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The Effect of Buffer Ions on Stearic Acid Monolayers in Relation to Foam Stability[1]

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Surface pressures and potentials of stearic acid monolayers were measured on buffered subsolutions at various pH values. The molecular area-pH plot for stearic acid monolayers at a surface pressure of 10 dynes/cm showed a maximum at pH 9.0. The surface potentials of stearic acid monolayers also showed a sharp change at about pH 9. The foaming characteristics of decanoic acid were studied at various pH values, which showed that the foam produced at pH 9.0 in tris-HCl buffer had the least stability. It is suggested from surface measurements that the maximum expansion of stearic acid monolayers on tris-HCl buffer at pH 9 is due to maximum repulsion between stearic acid molecules or to penetration of tris ions into the monolayer. This effect also reduces the foam stability of decanoic acid at pH 9.

INTRODUCTION

Earlier work on fatty acid monolayers was reported by Langmuir (1), Adam (2), and Schulman and Rideal (3–5). Using surface potential (ΔV) measurements, Schulman and Hughes (6) showed that the ΔV-pH plot for myristic acid monolayers resembled the titration curve for fatty acid solutions. This was followed by investigations from various laboratories, which have been summarized in recent review articles by Dervichian (7) and Shah (8). Most of these studies were done with subsolutions which were not buffered. The present studies report results with buffered subsolutions. The objective of the present study was to investigate fatty acid monolayers at various pH values and to correlate the surface properties with their foaming characteristics.

EXPERIMENTAL

Materials. The highly purified stearic acid was the same as used in the previous studies (9). Decanoic acid (purity > 99.5%) was purchased from K & K Laboratories, Inc. (Plainview, New York). 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 3–6, buffer solutions of citric acid-sodium citrate were used; for pH 7–9, buffer solutions of tris-HCl were used; for pH 10–11, buffer solutions of glycine-NaOH were used; for pH 12–13, 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 *Biochemists' Handbook* (10).

Monolayer Studies. The surface pressure was measured by a modified Wilhelmy plate method, and surface potential by a radioactive electrode as described previously (11). The state of the monolayers at about 20 Å²/molecule was determined by the talc method (12).

Foam Studies. The foams were studied in the following manner: 1 ml of warm decanoic acid (mp 31.5°C) was added to 20 ml of various buffer solutions in each 100 ml glass-stoppered cylinder, and the mixtures were shaken vigorously for 1 min. The foam characteristics were recorded and the cylinders were photographed at various time intervals.

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RESULTS

Monolayer Studies. Figure 1 shows the surface pressure-area curves of stearic acid monolayers on buffered subsolutions at different pH values. It is interesting to note that the surface pressure-area curve at pH 9.0 shows considerably higher initial surface pressure than that at pH 8 or 10. Figure 2 shows the molecular area of stearic acid at a surface pressure of 10 dynes/cm for various pH values. The plot of molecular area-pH shows a maximum at pH 9.0. It shows that a stearic acid molecule occupies a considerably larger area at pH 9 than at pH 8, 10, or 11, at a surface pressure of 10 dynes/cm.

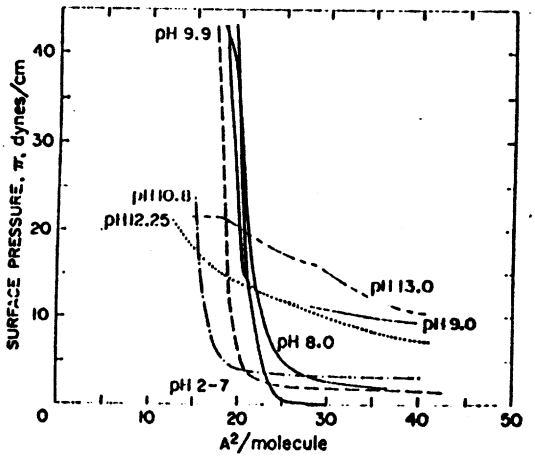

FIG. 1. Surface pressure-area curves of stearic acid monolayers on buffered subsolutions at various pH values at 22°C.

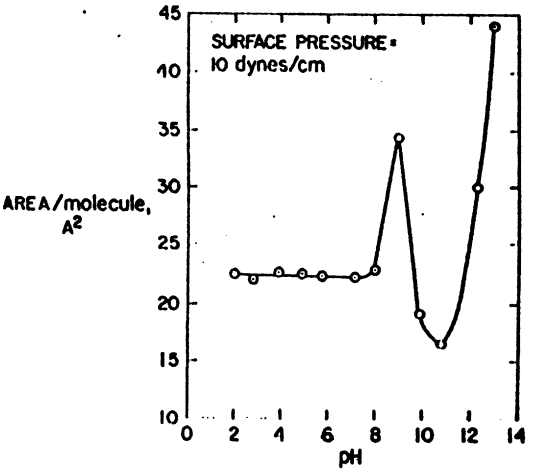

FIG. 2. Average molecular area of stearic acid at various pH values at a surface pressure of 10 dynes/cm.

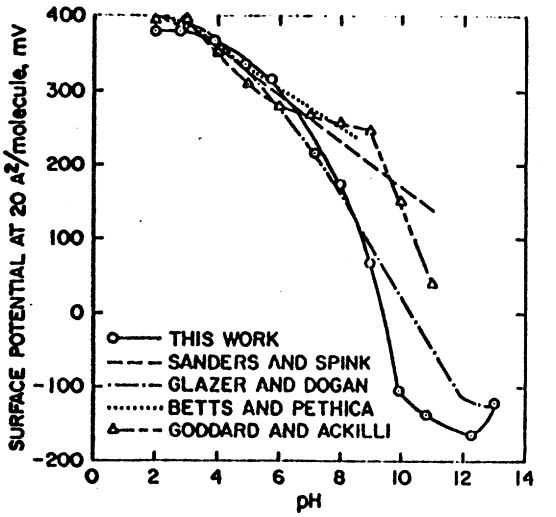

FIG. 3. Maximum surface potentials of stearic acid monolayers near 20 Å²/molecule at various pH values. Experimental data of other workers are included.

Figure 3 shows the maximum values of surface potentials of stearic acid monolayers at about 20 Å² per molecule at various pH values. For comparison, the surface potentials of stearic acid monolayers reported by other investigators are also shown in Fig. 3. Figure 4, which is plotted from the data in Fig. 3, shows the values of $-\delta(\Delta V)/\delta pH$ plotted against the pH of various subsolutions for stearic acid monolayers. The term $-\delta(\Delta V)/\delta pH$ represents a change in surface potential caused by a small change in the pH of the subsolution. It is evident from Fig. 4 that the maximum rate of change in the surface potential occurs at pH 9.5. However, there is also a small "hump" in the plot at pH 5.0.

It has been shown (9) that the term $\Delta V/n$ represents an average potential per molecule, which is also proportional to the surface dipole moment of the molecule (i.e., $\Delta V/n = K\mu = \Delta V \times 10^{-16}$ area per molecule in square Ångstroms). This parameter was found to be very useful for investigating interactions in mixed monolayers (9,12). Figure 5 shows the average potential per molecule $(\Delta V)/n$ plotted against the pH of subsolutions. The values of $\Delta V/n$ were calculated at a surface pressure of 10

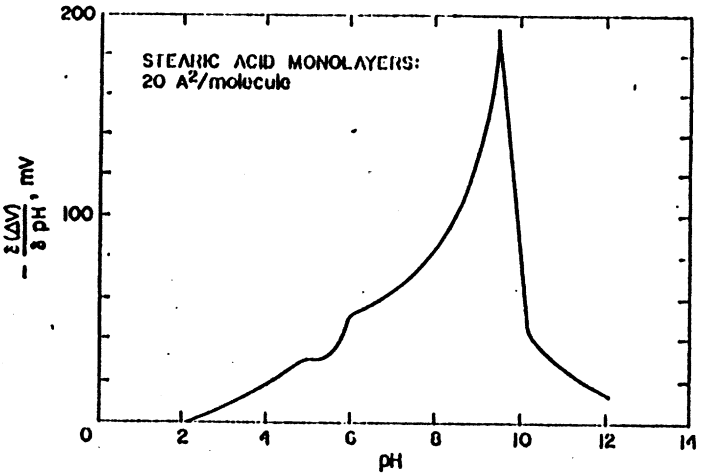

FIG. 4. Plot of $-\delta(\Delta V)/\delta pH$ - pH for stearic acid monolayers on buffered subsolutions at 22°C.

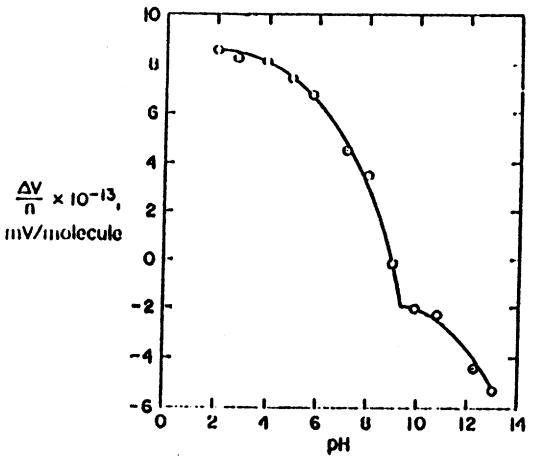

FIG. 5. Average potential per molecule ($\Delta V/n$)-pH plot for stearic acid monolayers on buffered subsolutions, 22°C, at a surface pressure of 10 dynes/cm.

dynes/cm. Here again, the average potential per molecule shows a sharp transition at pH 9.4 (Fig. 5).

Table 1 summarizes the state of stearic acid monolayers at 20 Å²/molecule for various pH values. For pH values 2–6, stearic acid monolayers are in the liquid state, whereas at pH 7–8, the monolayers are in the solid state near their limiting areas (≃20 Å²/molecule). For pH values between 9 and 12, the monolayers are in the gel state near the collapse pressure; however, it was inferred from the movement of talc particles that the surface viscosity gradually increased with the pH of the subsolution (Table 1). The transition from the liquid to the gel state takes place at rather low surface pressures in these monolayers.

Foam Studies. Figures 6 and 7 show the foam characteristics of decanoic acid at various pH values 5 min and 5 hours after formation of foams. It is evident that the foam at pH 9.0 has the largest volume and the least stability. Moreover, it is clear that decanoic acid does not produce foams below pH 7. The foam at pH 9 collapsed within 2 hours, whereas for other pH values it survived for more than 16 hours.

DISCUSSION

Monolayer Studies. Figure 1 shows the surface pressure-area curves of stearic acid monolayers on buffered subsolutions at various pH values. At pH 9.0, the initial surface pressure is considerably greater than that at other pH values (except pH 12–13). This suggests that the maximum expansion of stearic acid monolayers at pH 9 on subsolutions of tris-HCl buffer may be due to maximum repulsion between stearic acid molecules in the monolayer. Alternatively, it is also possible that the expansion at pH 9 is due to penetration of buffer ions (tris) into the monolayer. This effect may depend upon the concentration of tris ions since tris-HCl buffer at pH 7 and 8 does not cause such striking expansion of the monolayers.

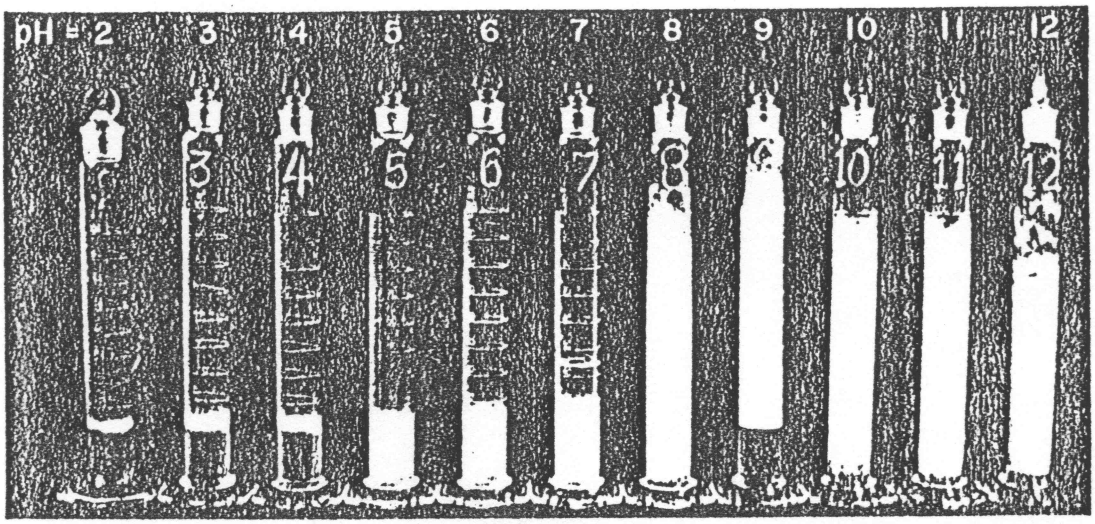

FIG. 6. Foam characteristics of decanoic acid in buffered solutions at various pH values 5 min after formation of foams, 22°C; 1 ml of decanoic acid is added to 20 ml of buffer solution in each cylinder.

It is difficult at this stage to prefer one mechanism over the other since we find that with various buffer subsolutions in the pH range 8–10, the initial surface pressure level in the plateau region increases with pH. The monolayers on subsolutions of tris buffer in the pH range 8–10 exhibit considerably greater initial surface pressure levels than those on other buffers.[3] The maximum in molecular area at pH 9 persists even in the 1:1 mixed monolayers of stearic acid and stearyl alcohol (13). The expansion in molecular area cannot be attributed to the presence of polyvalent metal ion impurities since, in general, this would tend to condense the monolayers. Moreover, the presence of a small amount of EDTA ($\approx 10^{-4}$ *M*) added to the subsolution did not influence this maximum in the molecular area. For pH 2–9, the limiting area of stearic acid is approximately the same ($\approx$20 Å^2/molecule), implying that the monolayers are stable in this pH range during the time interval of compression ($\approx$10 min). The reduction in the molecular area at pH 11–12 may be due to slight solubility or to structural changes in the monolayer (Fig. 2). The presence of 50 to 75 mole % of stearyl alcohol in stearic acid monolayers yields also a maximum in area per molecule at pH 9 and the molecular area of $\approx$20 Å^2 in the pH range 10–12 (13).

Previous workers (6,14,15) who also studied fatty acid monolayers as a function of pH failed to notice this maximum, presumably owing to their use of unbuffered subsolutions, though Goddard *et al.* (16)

[3] Our recent studies (unpublished) using subsolutions of HCl-Ammonia (pH 8.0–9.9), glycine-NaOH (pH 9.0–10.7), $NaHCO_3$-Na_2CO_3 (pH 9.0–10.6), boric acid-NaOH (pH 8.6–10.0), and tris-HCl (pH 8.0–9.4) buffers showed that with all these buffers the initial surface pressure level of the plateau region in the surface pressure-area curve increased with pH. If we assume that the initially high surface pressure level at pH 12–13 is due to ionic repulsion between molecules, then with all these buffers, the increasing initial surface pressure levels are due to ionization of carboxyl groups in the monolayer. However, the increase in the initial surface pressure level was maximum for tris-HCl buffer and minimum for $NaHCO_3$-Na_2CO_3 buffer. The other three buffer subsolutions showed approximately the same increase in surface pressure levels intermediate between those shown by tris-HCl and $NaHCO_3$-Na_2CO_3 buffers. This difference can be attributed either to the effect of various buffer ions on the degree of ionization of carboxyl groups or to the varying extent of penetration of these buffer ions in the monolayers. When C_{20} or C_{22} monolayers are studied on these buffers, the expansion effect is eliminated presumably because of increased cohesion between hydrocarbon chains.

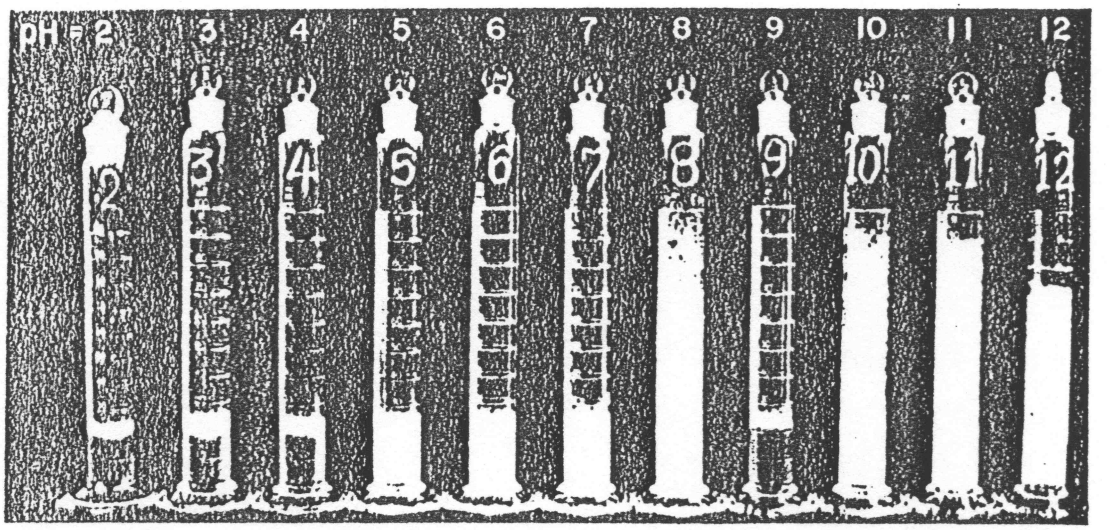

FIG. 7. Foam characteristics of decanoic acid in buffered solutions at various pH values 5 hours after formation of foams, 22°C.

have reported expansion of stearic, arachidic, and behenic acid monolayers on subsolutions of tetramethyl- and tetraethylammonium hydroxides.

Figure 3 shows the maximum surface potentials of stearic acid monolayers at various pH values at about 20 Å²/molecule. For a comparison, the data of other investigators are also plotted in Fig. 3. Betts and Pethica (17) and Sanders and Spink (18) used unbuffered subsolutions at high pH values. In the present work, the surface potentials at high pH values are considerably lower than those reported by other workers. This is presumably due to a greater extent of ionization or to interaction of buffer ions with the monolayers on buffered subsolutions.

Figure 4 is a $-\delta(\Delta V)/\delta pH$-pH plot derived from the data presented in Fig. 3. It shows that the maximum change in the surface potential of stearic acid monolayers occurs at pH 9.4. However, Fig. 4 shows a small "hump" at pH 5.0, which occurred at pH 4.0 in the work reported by Betts and Pethica (17). This presumably indicates that initial ionization occurs at this pH and the subsequent ion-dipole interaction results in the "hump" in the $-\delta(\Delta V)/\delta pH$-pH plot (Fig. 4). The observation that binding of Ca^{++} to stearic acid monolayers begins to occur at pH 5 also supports this conclusion (20,21).

It has been shown by Mattson and Volpenhein (22) and Benzonana and Desnuelle (23) from their titration studies of oleic acid that 50% ionization occurs at pH 8.8. Rosano and Feinstein (24) have reported from their studies on titration of micellar solutions of potassium laurate that buffering action occurs near pH 9.3. Bagg, Haber, and Gregor (25) have analyzed skimmed monolayers of stearic and behenic acids from sodium-containing subsolutions. They have reported the pK value of the fatty acid monolayers to be close to 8.9. Christodoulou and Rosano (26) have also reported the pK value of stearic and behenic acid to be close to 9.3 from surface potential measurements. The monolayer and foam studies presented in this paper also indicate that the area per molecule of stearic acid and the foam stability of decanoic acid are strikingly influenced by tris buffer at pH 9.

The State of Monolayers at Various pH Values. It is evident from Table I that at pH 7 and 8, the monolayers are in the solid state near their limiting area. This is another indication of ion-dipole interaction between ionized and un-ionized molecules. At lower pH values, the monolayers are in the liquid state owing to a lack of interaction (ion-

TABLE I

THE STATE OF STEARIC ACID MONOLAYERS AT 20 Å²/MOLECULE FOR VARIOUS pH VALUES[a]

pH	Subsolution	The state of monolayers	Surface pressure at which transition occurs
2.0	HCl solution	Liquid	
2.8	Citric acid-sodium citrate buffer	Liquid	
3.9	Citric acid-sodium citrate buffer	Liquid	
4.9	Citric acid-sodium citrate buffer	Liquid	
5.75	Citric acid-sodium citrate buffer	Liquid	
7.15	tris-HCl buffer	Solid	
8.0	tris-HCl buffer	Solid	Liquid → solid at 10 dynes/cm
9.0	tris-HCl buffer	Gel (+)[b]	Liquid → gel at 8 dynes/cm
9.9	Glycine-NaOH buffer	Gel (+)[b]	Liquid → gel at 2.5 dynes/cm
10.8	Glycine-NaOH buffer	Gel (++)[b]	Liquid → gel at 3.0 dynes/cm
12.25	NaOH solution	Gel (+++)[b]	Liquid → gel at 8.0 dynes/cm

[a] The solid, gel, and liquid states have been defined in the previous paper (12).

[b] The number of + signs indicates qualitatively the increasing surface viscosity of the monolayers.

dipole) in the monolayers. Qualitative observations indicate that above pH 9, the surface viscosity increases with pH. For these monolayers, the liquid to gel transition also occurs at low surface pressures.

Foam Studies. Figures 6 and 7 show the foam characteristics of decanoic acid in buffer solutions which were the same as those used in the monolayer studies at various pH values. Two major conclusions from the present study are: firstly, decanoic acid does not produce foam below pH 8.0; and secondly, at pH 9 the foam has the largest volume but collapses within 2 hours, whereas at other pH values it is stable for more than 16 hours. The characteristics of foam at pH 9 can be explained as follows: because of the maximum repulsion between molecules or the penetration of buffer ions at pH 9.0, the fatty acid molecules occupy a larger area per molecule in the monolayer and presumably in the foam lamellas. This reduces the surface viscosity in the lamellas and hence gives the largest amount of foam. However, the low surface viscosity causes a rapid rate of thinning (27) and the foam collapses within 2 hours at pH 9. As with monolayers of C_{20} and C_{22} fatty acids,[2] an increase in the chain length from C_{10} to C_{12} or C_{14} fatty acids could mask the effect of tris ions on foam stability. The ideas presented above do not represent a generalized theory of foam stability but are offered to explain a close correspondence between the foam characteristics of decanoic acid and the monolayer properties of stearic acid at pH 9.

In summary, we have shown that the average area per molecule, the surface potential, and the foaming characteristics of fatty acids strikingly change near pH 9.0 on tris-HCl buffer because of the maximum repulsion between molecules or the penetration of buffer ions.

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