

## Significance of the 1:3 Molecular Ratio in Mixed Surfactant Systems<sup>1</sup>

DINESH O. SHAH

*Departments of Chemical Engineering and Anesthesiology, University of Florida,  
Gainesville, Florida 32601*

Received February 8, 1971; accepted April 30, 1971

Effects of mixed surfactants on various interfacial phenomena are described. The mixed monolayers of egg lecithin-cholesterol and stearic acid-stearyl alcohol exhibit minimal area per molecule at the 1:3 molecular ratio. The rate of evaporation of water through mixed monolayers of stearic acid-stearyl alcohol is also minimal at the 1:3 molecular ratio. For foams of decanoic acid-decanol, the rate of drainage is minimal and the stability maximal at the 1:3 molecular ratio. Maximal solubilization of water as microemulsions occurs when molecular ratio of potassium oleate:hexanol is 1:3. The extraction of oil from emulsions stabilized by sodium dodecyl sulfate and hexadecyl pyridinium chloride is maximal also at the 1:3 molecular ratio. It is proposed that these striking changes in the properties of mixed surfactant systems at the 1:3 molecular ratio are due to two-dimensional hexagonal packing of molecules resulting in a closer molecular packing and a greater stability of mixed films at interfaces.

### INTRODUCTION

During the past 8 years, we have investigated various interfacial phenomena employing mixed surfactants. We have observed striking changes in the properties of these systems when the surfactants are in the 1:3 molecular ratio (1, 2). Similar observations have also been reported by other investigators (3, 4). The present paper summarizes these studies and proposes an explanation for the effects observed at the 1:3 molecular ratio.

### EXPERIMENTAL PROCEDURES

**Materials.** Chromatographically pure egg lecithin was supplied by the Sylvania Chemical Company (Orange, New Jersey). High-purity (>99%) cholesterol, stearic acid, and stearyl alcohol were purchased from Applied Science Laboratories, Inc. (State College, Pennsylvania 16801). Hexanol, decanol, and hexadecane of similar purity were obtained

from Chemical Samples Company (Columbus, Ohio). Decanoic acid (purity >99.5%) was obtained from K & K Laboratories, Inc. (Plainview, New York). All solvents used in monolayer studies were of spectroscopic grade. Inorganic chemicals of reagent grade, and twice distilled water were used in all experiments.

### Methods

**Monolayer Studies.** Lipid solutions (conc 0.8–1.0 mg/ml) were prepared in chloroform-methanol-hexane (in volume ratios of 1:1:3) of spectroscopic grade. The surface pressure was measured by the Wilhelmy plate method (5, 6) and the results were plotted as described previously (1, 7). Two mixed lipid systems, egg lecithin-cholesterol and stearic acid-stearyl alcohol, were studied by the monolayer technique; the former on the sub-solutions of 0.02 M NaCl, pH 5.6, and the latter on Tris-HCl buffer solutions in 0.02 M NaCl at pH 8.8.

**Evaporation Studies.** The effect of molecular ratios of mixed monolayers of stearic acid-stearyl alcohol on evaporation was

<sup>1</sup> Presented: 45th National Colloid Symposium at the Georgia Institute of Technology, Atlanta, Georgia, June 21–23, 1971.

measured simultaneously as follows. Twelve flat-bottomed crystallizing dishes (diam, 19 cm; height, 10 cm) were placed in a temperature controlled room at 22°C; each dish was filled with 250 ml of the same subsolution on which the mixed monolayers were studied. Stearic acid-stearyl alcohol solutions of various molecular ratios were spread in each dish until the added material did not spread, i.e., the monolayers existed at their equilibrium pressures with excess lipids. Three dishes containing the subsolution without monolayers were used as controls. The amount of solution remaining in each dish was measured after a time interval (145 hr) to determine the volume of water that had evaporated.

**Foam Studies.** One milliliter ( $\approx 0.9$  g) of the mixture of decanoic acid-decanol of various molecular ratios, was shaken vigorously for 1 min with 20 ml of the same subsolution used in the monolayer and evaporation studies of stearic acid-stearyl alcohol, in glass-stoppered 100 ml graduated cylinders. Foam heights were photographed at 5 min and 16 hr after production of foams. The amount of solution remaining under the foam column in each cylinder 10 min after foam formation was recorded.

**Microemulsion Studies.** Microemulsions, which are optically transparent isotropic oil-water dispersions, were produced by mixing hexadecane, hexanol, potassium oleate, and water. As the amount of water was increased, the microemulsion exhibited a clear to turbid to clear transition. We have shown previously (8) that the initial clear state consisted of the water-in-oil microemulsions. The effect of potassium oleate:hexanol ratio on solubilization of water was studied by observing the optical transparency and isotropic properties (i.e., the absence of birefringence) upon increasing the amount of water in microemulsions.

## RESULTS AND DISCUSSION

**Monolayers.** Figure 1 shows the average area/molecule plotted against the mole fraction for egg lecithin-cholesterol monolayers at various surface pressures. The maximal condensation observed at the molecular ratios of 3:1 and 1:3 between lecithin and

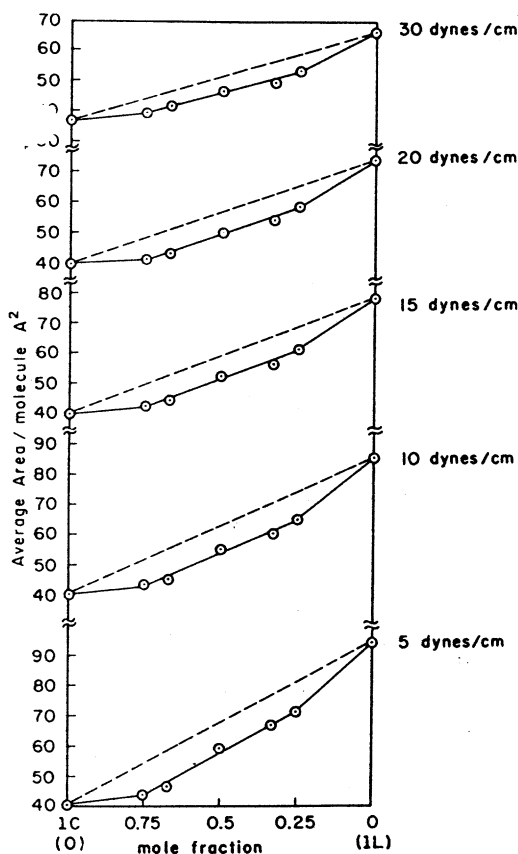


FIG. 1. Average area/molecule of egg lecithin-cholesterol monolayers at various surface pressures: The subsolution consists of 0.02 M NaCl, pH 5.6, at 25°C; (— —) the additivity rule of molecular areas.

cholesterol agrees with the results reported by DeBernard (4) for the mixed monolayers of egg lecithin and cholesterol.

Figure 2 shows the average area per molecule vs. mole fraction of stearic acid-stearyl alcohol in mixed monolayers at various surface pressures at pH 8.8. The stearic acid monolayers are expanded because of the repulsion between ionic carboxyl groups and the penetration of Tris ions into the monolayers (9). The cause of condensation close to the molar ratio 9:1 between stearic acid and stearyl alcohol is not yet understood. It may be due to aggregate formation or structural alteration or the solubility of molecules in the subsolution. However, the minimal condensation at the

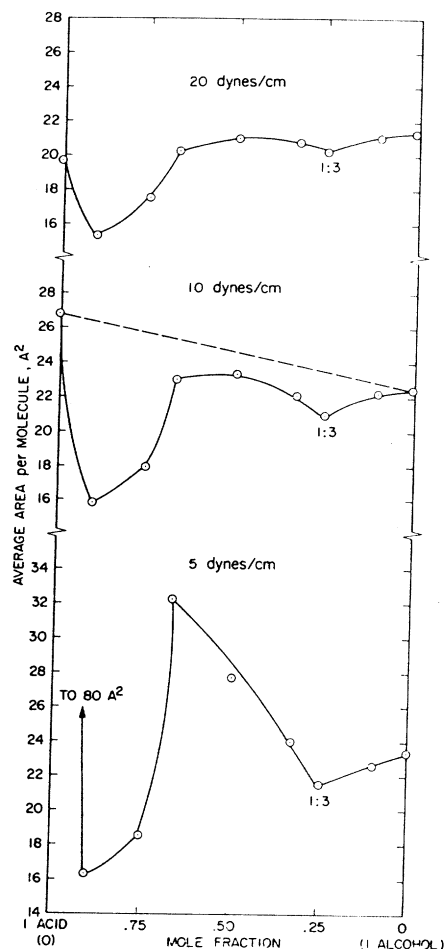


FIG. 2. Average area/molecule of stearic acid-stearyl alcohol monolayers on subsolutions of 0.05 *M* Tris-HCl buffer in 0.02 *M* NaCl, pH 8.8, at 22°C; (—) the additivity rule of molecular areas.

1:3 molecular ratio is well defined and the area per molecule of 20–21  $\text{\AA}^2$  is in agreement with the values reported for fatty acid monolayers (10, 11). The stability of mixed monolayers at and around the 1:3 molecular ratio was established by the observation that there was no significant change in the area of the monolayer with time if the surface pressure was maintained at 10 dynes/cm. We reasoned that if this 1:3 molecular association is real, it could influence other phenomena occurring at the air-water interface. Therefore, experiments on the evaporation of water through these mixed monolayers and on the foam characteristics of decanoic acid-decanol were performed.

**Evaporation.** The evaporation from all dishes without monolayers were the same for the same time interval, and the effects of the monolayers to retard evaporation were reproducible. Figure 3 shows that the lowest rate of evaporation through mixed monolayers of stearic acid-stearyl alcohol also occurs at the 1:3 molecular ratio. This agrees with the proposed explanation that the minimal area per molecule at the 1:3 molecular ratio is due to a tighter packing of molecules in the mixed monolayer. The lack of a minimum in evaporation at the 9:1 molecular ratio suggests that the reduction in average area per molecule observed in mixed monolayers at this ratio is not due to a tighter packing of molecules but may be due to other factors, e.g., structural alterations involving molecular aggregation or solubility. It is very likely that the structure of spread monolayers changes during the period of evaporation (145 hr), but the major point evident from the results is that this change must be minimal in the mixed monolayers of stearic acid-stearyl alcohol of the 1:3 molecular ratio, so as to produce maximum retardation of evaporation. Not only these stearic acid-stearyl alcohol mixed monolayers, but the nonionic mixed monolayers of  $C_{19}$ - $C_{20}$  alcohols also exhibit maximal retardation at the 1:3 molar ratio (12).

**Foams.** Figures 4 and 5 show foams of decanoic acid-decanol mixtures of various molar compositions at 5 min and 16 hr after production of foams. It is evident that the foam stability was maximal for the mixture in the 1:3 molecular ratio (cylinder no. 7 in Figs. 4 and 5). Figure 6 indicates the amount of buffer solution which came out of the foam column during the initial 10 min period after production of the foam. It is evident that the minimal amount of solution came out of the foam produced by decanoic acid-decanol mixture in the 1:3 molecular ratio. Within 2 hr, all cylinders showed about the same amount (20 ml) of solution under foam. Hence, the results shown in Fig. 6 suggest that the rate of drainage of foam is minimal at the 1:3 molecular ratio.

Davies (13) 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 the

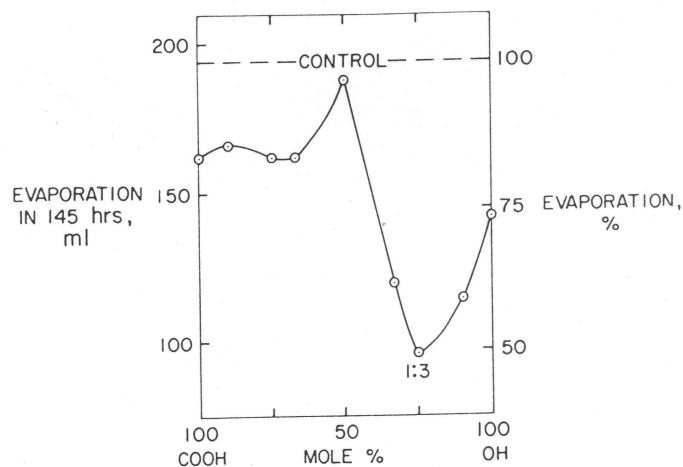


FIG. 3. Evaporation of water through various mixed monolayers of stearic acid-stearyl alcohol on subsolutions of 0.05 *M* Tris-HCl buffer in 0.02 *M* NaCl, pH 8.8, at 22°C; (--) the amount of evaporation without monolayers.

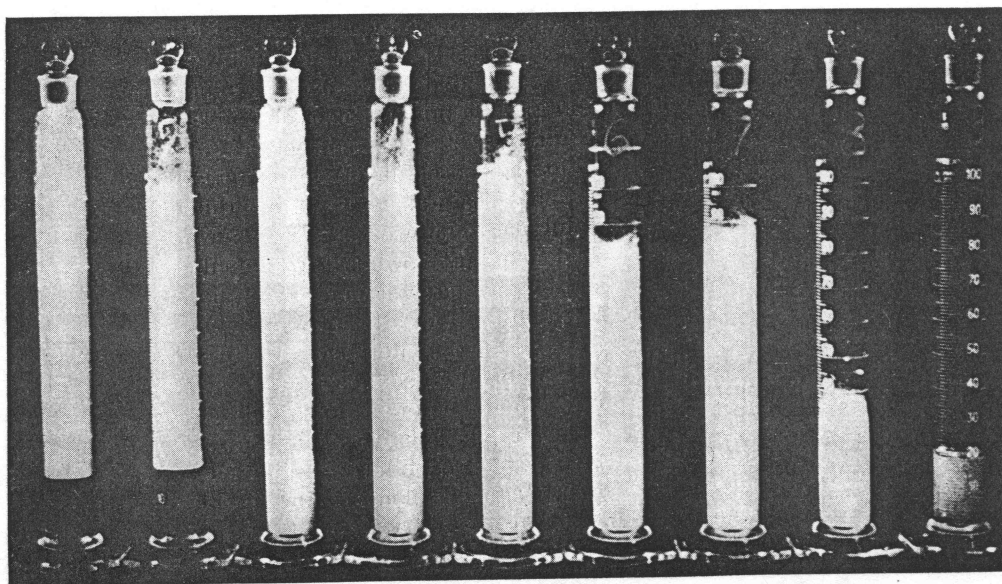


FIG. 4. Foam volume of decanoic acid-decanol mixtures of various molar compositions in 0.05 *M* Tris-HCl buffer in 0.02 *M* NaCl, pH 8.8, 5 min after formation of foams. The molecular ratios of decanoic acid and decanol in these cylinders are in the same order as shown in Fig. 6.

alcohol. Moreover, studies on sodium dodecyl sulfate solutions have shown that the presence of dodecanol increases the surface viscosity (14), decreases the rate of drainage from thin lamellae and increases the foam stability (15, 16). It should be noted that in this work the influence of decanol on the rate of drainage and foam stability is

optimum at a specific molecular ratio, namely 1:3, between decanoic acid and decanol, which can be explained as follows: If decanoic acid-decanol in foam lamellae form a 1:3 molecular association similar to that in mixed monolayers, then the tighter packing of molecules would result in an increase in surface viscosity, a decrease in the

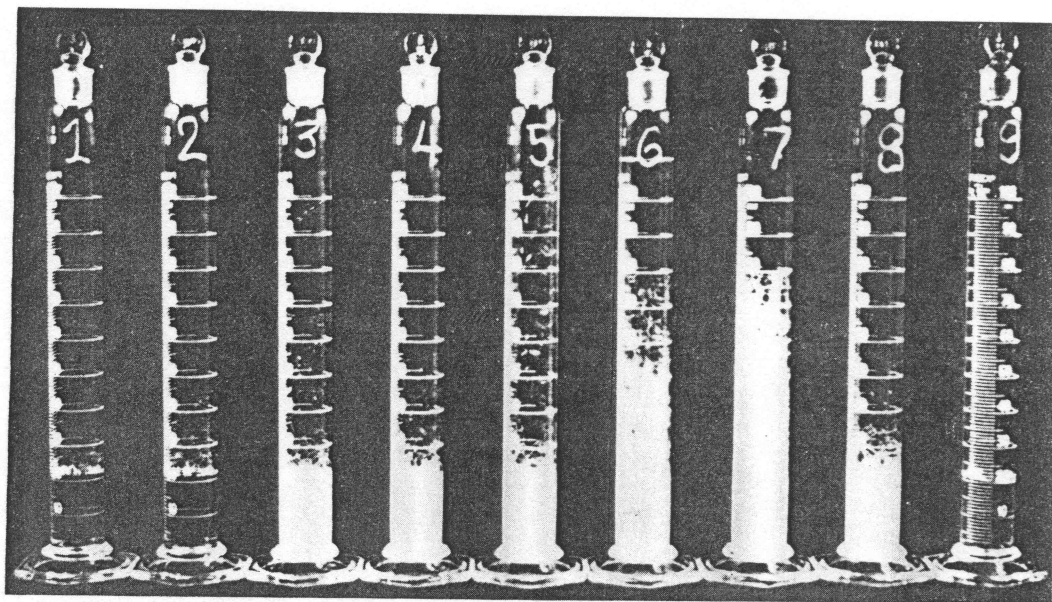


FIG. 5. Foam volume of the decanoic acid-decanol mixtures (shown in Fig. 4) 16 hr after formation of foams. The mixture in the 1:3 molecular ratio (cylinder no. 7) shows the maximum foam stability.

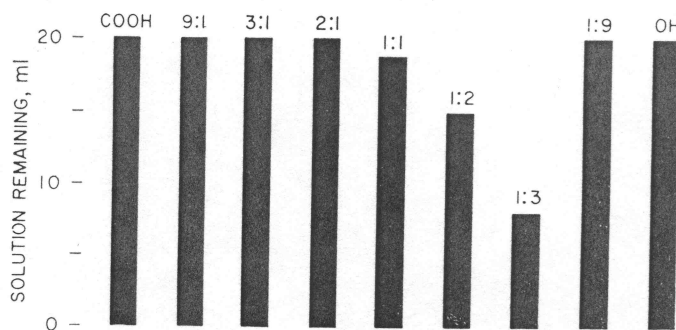


FIG. 6. Amount of buffer solution remaining under decanoic acid-decanol foam in each cylinder 10 min after formation of foams (Tris buffer + 0.02 M NaCl, pH 8.8): The maximal amount of buffer solution is retained in the foam produced by the mixture in the 1:3 molecular ratio.

rate of drainage, and an increase in foam stability in agreement with the results reported by other workers (2, 13-16). Again, it is emphasized that the composition of foam lamellae would change with time, but the significance of the results is that the initial composition of decanoic acid-decanol mixture in the 1:3 molecular ratio strikingly increases the foam stability as compared to other molecular ratios.

**Microemulsions.** Figure 7 shows the optical appearance of microemulsions with increasing content of water. The volume ratio of

hexanol:hexadecane (oil) was kept constant (0.4); whereas the concentration of potassium oleate was varied from 0.1 to 0.6 gm/ml of oil to study the effect of soap:hexanol ratio on microemulsions. We have shown (8) that the initial clear, isotropic region represents water-in-oil type microemulsions. It is clear from the results that the first clear region extends to the highest water:oil ratio ( $\approx 0.85$ ) for 0.3 gm of potassium oleate and 0.4 ml of hexanol, ml of oil. Here, also the molecular ratio of potassium oleate (0.3 gm) to hexanol (0.4 ml) is found to be close to

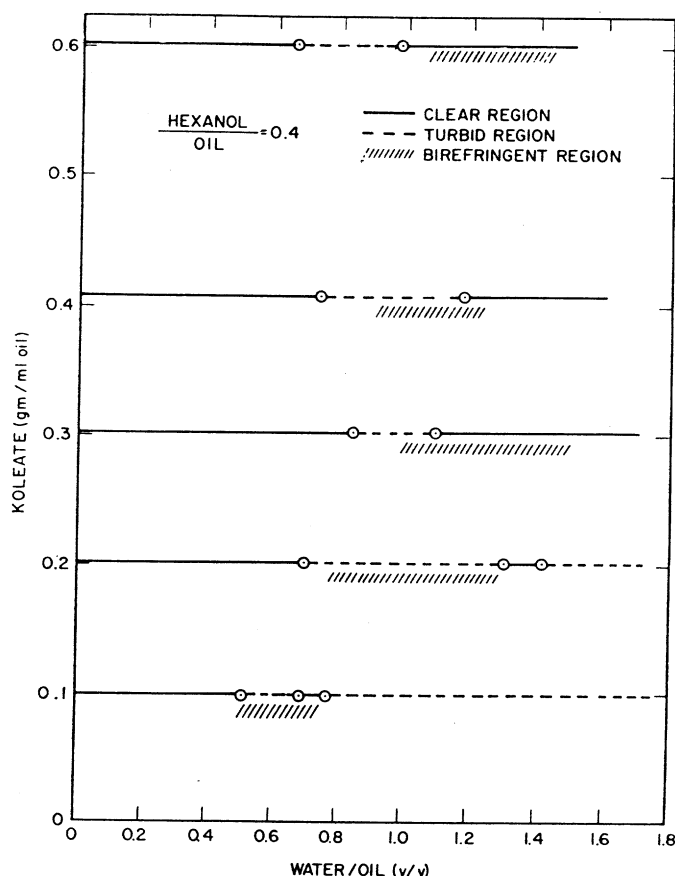


FIG. 7. Optical data vs. water content of microemulsions: The effect of potassium oleate:hexanol ratio on solubilization of water in the microemulsions. The maximal solubilization of water in the initial clear region occurs at potassium oleate conc of 0.3 gm/ml of oil. Here, the molecular ratio of potassium oleate:hexanol is close to 1:3.

1:3. Using another approach, Bowcott and Schulman (17) showed that the molecular ratio of potassium oleate:hexanol at the interface was 1:3 for maximal solubilization of water in microemulsions (i.e., the molecular ratio of water:potassium oleate of 70). This suggests that the 1:3 molecular association also exists at the oil/water interface. However, other ratios of soap and alcohol at the interface have been reported (18). Our electrical, nuclear magnetic resonance, and viscosity studies on birefringent and second clear regions will be reported elsewhere.

*Macroemulsions.* It is interesting that not only microemulsions described above show the effect of the 1:3 molecular association, but macroemulsions stabilized by sodium dodecyl sulfate and cetyl pyridinium chloride

also exhibit a similar association when oil is extracted from them. Figure 8 is taken from the original work of Booiij (3), which shows that the extraction of oil from emulsions is maximum when the surfactants are in the 1:3 molecular ratio. This can be explained as follows: If the surfactants form a tightly packed association in the 1:3 molecular ratio at the oil-water interface similar to that in monolayers, then penetration of oil molecules within the surfactant film would be minimal, and hence, most of the oil would be extracted from the emulsions at this molecular ratio. In this system, the maxima occur both at the 1:3 and 3:1 ratios; however, there are qualitative differences between the two maxima. The maximal extraction of oil and the formation of poor

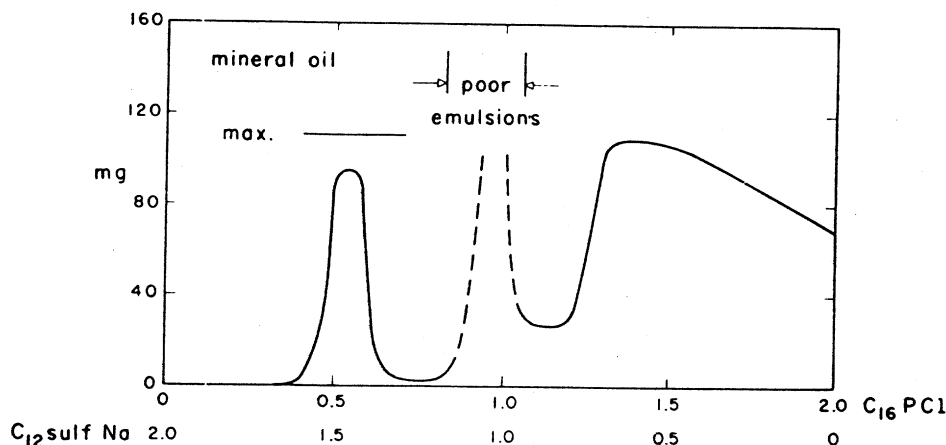


FIG. 8. Extraction of mineral oil from emulsions prepared with mixtures of sodium dodecyl sulfate and hexadecyl pyridinium chloride: (abscissa) concentration of surfactants in millimoles per liter [Ref. (3)].

emulsions at the molecular ratio 1:1 can be attributed similarly to the formation of 1:1 association between these cationic and anionic surfactants. The evidence for the existence of such 1:1 and 1:3 stable molecular associations was also obtained from penetration of a soluble surfactant into an insoluble monolayer as discussed below.

**Monolayer Penetration.** Schulman and Stenhagen (19) showed that penetration of hexadecanol monolayers by sodium hexadecyl sulfate results in 1:1 and 1:3 stable molecular association between hexadecanol and hexadecyl sulfate, depending upon the available area in the mixed monolayers. The 1:2 molecular association in the mixed monolayer was found to be relatively unstable. A similar conclusion was also reached by Joly (20), who used a different procedure to study penetration in monolayers. He also obtained evidence for association in such molecular ratios in mixed monolayers of lysolecithin-sodium palmitate, lecithin-digtonin, and heptadecylamine-digtonin. It is evident from the review of the work in this area that in several instances the stable molecular association in 1:3 ratio occurs upon penetration, if the area is available in the monolayer. It should be pointed out that there are certain steric requirements for the formation of such a 1:3 association of mixed surfactants at the air-water and oil-water interfaces. These are described in the next section.

#### SIGNIFICANCE OF THE 1:3 MOLECULAR RATIO IN MIXED SURFACTANT SYSTEMS

We propose that the striking changes observed in the properties of mixed surfactant systems at the 1:3 molecular ratio are not coincidents, but are due to a fundamental factor present in these systems. The combinations of molecules involved in the 1:3 association described above are zwitterionic-nonionic, anionic-nonionic, nonionic-nonionic, and cationic-anionic types. This molecular association is influenced often by changing the chain length of the molecules (3, 12). From careful review of the work (1, 3, 12, 21) on mixed surfactant systems, it appears that the molecular areas of the two components at the interface are always unequal when this association occurs. In the 1:3 molecular association, the component with the smaller area/molecule generally forms the larger fraction (0.75) in the mixed surfactant systems (e.g., stearic acid-stearyl alcohol monolayers). In several, mixed surfactant systems (e.g., egg lecithin-cholesterol monolayers,  $C_{12}$  sulfate- $C_{16}$  pyridinium stabilized emulsions) both 1:3 and 3:1 molecular associations are observed, whereas in others 3:1 association is not observed. This is particularly true when the component with the larger area/molecule forms the greater fraction (e.g., stearic acid-stearyl alcohol mixed monolayers, decanoic acid-decanol foams). This suggests that the

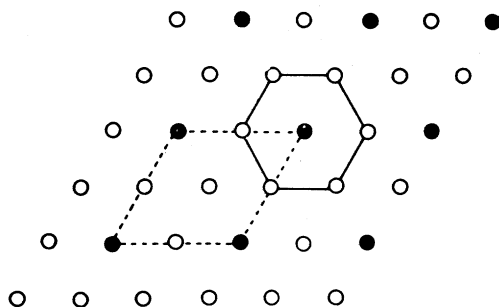


FIG. 9. A proposed two-dimensional hexagonal arrangement of molecules at the 1:3 molecular ratio in mixed surfactant systems: Molecules of one type occupy the corners and those of the other type occupy the centers of hexagons.

molecular association depends upon the molecular area and, hence, on the intermolecular spacing and, in turn, on geometrical factors or arrangements of surfactant molecules at the interface. It is known (22) that only the hexagonal arrangement of molecules can provide the closest packing possible in two dimensions. As shown in Figure 9, two types of molecules can be arranged in monolayers so that molecules of one type occupy the centers and those of the other type occupy the corners of hexagons. This type of hexagonal packing would not only yield the minimal area per molecule due to close-packing, but would also make the 3:1 and 1:3 ratios possible by simple interchangeability of positions between the two types of molecules. Therefore, we propose that the striking changes observed in the properties of mixed surfactant systems at the 1:3 molecular ratio are due to a hexagonal packing of molecules at the interface. It should be pointed out that for molecules having identical area, hexagonal packing is possible in monolayers, but for two types of molecules having nonidentical area, it appears that hexagonal packing occurs only when the molecules are in the 1:3 ratio. The data presented on foams, and macro- and microemulsions also imply that such hexagonal packing of molecules occurs both at air-water as well as at oil-water interfaces. Cook and Ries (23) have proposed a similar hexagonal arrangement of stearic acid and hexadecane molecules to account for the effects observed at the 1:3 molecular ratio

in mixed monolayers at the air-water, as well as at the solid-liquid interfaces. In agreement with this concept are the electron diffraction studies of Havinga and De Wael (24) and also of Germer and Storks (25), who showed that for monolayers deposited on a supporting base, the arrangement of molecules is that of hexagonal symmetry.

The regular arrangement of molecules would require sufficient intermolecular interaction which is possible if the corners of hexagons are occupied by molecules having a smaller area per molecule than those occupying the centers of hexagons. The molecules having a larger area per molecule may not form such hexagons, since the increase in intermolecular spacing would reduce the intermolecular interaction and, hence, decrease the order (or the hexagonal arrangement) in the mixed monolayers. Therefore, in several systems having 0.75 mole fraction of molecules with a larger area per molecule, 3:1 association is not observed.

In summary, the present paper proposes, on the basis of available theoretical and experimental data, the hexagonal arrangement of the polar groups of surface-active molecules at the interface to account for the striking changes observed at the 1:3 molar ratio in the properties of mixed surfactant systems studied.

#### ACKNOWLEDGMENTS

The author expresses his sincere appreciation and thanks to Professors R. D. Walker, Jr., and J. H. Modell, of the University of Florida, Drs. O. A. Roels, R. O. Anderson, G. M. Sharma, Mr. Roy Hamlin, Jr., Miss C. A. Dysleski, and Mrs. P. H. Kilian of Columbia University, and Drs. L. P. Zill and M. R. Heinrich of NASA Ames Research Center for their stimulating comments, discussions, and cooperation in this work. This work was supported in part by Grant WP-15080 from Federal Water Quality Administration, and in part by funds from the Departments of Anesthesiology and Chemical Engineering of the University of Florida.

#### REFERENCES

1. SHAH, D. O., AND SCHULMAN, J. H., *J. Lipid Res.* **8**, 215 (1967).
2. SHAH, D. O., AND DYSLESKI, C. A., *J. Amer. Oil Chem. Soc.* **46**, 645 (1969).
3. BOOIJ, H. L., *J. Colloid Interface Sci.* **29**, 365 (1969).



4. DEBERNARD, L., *Bull. Soc. Chim. Biol.* **40**, 161 (1958).
5. SHAH, D. O., AND SCHULMAN, J. H., *J. Lipid Res.* **6**, 341 (1965).
6. SHAH, D. O., AND SCHULMAN, J. H., *Lipids* **2**, 21 (1967).
7. SHAH, D. O., *J. Colloid Interface Sci.* **32**, 577 (1970).
8. SHAH, D. O., AND HAMLIN, R. M., *Science* **171**, 483 (1971).
9. SHAH, D. O., *J. Colloid Interface Sci.* **32**, 570 (1970).
10. GODDARD, E. D., AND ACKILLI, J. A., *J. Colloid Sci.* **18**, 585 (1963).
11. SEARS, D. F., AND SCHULMAN, J. H., *J. Phys. Chem.* **68**, 3529 (1964).
12. SIMKO, A. J., AND DRESSLER, R. G., *Ind. Eng. Chem., Prod. Res. Develop.* **8**, 446 (1969).
13. DAVIES, J. T., *Proc. Int. Congr. Surface Activ.*, 2nd, **1**, 220 (1957).
14. BROWN, A. G., THUMAN, W. C., AND MCBAIN, J. W., *J. Colloid Sci.* **8**, 491 (1953).
15. ROSS, J., *J. Phys. Chem.* **62**, 531 (1958).
16. MILES, G. D., ROSS, J., AND SHEDLOVSKY, L., *J. Amer. Oil Chem. Soc.* **27**, 268 (1950).
17. BOWCOTT, J. E., AND SCHULMAN, J. H., *Z. Elektrochem.* **59**, 283 (1955).
18. PRINCE, L. M., *J. Colloid Interface Sci.* **23**, 165 (1967).
19. SCHULMAN, J. H., AND STENHAGEN, E., *Proc. Roy. Soc., Ser. B* **126**, 356 (1938).
20. JOLY, M., *Nature (London)* **158**, 26 (1946).
21. SHAH, D. O., *Advan. Lipid Res.* **8**, 347-431 (1970).
22. AZAROFF, L. V., "Introduction to Solids," pp. 56-57. McGraw-Hill, New York (1960).
23. COOK, H. D., AND RIES, H. E., *J. Phys. Chem.* **63**, 226 (1959).
24. HAVINGA, E., AND DE Wael, J., *Recl. Trav. Chim. Pays-Bas* **56**, 375 (1937).
25. GERMER, L. H., AND STORKS, K. H., *J. Chem. Phys.* **6**, 280 (1938).