Surface Active Properties of Combinations of Soap and Lime Soap Dispersing Agents[1]

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ABSTRACT AND SUMMARY

Surface tension versus log concentration curves were obtained for combinations of a variety of lime soap dispersing agents (LSDA) with sodium oleate. Salient features of the curves for these mixtures were: (a) criticial micelle concentration (CMC) close to that for LSDA alone; (b) absence of a surface tension minimum or substantial reduction in the minimum, which was often found with LSDA alone; (c) surface tension values above the CMC very close to those found for soap alone above its CMC; and (d) slope below the CMC greater than that for soap alone, more like that for soap with alkali added or lime soap dispersing agent alone. Higher CMC values were confirmed by dye solubilization measurements. The surface tension curves provided further evidence for the mixed micellar nature of soap-LSDA mixtures and suggested that the addition of LSDA to soap increased the surface concentration of surfactant.

INTRODUCTION

The disadvantages of soap in hard water can be overcome by proper formulation with lime soap dispersing agents (LSDA) (1). Detergency of formulations containing tallow soap, LSDA, and an inorganic builder such as a sodium silicate was found to be equal to that of commercial detergents containing 50% sodium tripolyphosphate. Unlike soap alone, these formulations did not leave any more deposit on the fabric than the phosphate built formulations (2).

Analysis of lime soap dispersions showed that the suspended particles were intimate mixtures of soap and lime soap dispersing agents (LSDA) in the same ratio as that of the starting mixtures (3). The finely dispersed particles were capable of supplying surface active ions to the system and made a significant contribution to the detergency process. The purpose of the present study is to confirm the mixed micellar nature of soap-LSDA combinations and compare surface properties of such mixtures with those of their components. Examples of anionic and amphoteric surfactants with different carbon chain lengths have been selected for this study (Table I). To simplify the system for surface tension study, purified soap (sodium oleate) in combination with pure lime soap dispersing agents were used in water of zero hardness.

Since the surface tension curves were not used for accurate determination of surface concentration, simplifications were made in the usual rigorous control of solvent purity, counterion concentration, and temperature. For this study, slopes below the CMC were used to make qualitative comparisons of surface concentrations. Critical micelle concentration (CMC), minima at the CMC, and surface tension values above the CMC were also compared.

Dye solubilization measurements were carried out to confirm CMC values and to obtain more information on colloidal properties above the CMC. Good solubilization curves were obtained only after alkali was added to prevent hydrolysis of the soap.

EXPERIMENTAL PROCEDURES

Materials

Sodium oleate was prepared by neutralization of an alcohol solution of pure oleic acid (99+%, Applied Science Laboratories, Inc., State College, PA) with aqueous reagent grade sodium hydroxide. Sodium analysis of the dried soap was found to agree with theory, and a 0.1% ethanolic solution was neutral to phenolphthalein. References that describe the preparation of lime soap dispersing agents, along with the chemical formulas and abbreviations used throughout this paper, are listed on Table I.

Tap water was deionized by passing through two Type II Research Model mixed bed demineralizers (Illinois Water Treatment, Rockford, IL). The treated water had a conductance of 1 μ/cm^2 and a surface tension of 69 ± 1 dynes/cm (uncorrected for contact angle, 15-20 Deg). Distillation of the water from alkaline permanganate in a glass still, which had been thoroughly steamed and leached with distillate, did not change its surface tension.

Solutions were prepared by dilution from 0.1% stock solutions. To avoid concentration changes due to surface adsorption at low concentrations, the dishes used for the surface tension measurements and the flasks used for dilution were first rinsed with the solutions prior to filling. Two to five replicate measurements for each compound were made with solutions prepared freshly each time as described above.

Oil Orange (phenyl-azo-2-napthol, C.I. No. 12055) was obtained through the courtesy of E.I. DuPont de Nemours & Co., Wilmington, DE, and was purified by two crystalliza-

TABLE I

Lime Soap Dispersing Agents

Compound	Code	Reference
$C_{15}H_{31}CONH(CH_2)_3\overset{+}{N}(CH_3)_2(CH_2)_3SO_3^-$	PASB	4
$C_{13}H_{27}CONH(CH_2)_3\overset{+}{N}(CH_3)_2CH_2CHOHCH_2SO_3^-$	MAHSB	5
$C_{16}H_{33}\overset{+}{N}(CH_3)_2(CH_2)_3SO_3^-$	HSB	4
$C_{17}H_{35}CONHCH_2CH(CH_3)OSO_3Na$	SAM	6
$C_{14}H_{29}CH(CO_2CH_3)SO_3Na$	PMS	7

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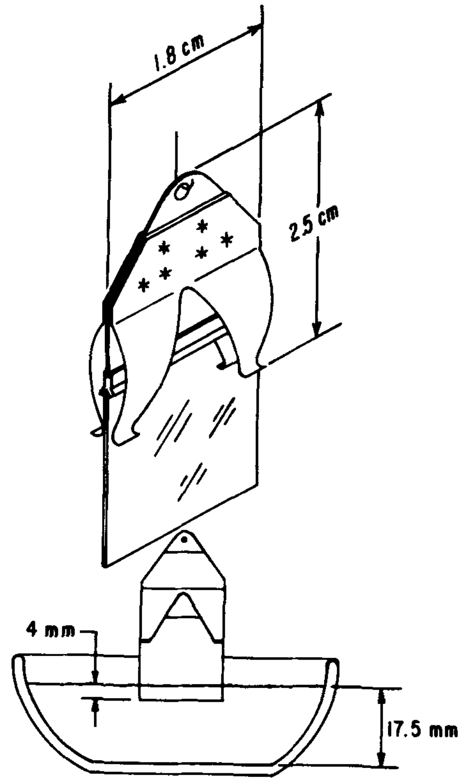

FIG. 1. Apparatus for suspending microscope cover glass in solution for surface tension by Wilhelmy method.

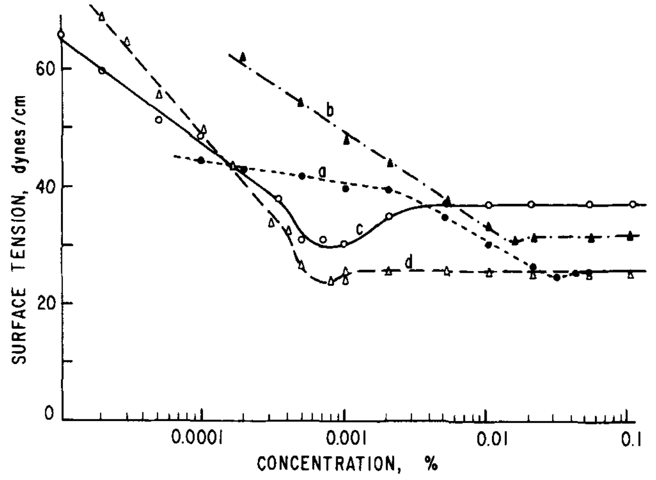

FIG. 2. Surface tension versus concentration for: (a) sodium oleate in deionized water; (b) sodium oleate in 0.005 N NaOH; (c) PASB in deionized water; and (d) 20% PASB-80% sodium oleate in deionized water.

tions at O C from a mixture of 85% petroleum ether and 15% acetone by volume. The long orange needles melted at 123 C and had a specific absorption (1%) of 628 at 480 nm.

Surface Tension Measurement

The Wilhelmy method was used to measure surface tension. New microscope cover glasses, 1.82 cm x 1.84 cm x 0.0140 cm, were suspended in 30 ml of test solution in a 7 cm diameter dish with edges sloping outward. The device used for attaching the glass cover slip to the hangdown wire is shown in Figure 1. The dish and glass sensor were enclosed in a weigh-below chamber to eliminate draughts and minimize variations in water vapor content. Surface tension was measured with a Cahn Electrobalance, RM-2 (Ventron Corp., Paramount, CA) and recorded continuously with a Speedomax recorder (Leeds & Northrup Co., North Wales, PA). Whenever the readings drifted, a sufficient period of time was allowed to elapse until a steady value was attained. Buoyancy corrections were applied for 4 to 10 mm immersion of the glass sensor. All measurements were made at 25 ± 1 C. Reproducibility of surface tension measurements under these conditions was ± 0.5 dynes per cm. Figures 2 and 3 are typical surface tension curves, and Table II lists the principal features of these and other curves.

Dye Solubilization Measurements

Thirty ml of each solution and an excess (ca. .1 mg) of dye crystals were mixed in an 8 oz bottle on a Gyrotory shaker (Brunswick Scientific Co., New Brunswick, NJ) operating at 150 rpm for 20 hr in a room regulated at 24 ± 0.5 C. Dye solubilization under these mixing conditions was found to be greater than 90% of that found after mixing until equilibrium was reached. Excess dye was removed by filtration through a No. 12 fluted filter paper, and clarity of the filtrate was insured by diluting a 25 ml aliquot to 50 ml with ehtnaol. Optical density was measured at 480 nm in a 25 mm cell with the aid of a Beckman Model B spectrophotometer. A plot of absorbance versus concentration was used to locate the CMC values and to calculate the dye solubilizations shown in Table III.

RESULTS AND DISCUSSION

Since at concentrations below the CMC the surface tension values drifted frequently for an hour or more before reaching equilibrium, it was advantageous to use a Wilhelmy plate attached to an electronic balance whose output was recorded continuously. The use of platinum plates was troublesome because they were difficult to clean and rinse. Therefore, we used new microscope cover glasses, which were readily wet by the test solutions and could be reproducibly positioned when suspended by the holder shown in Figure 1.

Figure 2 shows the surface tension curves for sodium oleate in deionized water (curve a); sodium oleate in the presence of 0.005 N sodium hydroxide, at a pH of 11.3 (curve b); the amphoteric lime soap dispersant PASB alone (curve c); and the mixture of 80% sodium oleate and 20% of PASB (curve d). The slope of curve "a" below the CMC was not constant, suggesting that fatty acid was formed by hydrolysis of the soap at these high dilutions. Fatty acids, if present in neutral soap solutions, do not produce a minimum near the CMC of soap surface tension curves. Flengas and Rideal (8) also found surface tension curves for soap to be minimum free.

In alkaline solution, sodium oleate gave a surface tension curve "b" which had a constant slope below the CMC, and this slope was steeper than that of any analogous portion of curve "a", which indicates a higher surface concentration for this highly ionized material.

Mixtures of two or more surfactants usually form mixed micelles in aqueous solution. Surface tension curves for mixed micellar systems should have a single sharp break at the CMC, like that of a single surfactant. The presence or absence of a minimum at the CMC and its shape depend on the nature of the second component of the mixture, which may function as an impurity (9). Shinoda (10) and Schick and Manning (11) have shown that the CMC of mixtures is always between those of the individual components.

Curve "c" of Figure 2 (for PASB by itself) shows a large minimum at the CMC, presumably due to impurities in the sample. However, the soap-PASB mixture (curve d) shows a much smaller minimum at the CMC than the PASB by itself.

The slope below the CMC for the PASB-soap mixture (curve d) more closely resembles the steeper PASB slope than that for soap in deionized water, even though soap is the major component. This indicates that the addition of amphoteric lime soap dispersing agent to soap increases total surface concentration. This critical micelle concentration of the blend is nearly the same as that of PASB alone rather than lying between those of the two components as has been shown for other mixtures (10,11). The surface tension of the blend (curve d) above the CMC is much closer to that of sodium oleate (curve a) than to that of the PASB. Klevens and Raison made similar observations when they found that mixture of perfluorooctadecanoic acid and sodium lauryl sulfate had surface tnesion values above the CMC close to that of the perfluorinated acid by itself (12).

This phenomenon, as well as that of the obscuring of the minimum at the CMC, may be due to preferential adsorption of soap at the interface.

Figure 3 shows the analgous surface tension curves for the anionic lime soap dispersant PMS. Curves "a" and "b" are the same two reference curves for sodium oleate as shown in Figure 2. While curve "c" for PMS alone exhibits a minimum at the CMC, the minimum disappears entirely from the curve "d" for the soap-PMS blend. The blend behaves as if it were a single surfactant, demonstrating the mixed micellar nature of the blend in aqueous solution.

Data for various soap-lime soap dispersant blends are given in Table II. For most blends the CMC is closer to that of the lime soap dispersant than to that of the soap, and in some cases the CMC of the 80:20 mixture of soap and dispersant is identical to that of the dispersant. The blends exhibit either no minimum or greatly reduced minima. The surface tension of solutions of the blends above the CMC are close to that of soap lone regardless of the nature of the dispersant or the soap:dispersant ratio. This indicates preferential adsorption of soap at the air-liquid interface, as pointed out above. The slopes of the curves for the blends below the CMC are greater than that for soap alone and are generally close to those for the dispersants by themselves.

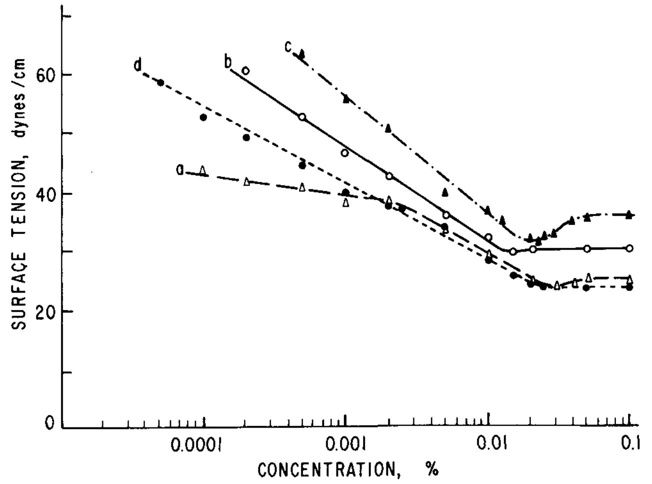

FIG. 3. Surface tension versus concentration for: (a) sodium oleate in deionized water; (b) sodium oleate in 0.005 N NaOH; (c) PMS in deionized water; and (d) 20% PMS-80% sodium oleate in deionized water.

Dye solubilization measurements were conducted to corroborate CMC values obtained by the surface tension method. Neutral solutions of soap and soap-LSDA mixtures did not give reliable solubilization curves. These difficulties were apparently caused by soap hydrolysis, since smooth curves with sharp breaks at the CMC were obtained in 0.01 N sodium hydroxide solutions. Table III shows good agreement between the CMC values determined by surface tension and dye solubilization methods for MAHSB and PMS

TABLE II

Surface Active Properties in Deionized Water[a]

Composition	CMC, g/liter	Minimum, dynes/cm	γ at 0.1%,[b] dynes/cm	-d γ/d ln c[c]
100% Na oleate	0.22	None	25	5.9
10% PASB – 90% Na oleate	0.0074	None	24	7.6
20% PASB – 80% Na oleate	0.0075	1.5	25	11.4
100% PASB	0.007	7.0	36	7.6
10% HSB – 90% Na oleate	0.011	None	24	7.7
20% HSB – 80% Na oleate	0.011	None	24	9.0
50% HSB – 50% Na oleate	0.0046	None	24	10.4
100% HSB	0.0045	4.0	32	11.1
20% MAHSB – 80% Na oleate	0.021	None	24	8.1
100% MAHSB	0.022	None	35	8.0
20% SAM – 80% Na oleate	0.1	None	24	7.0
100% SAME	0.035	3.0	42	7.7
20% PMS - 80% Na oleate	0.25	None	24	8.7
100% PMS	0.22	4.0	36	9.0

[a]Data obtained from surface tension curves.

[b]Surface tension by the Wilhelmy method.

[c]Slope below the critical micelle concentration in dynes per cm.

TABLE III

CMC Values and Dye Solubilization

Detergent	CMC (in 0.01 N NaOH by surface tension g/liter	CMC (in 0.01 N NaOH by dye solubilization) g/liter	Solubilization at 0.5 g/liter (in 0.01 N NaOH) mg/liter
Na oleate	0.1	0.1	4.1
20% MAHSB – 80T Na oleate	0.04	0.045	4.4
100% MAHSB	0.04	0.048	6.5
20% PMS – 80% Na oleate	0.10	0.094	4.1
100% PMS	0.10	0.090	3.4

and their mixtures. Values for the CMC of HSB and PASB were too low to permit accurate measurement by dye solubilization. The data for PASB and its mixture indicated that the CMC was below 0.01 g per liter. Good solubilization curves for SAM could not be obtained, probably because of hydrolysis in 0.01 N sodium hydroxide.

Table III also shows a comparison of the amount of dye solubilzied by different detergent compositions at a total concentration of 0.5 g per liter. Although the two LSDAs by themselves had different dye solubilzing power, both of the soap-LSDA combinations solubilized nearly the same amount of dye as did soap alone. This is in agreement with surface tension findings that above the CMC the mixture has essentially the colloidal properties of soap.

The measurements of this study leave little doubt as to the mixed micellar nature of soap-LSDA blends. Critical micelle concentrations are clearly identified as single breaks in the surface tension curve and dye solutilization curves at a concentration close to that for the LSDA alone. The LSDA appears to aid ionization of soap at the interface because hydrolysis is not a problem in surface tension measurement of these mixtures and surface concentrations are similar to those of highly ionized surfactants. Above the CMC, the mixture takes on the characteristics of soap.

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