Solubilizing Power of Some Anionic Surface Active Agents

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ABSTRACT

Solubilizing power of anionic surfactants was studied with the aid of turbidimetry. The work was based on the finding that although the calcium salts of anionic surfactants are insoluble in water and produce turbidity, they become soluble in the presence of excess calcium ions. The critical micelle values obtained by the turbidimetry were in good agreement with those of other authors.

INTRODUCTION

Solubilizing power is one of the most important properties of surfactants. There are a few methods known by which critical micelle concentration (CMC) of surfactants can be experimentally determined through the use of solubilization measurements. A number of approaches have been taken to measure solubilizing phenomena. One of these is a colorimetric method (1-4) in which oil soluble dyes, such as orange OT (Benzidine orange), dimethylaminoazobenzene (DMAB), and azobenzolazo-β-naphthol (SUDAN III) are dissolved above the CMC of the surfactants, and the solubilizing power of the surfactants is measured by optical density. Harkins (5) adopted a method of measuring the solubility of colored substances by colorimetry. In our study, it was found that the calcium salts, in contrast to the sodium salts, of anionic surfactants generally used for detergents, are insoluble in water, making the solution turbid. Furthermore, in the presence of excess calcium ions, these calcium salts become soluble in the solution of the surfactants giving rise to transparent solutions. In connection with the above finding, the formation of the calcium salts of surfactants was closely examined, the solubilizing capacity of surfactants was measured by a turbidimetry method devised by us, and from this, CMC values were obtained, which agreed very well with the results of other authors.

EXPERIMENTAL PROCEDURES

Materials

The surfactants used were as follows: Linear alkyl benzene sulfonate (LAS) (5&6-phenyl, 43.1%; 4-phenyl, 22.0%; 3-phenyl, 20.7%; 2-phenyl, 14.2%) and alkyl benzene sulfonate ABS (tetra propylene benzene sulfonate [TPBS]) (Nissan-Kagaku Kogyo Co., Ltd., Tokyo, Japan), alpha olefin sulfonate (AOS) (C_{15}, 31%; C_{16}, 30%; C_{17}, 25%; C_{18}, 13%) (Lion Fat and Oil Co., Ltd., Tokyo, Japan), sodium alkane sulfonate (SAS) (C_{13}, 6.7%; C_{14}, 90.6%; C_{15}, 2.7%) (Farbwerke Hoechst A.G., Frankfurt, West Germany), and sodium lauryl sulfate (SLS) of reagent grade. The surfactants were extracted with ether and recrystallized from ethanol.

Apparatus and Conditions

Colorimetric determinations were carried out with an Electro photocolorimeter, Hirama 2B type with a filter 655 mμ, cell length of 10.0 mm, at 28.0 C ± 0.1 C. The concentrations of solutions in this study followed the Lambert-Beer Law.

Formation of Calcium Salts of Surfactants

Solutions of surfactants were prepared at concentrations of 0.10, 0.20, 0.25, and 0.50% by wt in carbon dioxide-free distilled water. The hard water used contained calcium ions at levels equivalent to 100, 200, and 300 ppm as calcium chloride. A 10 ml solution containing surfactant and 10 ml of hard water was placed separately into 50-ml glass stoppered flasks and allowed to stand for 30 min at 28 C. The 2 solutions then were mixed at once with vigorous stirring. The turbidity of the solution was measured with an Electro Photocolorimeter at regular intervals.

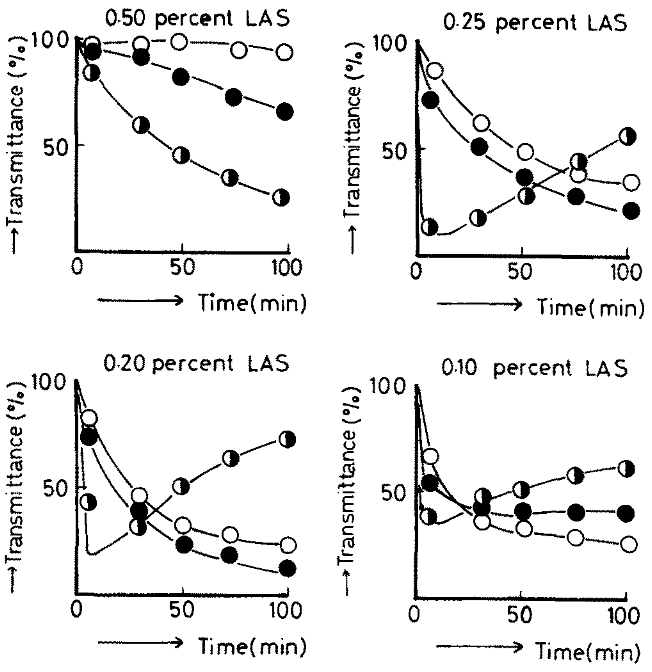

FIG. 1. Formation of calcium salts by linear alkyl benzene sulfonate (LAS). Calcium ion concentration: ○ = 100 ppm; ● = 200 ppm; ◑ = 300 ppm.

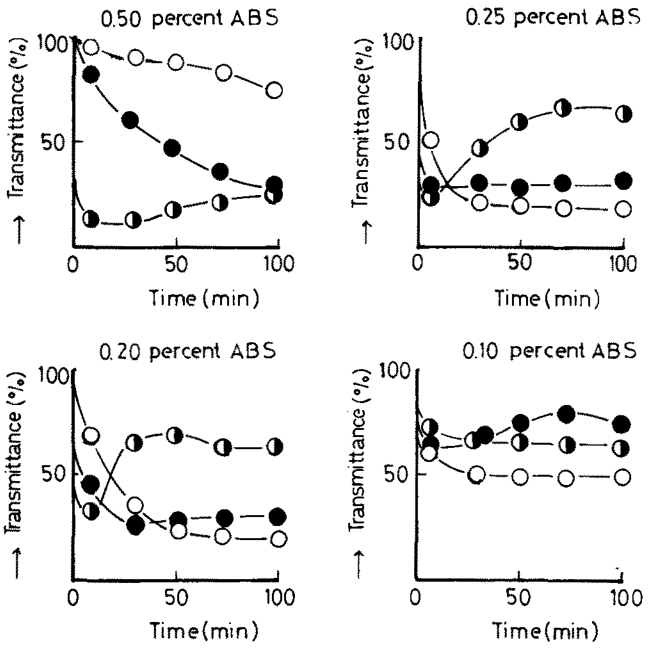

FIG. 2. Formation of calcium salts by alkyl benzene sulfonate (ABS). Calcium ion concentration: ○ = 100 ppm; ● = 200 ppm; ◑ = 300 ppm.

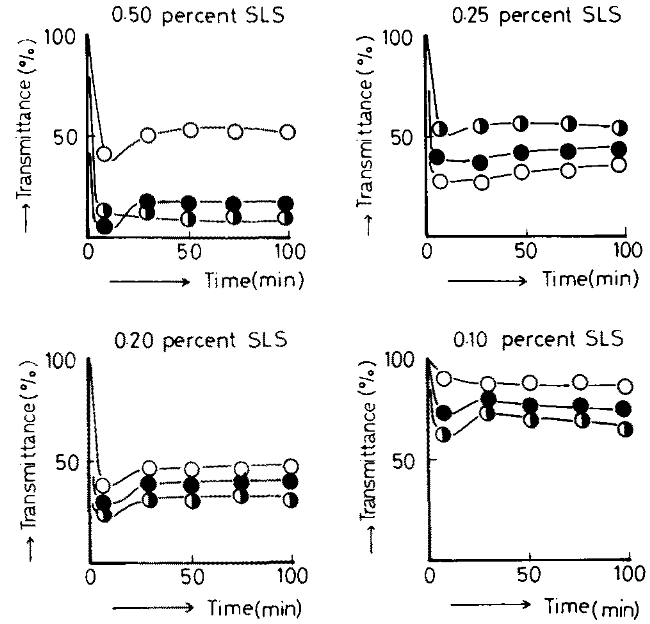

FIG. 3. Formation of calcium salts by sodium lauryl sulfonate (SLS). Calcium ion concentration: ○= 100 ppm; ●= 200 ppm; ◑= 300 ppm.

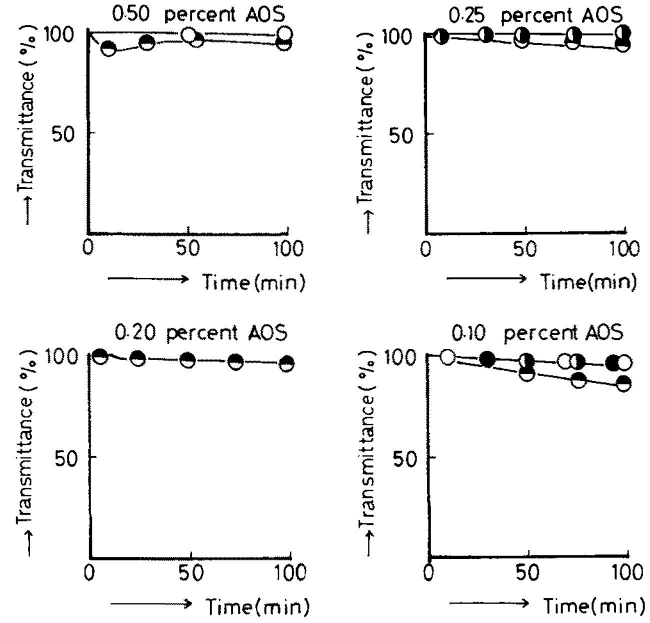

FIG. 4. Formation of calcium salts by alpha olefin sulfonate (AOS). Calcium ion concentration: ○ = 100 ppm; ● = 200 ppm; ◑ = 300 ppm; ⊖ = 500 ppm.

Solubility Measurement of Calcium Salts of Surfactant and Determination of CMC

Calcium salts of anionic surfactants, except AOS, were prepared from the surfactants and calcium chloride solutions by precipitation, filtration, washing with water, drying in a vacuum, and keeping in a desiccator for ca. 2 months. Into a 50-ml glass stoppered Erlenmeyer flask in which a given amount of calcium salt of a surfactant had been placed, 20 ml surfactant solution was added with thorough stirring. After equilibrium was established, the turbidity of the solution was measured. The CMC of the anionic surfactants was determined from the solubilities of calcium salts of surfactants in the surfactant solutions at various concentrations.

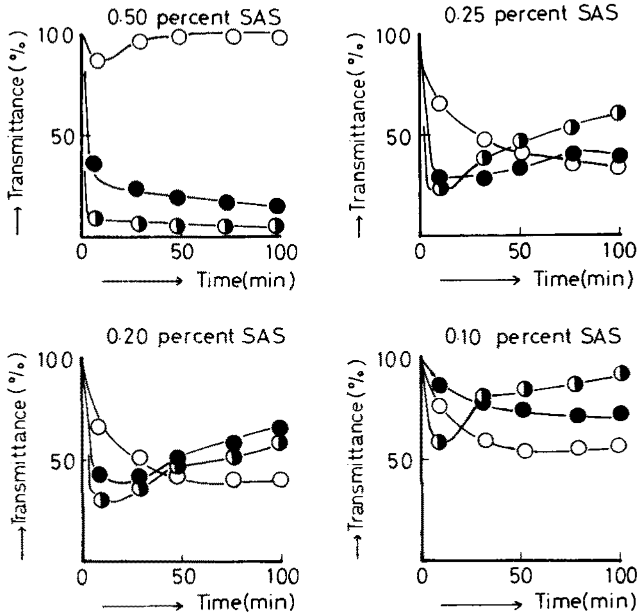

FIG. 5. Formation of calcium salts by sodium alkane sulfonate (SAS). Calcium ion concentration: ○ = 100 ppm; ● = 200 ppm; ◑ = 300 ppm.

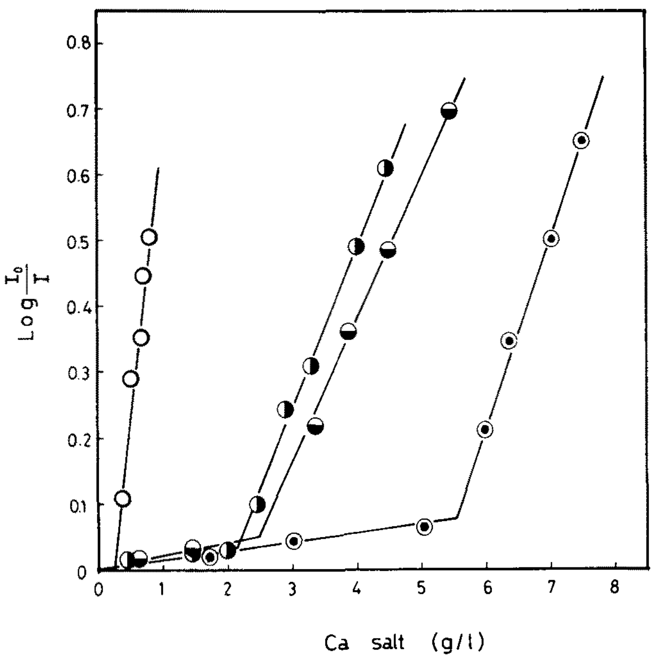

FIG. 6. Optical density of various concentrations of linear alkyl benzene sulfonate (LAS) solution with increasing amount of dissolved calcium salt. ○= 0.10% LAS; ◑= 0.20% LAS; ⊖= 0.25% LAS; ⊙ = 0.50% LAS; I = intensity of permeable light; I_0 = intensity of incident light.

RESULTS AND DISCUSSION

Behavior of Anionic Surfactants in Hard Water

Figures 1-5 show the formation of calcium salts by reaction of calcium ion with surfactants. In 100 and 200 ppm hard water, the solution became gradually turbid at different concentrations of LAS due to the formation of white precipitates of calcium sulfonate, while in 300 ppm hard water, the turbidity increased rapidly at first, but later decreased gradually, except for 0.50% LAS (Fig. 1). Table II shows the material balances for respective concentrations of LAS and calcium ion in solution. It is shown in Table II that in the case of 100 ppm of calcium ion, where there is

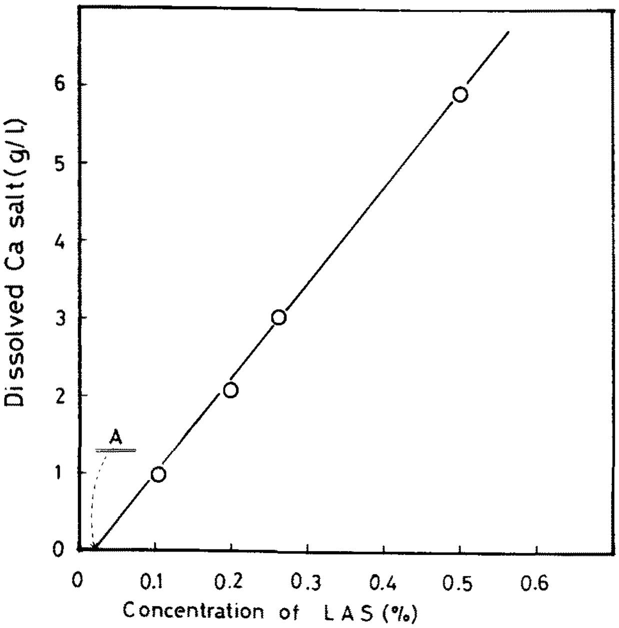

FIG. 7. Solubilization power and critical micelle concentration of linear alkyl benzene sulfonate (LAS). A = Critical micelle concentration of LAS in water.

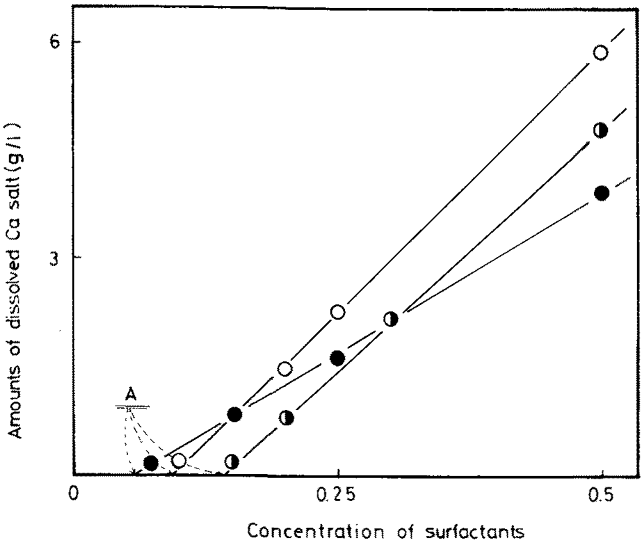

FIG. 8. Solubilization power and critical micelle concentration of: ○ = alkyl benzene sulfonate (ABS); ● = sodium lauryl sulfonate (SLS); and ◑ = sodium alkane sulfonate (SAS).

TABLE I

Critical Micelle Concentration
(CMC) of Anionic Surface Active Agents

	CMC	
Sample[a]	Observed (% by wt)	Reference[b] (% by wt)
LAS	0.025	0.025(8)
ABS	0.035	0.041(9)
SLS	0.14	0.20(10)
AOS	0.028	0.031(11)[a]
SAS	0.14	0.1(12)

[a] LAS = linear alkyl benzene sulfonate; ABS = alkyl benzene sulfonate; SLS = sodium lauryl sulfonate; AOS = alpha-olefin sulfonate; SAS = sodium alkane sulfonate.

[b] ( ) = reference number.

[c] Because insoluble calcium salt of AOS are not formed, the CMC value was determined by using conductivity method.

TABLE II

Material Balance of Each Concentration of Linear Alkyl Benzene Sulfonate (LAS) and Calcium Ion in Solution

Calcium concentration (ppm)	LAS concentration (%)	LAS Mole number (10^{-3} mole/liter)	Ca^{2+} Mole number (10^{-3} mole/liter)	Excess substance	Unreacted LAS (10^{-3} mole/liter)	Unreacted Ca^{2+} (10^{-3} mole/liter)	Unreacted Ca salt (10^{-3} mole/liter)	Formed NaCl (10^{-3} mole/liter)
100	0.10	1.45	0.63	LAS	0.20	0	0.63	1.25
100	0.20	2.90	0.63	LAS	1.65	0	0.63	1.25
100	0.25	3.63	0.63	LAS	2.38	0	0.63	1.25
100	0.50	7.25	0.63	LAS	6.00	0	0.63	1.25
200	0.10	1.45	1.25	Ca^{2+}	0	0.53	0.73	1.45
200	0.20	2.90	1.25	LAS	0.40	0	1.25	2.50
200	0.25	3.63	1.25	LAS	1.13	0	1.25	2.50
200	0.50	7.25	1.25	LAS	4.75	0	1.25	2.50
300	0.10	1.45	1.88	Ca^{2+}	0	1.15	0.73	1.45
300	0.20	2.90	1.88	Ca^{2+}	0	0.43	1.45	2.90
300	0.25	3.63	1.88	Ca^{2+}	0	0.06	1.82	3.63
300	0.50	7.25	1.88	LAS	4.50	0	1.88	3.75

an excess of LAS and no free calcium ions are present in the solution, a rapid decrease in the turbidity of the solutions with increasing concentrations of LAS was not observed. In 200 ppm of calcium ion, turbidity measurements looked similar to those for 100 ppm of calcium ion, except for the 0.10% LAS solution. When 300 ppm of calcium ion were mixed with solutions of 0.50% LAS, results were similar to those for 100 ppm and 200 ppm of calcium ion because of the absence of free calcium ion. In reactions of 300 ppm of calcium ion with 0.10, 0.20, and 0.25% LAS, the counter ion effect appeared for the first time, exhibiting an unusual feature, as shown in Figure 1, for solutions of 0.20 and 0.25% LAS. This was due to the effect of free calcium ions and large quantities of sodium chloride on the micelle formation, and can be explained in terms of metathesis to form calcium salts of surfactants and sodium chloride. On the other hand, a large excess of calcium ions facilitated either a lowering of the CMC or a formation of more micelles of smaller size. In other words, tendency for micelle formation depended on the builder effects due to counter ions, and we would have expected the turbidity of the solutions to decrease.

As is evident from Figure 2, ABS behaved like LAS, but differed with respect to the reaction of 200 ppm of calcium ion with various concentrations of ABS. When 300 ppm calcium ion was mixed with solutions of 0.50% ABS, the turbidity of the solutions decreased slightly in spite of the absence of free calcium ion, indicating that calcium salt was dispersed by the surfactant anion. In a comparison of Figures 1 and 2, the difference between normal paraffinic chain compounds and branched chain compounds was obvious.

SLS behaved very differently from LAS or ABS as shown in Figure 3. In the case of SLS, the solubilization was almost independent of the presence of free calcium ion and of inorganic electrolytes. The structure of SLS, a sulfate, is different from that of the sulfonates, of LAS or of ABS. SLS plus calcium ion formed an insoluble salt.

The results for AOS are shown in Figure 4. As is evident from the Figure 4, the turbidity curves were very different from the 3 surfactants mentioned above. All curves lay in the 90-100% transparency region and remained almost unchanged. This was due to the effects of the hydroxyl group and the double bond in the AOS molecule (6-7). In the presence of calcium ion, the protons from the hydroxyl groups of adjacent AOS molecules were replaced by calcium ion. Insoluble calcium salts, thus, were not formed because the calcium ion was packed within the AOS molecules. This explained why the turbidity of the solutions was not increased. Details on this will be reported in the near future. SAS, shown in Figure 5, is a biodegradable commercial anionic surfactant and behaved like LAS and ABS.

In summary, our interpretation of the results is that all sulfonates, except AOS, form insoluble calcium salts, and these salts are partially solubilized by a large excess of calcium ion. However, AOS was not affected by the amount of calcium ion present. Furthermore, in the sulfonate series, there was a large difference between normal parafinic and branched chain compounds.

SLS, a sulfate, produced an insoluble calcium salt which was not solubilized readily by large amounts of calcium ion; hence SLS was not affected by a large excess of calcium ion.

Solubilizing Capacity and Determination of CMC

Figure 6 shows the optical density of various concentrations of LAS solution with increasing amounts of dissolved calcium salt of surfactant. The increase of log I_0/I was rapid when insoluble calcium salts particles first appeared. The point of intersection with the abscissa was considered to indicate the solubility of calcium salt in the surfactant solution.

Figure 7 shows the solubility of the calcium salt of LAS in dilute LAS solutions. The solubility remained constant until the critical concentration was reached beyond which there was a sharp increase in surfactant micelles due to solubilization. Point A shows the CMC of LAS in water. The CMC of LAS (0.025% by wt) obtained here is in good agreement with published data (8-12).

Figure 8 shows the solubilizing power and the CMC of ABS, SLS, and SAS, respectively. A comparison of our results with those of other investigators is shown in Table I. The CMCs of the surfactants measured are in good agreement with the data of other authors.

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