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A correlation of foam stability with surface shear viscosity and area per molecule in mixed surfactant systems

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With 7 figures

Introduction

Foams and bubbles are interesting systems for the study of the behavior of soluble surfactants at the gas/liquid interface. On the other hand, monolayers are suitable for the study of the behavior of insoluble surfactants at the gas/liquid interface. *Shah* and *Schulman* (1) and *Shah* (2) have shown that in mixed surfactant systems the stoichiometric association between the surfactant molecules can strikingly alter the properties of the system. In recent years reliable techniques for measuring surface shear viscosity have been developed by *Burton* and *Mannheimer* (3); *Mannheimer* (4); *Mannheimer* and *Schechter* (5); *Pintar, Israel, and Wasan* (6); *Wasan* and *Gupta* (7); *Goodrich, Allen*, and *Poskanzer* (8); and *Poskanzer* and *Goodrich* (9). The present study attempts. to explore the influence of the molecular association between the surfactants and their effect on average area per molecule, surface shear viscosity, rate of drainage, and foam stability in mixed surfactant systems.

Experimental procedures

1. Materials: High purity (> 99%) stearic acid, stearyl alcohol, and dodecanol were purchased from Applied Science Laboratories, Inc. (State College, Pa.); l-octanoic acid and l-decanoic acid were obtained from *K* and *K* laboratories (Plainsview, N.Y.); l-octanol and l-decanol were obtained from Chemical Sample Co. (Columbus, Ohio); and high purity (98%) sodium dodecyl sulfate was generously supplied by Alcolac, Inc. (Baltimore, Md.) and further purified by the method of foam fractionation described elsewhere (10). All inorganic chemicals were of reagent grade. Solvents

of spectrophotometric grade and double-distilled water were used in all experiments.

2. Foam Studies: a. Sodium dodecyl sulfate-dodecanol: The technique described by *Brown* et al. (11) was employed in preparing aqueous solutions of sodium dodecyl sulfate-dodecanol. The solutions were prepared at different relative concentrations of dodecanol, K, defined as

$$K = \frac{\text{Concentration of sodium dodecyl sulfate (g/l)}}{\text{Concentration of dodecanol (g/l)}}$$

The standard foam meter, first introduced by *Bikerman* (12), was used to measure foam persistance and the amounts drained at various intervals. A schematic diagram of the foam meter is shown in figure 1. It consists of a glass column 75 cm long and 2 cm in diameter. A sintered glass disc (40-60 porosity) is attached to the lower end of the column. To maintain the foam at a constant temperature of 25 ± 1 °C, the column is surrounded by a water jacket and water is allowed to circulate from a constant temperature bath. Ten milliliters of solution was pipetted into the column and high purity prehumidified nitrogen gas was bubbled through the solution at a flow rate of 20 cc/min until the solution was converted to foam. The initial volume of foam and the time of complete collapse were recorded. Also recorded were the times of drainage of each 0.2 ml of liquid.

b. Fatty acid – fatty alcohol: The stability of the foams produced by octanoic acid-octanol and decanoic acid-decanol, was studied in the following manner: 1 ml of each lipid mixture, containing different molar ratios of the fatty acid to the fatty alcohol, was placed in a 100 ml glass-stoppered graduated cylinder and shaken vigorously with 20 ml. of 0.05 M tris-HCl buffer (13) in 0.02 M-NaCl, pH 8.8. The amount of solution accumulated (drained) under the foam in each cylinder was recorded 10 minutes from foam formation. The foam height after 16 hours of waiting time was also recorded. Photographs of the cylinders were taken at various instants of time.

3. Surface shear viscosity: The modified deep channel viscous traction viscometer described elsewhere (6, 7) was used to determine the surface shear viscosity of
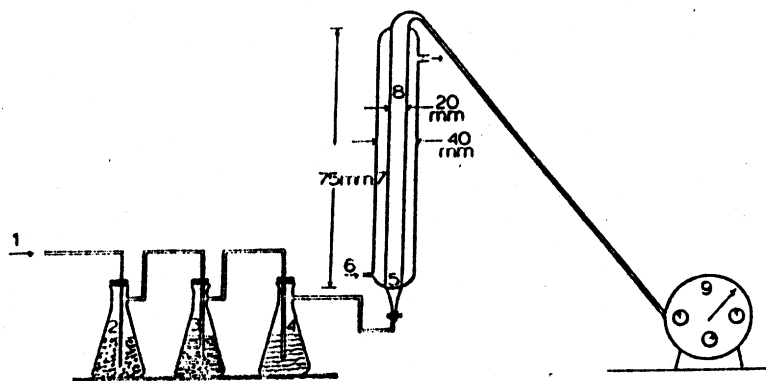
Fig. 1. Schematic diagram of foam meter
1. high purity N_2.
2. ascarite.
3. glass wool.
4. distilled H_2O.

5. sintered glass disc.
6. water from a constant T bath.
7. water jacket.
8. foam column.
9. dry test meter.

each solution. For systems of sodium dodecyl sulfate-dodecyl alcohol, the surface shear viscosity of the adsorbed film was determined. However, for octanoic acid-octanol and decanoic acid-decanol, because of their relatively poor solubility in the buffer solution, it was found convenient to spread monolayers of these mixtures at about 20 Å^2/molecule (i.e. to a state of close packed molecules) in the surface viscometer. Monolayers were spread from fatty acid-fatty alcohol solution in a mixture of chloroform-methanol-hexane (1:1:3 V/V/V). Since these systems do not form stable monolayers, the absolute value of surface shear viscosity changed with time, however, the relative order of the initial values of surface shear viscosity remained reliable and reproducible.

4. Mixed Monolayers: Solutions of stearic acid and stearyl alcohol were prepared in chloroform-methanol-hexane (1:1:3 V/V/V) mixture. The surface pressure was measured by the modified Wilhelmy plate method (14). The average area per molecule was calculated from the total number of molecules in the monolayer. The monolayers were studied on the same buffer subsolution used in the foam studies of fatty acid-fatty alcohol systems. The average area per molecule in mixed monolayers was plotted as a function of the molar ratio of the two components at constant surface pressure.

Fig. 2. Surface shear viscosity and the average rate of drainage versus sodium dodecyl sulfate concentration at various K values

Results and discussion

The results presented in this paper show a definite trend. Aqueous solutions of single surfactants such as sodium dodecyl sulfate exhibit low surface shear viscosity (10^{-4} S.P.) and yield relatively unstable foam with a high drainage rate. Figure 2 depicts the influence of dodecanol on the surface shear viscosity and the drainage rate of SDS solutions. For a given
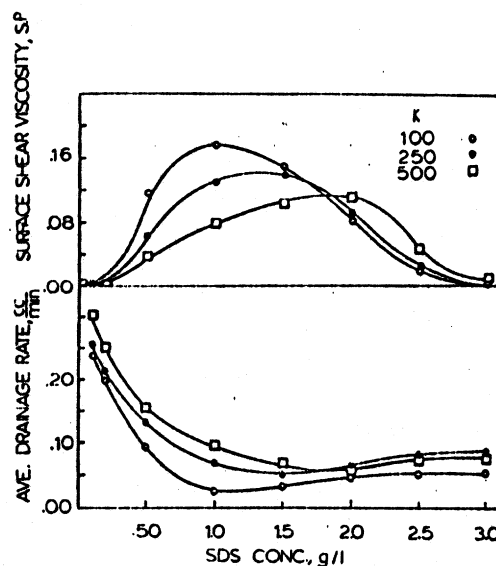
K (ratio of SDS concentration to DOH concentration) surface shear viscosity is relatively low, increases rapidly as the surfactants concentration is increased, reaches a maximum, then decreases rapidly to a negligible value (10^{-4} S.P.). Foam stability data show similar trend while the drainage rate data show an opposite trend (i.e. decrease to a minimum followed by an increase). The concentration at which the maximum in surface shear viscosity (minimum drainage rate) occurs depends on
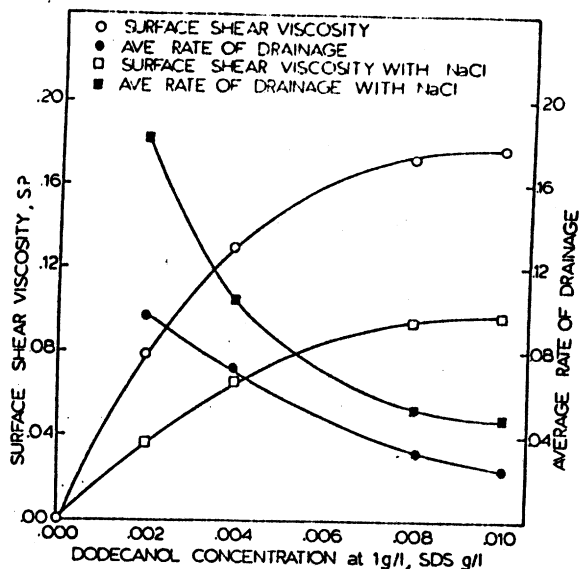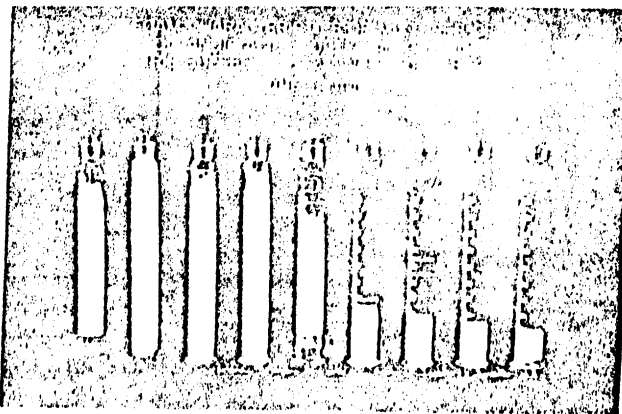
Fig. 3. Surface shear viscosity and the average rate of drainage versus dodecanol concentration for SDS–DOH at an SDS concentration of 1.0 g/l with and without 0.02 M NaCl

surface excess concentration of SDS-to-DOH is 2:3 with a loosely packed film. Holding the molar ratio constant at 64:1 and increasing the bulk concentrations causes the surface excess ratio to increase until it reaches a maximum of 1:1 at an SDS concentration of 1 g/l (a DOH concentration of 0.01 g/l). This increase is also accompanied by closer molecular packing. If the bulk concentration of the two surfactants are increased further, the surface excess ratio decreases back to 2:3 with a loosely packed film. This indicates that DOH is more surface active than SDS since it is more preferentially adsorbed at the surface. Furthermore, this indicates that there is a unique

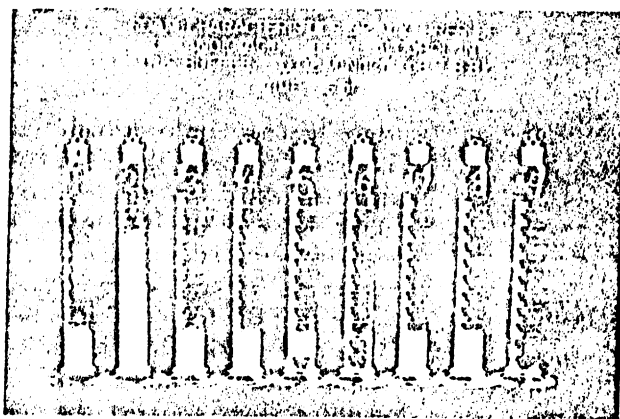the value of K and increases as K decreases (as DOH concentration decreases).

The addition of a strong electrolyte, sodium chloride, to aqueous solution of SDS-DOH, at SDS concentration = 1 g/l, while decreasing the surface tension, strikingly decreases the magnitudes of surface shear viscosity and foam stability and increases the rate of drainage (fig. 3). This is in contrast with the findings of *Shih* and *Lemlich* (15) who found that the addition of potassium chloride had no effect on the stability of foams produced by Triton X-100, albumin, and saponin. This is probably due to the nonionic nature of the surfactants used by these investigators versus the ionic nature of the surfactants used in the current study. *Burcik* (16) suggests that the addition of an electrolytic salt to an aqueous solution of an ionic surfactant decreases the surface tension and enhances the rate of equilibrium surface tension attainment, i.e. increases the rate of foam collapse. The results of our work favor this conclusion.

Using the foaming method *Wasan* and co-workers (17) determined the surface excess concentrations of several mixed surfactant systems. For SDS–DOH, $K = 100$, they found that while the ratio of the *molar* concentration of SDS to that of DOH is 64:1, the ratio of the

4 a

4 b

Fig. 4. (a) Foam volume of octanoic acid-octanol mixtures of various molar compositions, 5 minutes after the formation of foam; (b) Foam volume of octanoic acid-octanol mixtures of various molar compositions, 16 hours after the formation of foam
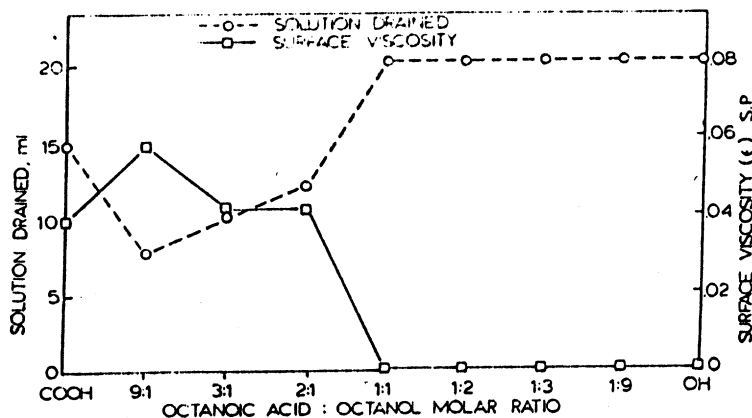
Fig. 5. Accumulated amount of buffer solution under octanoic acid-octanol foam in each cylinder 10 minu
after formation of foams (Tris-HCl buffer + 0.02 M NaCl, pH 8.8): The maximal amount of buffer soluti
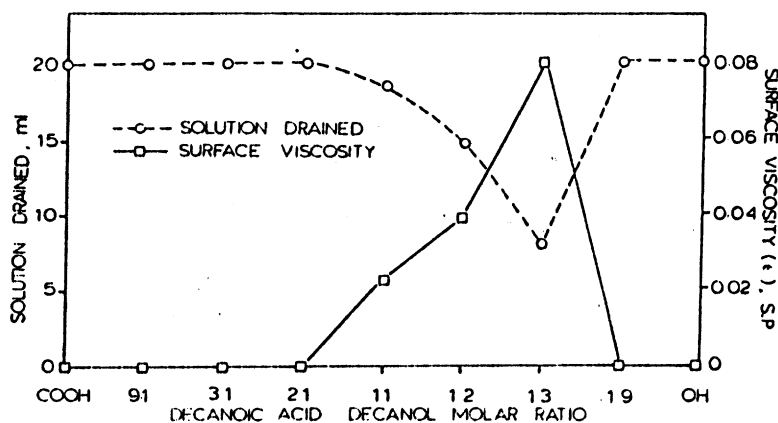is retained in the foam produced by the mixture in the 9:1 molecular ratio

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

surface excess ratio which corresponds to maximum surface shear viscosity and this unique surface excess ratio is also the maximum.

This hypothesis is further supported by considering the foam characteristics of octanoic acid-octanol mixtures (fig. 4 (a) and (b)). It is evident that the foam stability is maximum at a 9:1 molar ratio in octanoic acid-octanol system. Similar studies with decanoic acid-decanol system showed the maximum foam stability at a 1:3 molar ratio (2). It is striking that an increase of two methylene groups from C_8 to C_{10} brings the maximal foam stability and the maximal surface shear viscosity from 9:1 to 1:3 molar ratio between the fatty acid and the fatty alcohol (fig. 5 and 6).

It is interesting that the minima in area molecule in mixed monolayers of stearic acid-stearyl alcohol also occur at the 9:1 and 1:3 molar ratio (fig. 7). From measurements of evaporation through these mixed monolayers, Shah has shown (2, 18, 19) that the minimum at the 1:3 molar ratio between stearic acid-stearyl alcohol is due to closer packing of molecules since he also observed the minimum evaporation rates. In contrast, there was no corresponding minimum in evaporation rate at the 9:1 ratio suggesting that the minimum in area/molecule at the 9:1 molar ratio is not due to a closer packing of molecules but presumably due to structural alterations within the mixed monolayer at this molar ratio. This con

STEARIC ACID - STEARYL ALCOHOL
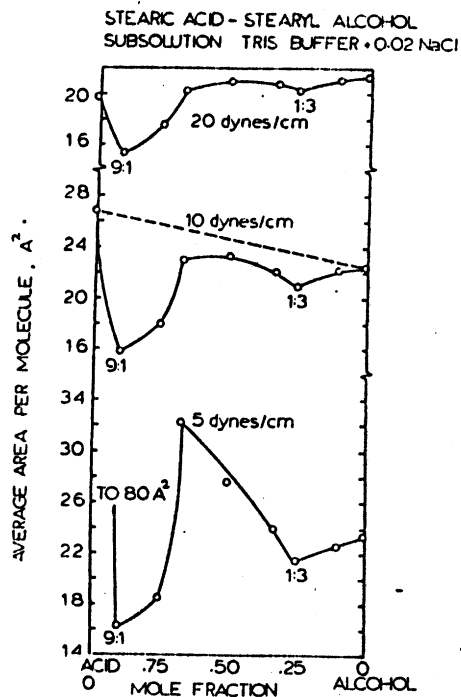SUBSOLUTION TRIS BUFFER • 0.02 NaCl

Fig. 7. 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. The minimal condensation occurs at 9:1 and 1:3 molecular ratio between stearic acid and stearyl alcohol

cept of structural alteration which may include aggregate, micelle or liquid crystal formation within the mixed monolayer (i.e. a deviation from a strictly monolayer state), is further supported by the observation that the area of 16Å² per molecule at the 9:1 ratio is considerably smaller than that in a closed packed monolayer. This suggests that perhaps a small fraction (about 10 mole %) of alcohol molecules may act as condensation nuclei around which the fatty acid molecules may aggregate and cause structural alterations including a deviation from the two-dimensional state of the monolayer (20).

The minimum in the average area per molecule observed at the molecular ratio of 9:1 between stearic acid and stearyl alcohol does not appear to be a specific molecular complex, but it indicates the situation in which one component (nonionic) is present at a relatively low concentration serving as nucleation centers. Recently, it has been shown by *Ahmad* and *Friberg* (21) that the surfactant solutions

containing liquid-crystalline phases can exhibit enhanced foam stability. From the phase diagram of octanol-sodium octanoate-water given by *Lumb* (22), it can be suggested that the molecular ratio of 9:1 between octanoic acid and octanol at pH 8.8 may cause the formation of such liquid-crystalline structures in the foam lamellae, which subsequently can enhance the foam stability.

Based upon our studies on mixed monolayers of stearic acid and stearyl alcohol, we propose that if such tight packing of decanoic acid and decanol molecules occurs in the foam lamellae in the molecular ratio of 1:3, then this would increase the surface viscosity, would decrease the rate of drainage and subsequently would increase the foam stability. The last three expected phenomena were in fact experimentally observed (figs. 4 and 5). *Shah* has (18 and 19) also proposed that in mixed surfactant systems of 1:3 molar composition, the two types of molecules arrange in a hexagonal pattern so that the molecules of the larger fraction occupy the corners and those of the smaller fraction occupy the centers of hexagons. The hexagonal arrangement seems to provide the closest possible packing of molecules at interfaces.

Theoretical analysis of flow characteristics in thin liquid films have been attempted by several workers who used a form of the Navier-Stokes equations similar to those encountered in lubrication theory (23-26). The recent work of *Ruckenstein* and *Jain* (25, 26) shows that the presence of surface active substances causes an increase in the surface viscosity of the film and results in increasing the rupture time of the film by several orders of magnitude. The results of our work favor their conclusion. In summary, our experimental results clearly establish the following interrelationship: foam stability → rate of drainage → surface viscosity → molecular packing in surfactant film.

The preceding is by no means a complete explanation of all the factors governing foam stability. Surface shear viscosity is indeed an important factor because it influences the rate of drainage thus increasing (or decreasing) the rate at which the lamella attains its critical thickness. The critical thickness itself is governed by the electrical repulsion of the ionic double layer (27) and the van der Waals attraction. Once the lamella attains its critical

thickness its persistence is governed by local surface tension gradients which gives rise to Gibbs elasticity. This effect was pointed out by the analysis of *Ruckenstein* and *Jain* (25, 26) who found that the presence of surface active materials influence the compositional elasticity of the film as well as its surface viscosity. Recently, several researchers have indicated the importance of surface dilational viscosity in foam stability (28). Preliminary experiments conducted by *Wasan* and co-workers (29) indicate that surface dilational viscosity is indeed an important factor. Only when these factors are researched to the fullest and explained in terms of molecular association a complete description of the factors affecting foam stability can be possible.

Acknowledgement

Summary

Aqueous solutions of sodium dodecyl sulfate yield very unstable foam with a very high rate of drainage because they exhibit a relatively low surface shear viscosity. When a solubilizate, such as dodecanol is present in the system, the rate of drainage and thus foam stability prove to be a function of surface shear viscosity. In itself surface shear viscosity appears to be a function of the state of the film as well as the relative amount of the surfactants that is adsorbed at the surface. Systems of fatty acid – fatty alcohol (decanoic acid – decanol, octanoid acid – octanol) exhibit maximum foam stability at molar ratios of 1:3 and 9:1, respectively. At the same molar ratios in these systems, the rate of drainage is minimum and surface shear viscosity is maximum. Studies on mixed monolayers of stearic acid – stearyl alcohol showed minima in the average area per molecule at the 9:1 and 1:3 molar ratios.

It is proposed that the molecular interaction which causes the reduction in the average area per molecule in the mixed monolayer also causes the maximum in surface shear viscosity, the minimum in the rate of drainage, and the maximum in foam stability.

Zusammenfassung

Wäßrige Lösungen von Natriumdodecylsulfat haben sehr instabile Schäume mit einer hohen Draingeschwindigkeit, die mit der relativ niedrigen Oberflächengeschwindigkeit zusammenhängt. Bei Gegenwart eines Solubilisators, wie z. B. Dodecanol, wird die Draingeschwindigkeit und die Schaumstabilität eine Funktion der Oberflächenscherviskosität. Die Oberflächenscherviskosität selbst scheint eine Funktion des Filmzustandes und der relativen Tensidmenge zu sein, die an der Oberfläche adsorbiert ist. In den Systemen Fettsäure-Fettalkohol treten Maxima d Schaumstabilität bei Molverhältnissen 1:3 bzw. 9 auf. Bei den gleichen Molverhältnissen hat die Drai geschwindigkeit ein Minimum und die Oberfläche scherviskosität ein Maximum. In Monoschichten v Stearinsäure und Stearylalkohol erreicht der Platzb darf pro Molekül Minima bei Molverhältnissen v 9:1 und 1:3.

Es wird angenommen, daß die gleichen Wechse wirkungen, welche zur Reduktion des Platzbedarfs den gemischten Monoschichten führen, auch d Maxima in der Oberflächenscherviskosität und d Minima in der Draingeschwindigkeit und damit d Maxima in der Schaumstabilität bedingen.

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