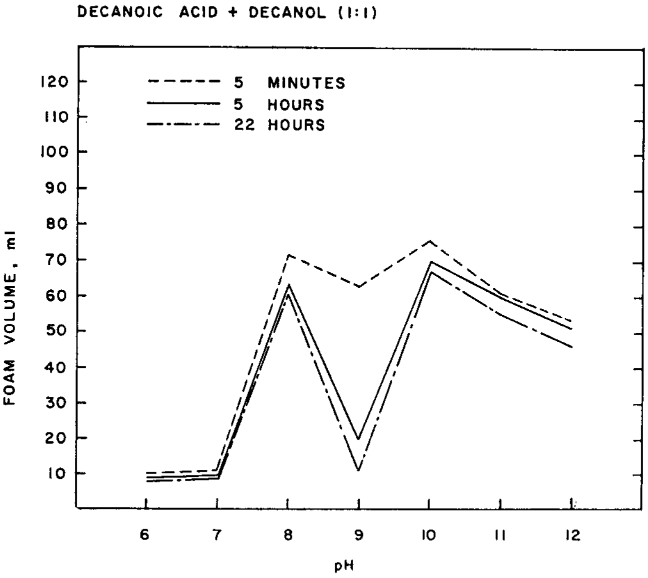

Fig. 5. Foam volume of 1:1 molar mixtures of decanoic acid-decanol in buffered solutions at various pH values 5 min, 5 hr and 22 hr after formation of foams, 22 C.

To investigate the effect of dilution of carboxyl groups, the foam characteristics of 1:1 mixture of decanoic acid-decanol were studied 5 min, 5 hr and 22 hr after foam formation (Fig. 5). It is evident that the foam at pH 9 has the least stability. Therefore, it appears that the properties of decanoic acid are not significantly influenced by the presence of equal amounts of decanol in the solution.

We have shown previously (4,5) that at pH 8.8 stearic acid and stearyl alcohol form a molecular complex in a 1:3 molar ratio which gives a minimum average area per molecule. Therefore, we decided to study the foaming properties of decanoic acid/decanol (1:3) mixture at various pH values (Fig. 6). In contrast to pure decanoic acid or 1:1 mixture of decanoic acid-decanol, the foam stability of the 1:3 mixture of decanoic acid-decanol is maximum at pH 9.

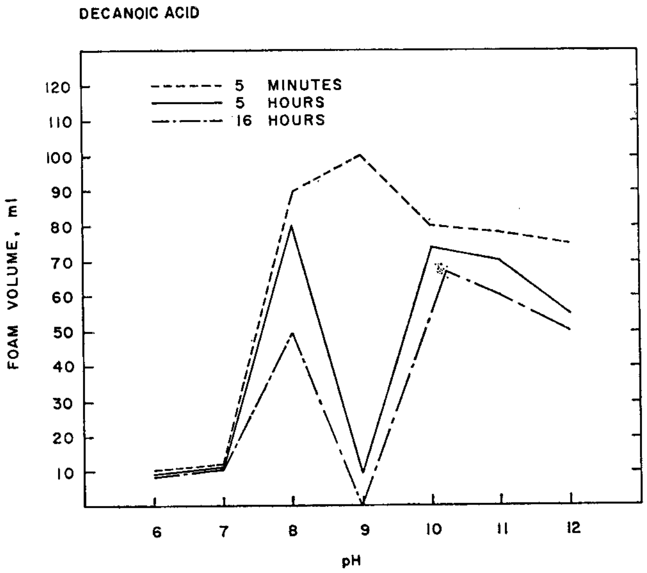

Fig. 4. Foam volume of decanoic acid in buffered solutions at various pH values 5 min, 5 hr and 16 hr after formation of foams, 22 C.

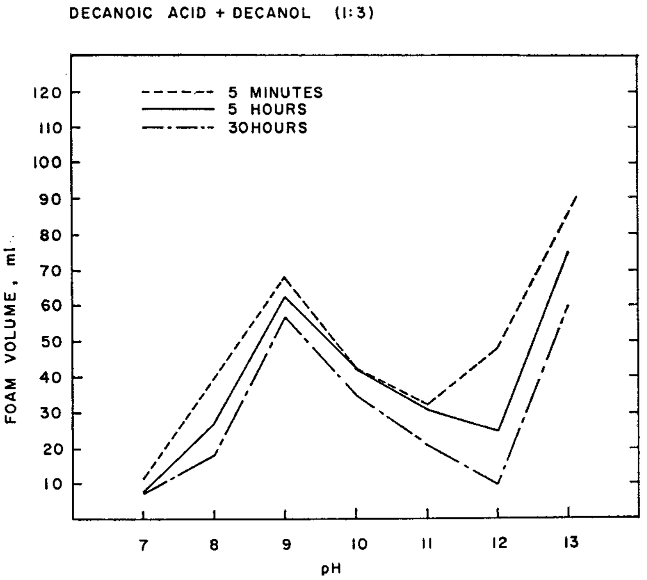

Fig. 6. Foam volume of 1:3 molar mixtures of decanoic acid-decanol in buffered solutions at various pH values, 5 min, 5 hr and 30 hr after formation of foams, 22 C.

These results suggest that the molecular association in a 1:3 molar ratio between the fatty acid and alcohol reduces the area per molecule and increases the foam stability at pH 9 (Figs. 1 and 6). It is also evident that a 1:3 molecular complex of decanoic acid-decanol has completely opposite foam stability to those of pure decanoic acid or 1:1 mixture of decanoic acid-decanol at pH 9.0. The increase in the foam stability at pH 9 is presumably due to increase in surface viscosity of the 1:3 mixed films because of the decrease in area/molecule. Davies (15) has reported that the increase in foam stability of sodium laurate solutions in the presence of lauryl alcohol is due to the increase in surface viscosity caused by this additive.

It should be emphasized that the results reported in this paper indicate that the influence of the fatty alcohol on foam stability is optimum at a specific molar ratio which depends upon the pH of the solution. These studies also indicate that information obtained from mixed monolayers may explain foam characteristics.

ACKNOWLEDGMENTS

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