

CRITICAL MICELLE CONCENTRATIONS OF α -SULFONATED FATTY ACIDS AND THEIR ESTERS¹

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Conductance, surface tension and dye titration methods have been used to determine the c.m.c. of α -sulfo-myristic acid, α -sulfo-palmitic acid, α -sulfo-stearic acid and sodium salts of methyl, ethyl, propyl and 2-sulfoethyl esters of α -sulfonated palmitic and stearic acids. Increase in length of the carbon chain of the fatty acid results in a decrease in c.m.c. in accordance with the usual logarithmic relationship. Disodium 2-sulfoethyl α -sulfo-palmitate has a c.m.c. which is a little greater than that reported for sodium dodecyl sulfate. Disodium 2-sulfoethyl α -sulfo-stearate has a c.m.c. which is about midway between that reported for sodium dodecyl sulfate and sodium tetradecyl sulfate. This may account for the similarity of these compounds in detergency and response to building.

Sodium salts of α -sulfonated fatty acids [RCH(SO₂Na)COOH and RCH(SO₂Na)COONa] and their esters [RCH(SO₂Na)COOR' where R' is alkyl or -CH₂CH₂SO₂Na] have been prepared in high purity^{3,4} and their detergent properties have been evaluated.^{4,5} It is of interest to study the micellar properties of solutions of these compounds in order to correlate their surface active properties with critical micelle concentration (c.m.c.). The esters are of particular interest because their structure can be varied at both the fatty acid and the alcohol portion of the molecule. The disodium salts of 2-sulfoethyl esters and the simple disodium salts of α -sulfonated fatty acids are interesting examples of surfactants with two hydrophilic groups.

There are sources of error in the methods used for these studies. Impurities affect the accuracy of the surface tension method; in the dye titration method, dyes have been shown⁶ to initiate the formation of micelles at slightly lower concentrations; and in the conductance method difficulties are encountered when the conductivities are low. Therefore all three methods were used whenever applicable and an attempt was made to correlate them.

Experimental

Surfactants used were those described in earlier publications.^{3,4} In all cases an attempt was made to purify the compounds until the surface tension *versus* concentration curve of the aqueous solutions did not show a minimum. α -Sulfo-myristic acid and α -sulfo-palmitic acid were found to be free of surface tension minima after five crystallizations from chloroform. Crystallization from chloroform did not purify α -sulfo-stearic acid to this degree.

Simple esters such as sodium ethyl α -sulfo-palmitate were extracted with ether in a Soxhlet extractor for six to eight hours and found to be free of surface tension minima. Ether extraction failed to remove the minimum from disodium 2-sulfoethyl α -sulfo-stearate but foam fractionation⁷ followed by freeze drying was found to be successful.

Surface Tension.—The du Noüy tensiometer was used for all surface tension measurements. Since little change in

surface tension with temperature was observed with these compounds, and since it has been shown that the c.m.c. is nearly independent of temperature,⁸ all surface tension measurements were made at room temperature, 28 ± 1°. Appropriate corrections were applied to the tensiometer readings to give surface tension in dynes per centimeter.

Conductance.—A Leeds and Northrup conductivity bridge operating at 1,000 cycles was used to measure conductance. The bridge was capable of measuring resistance up to 20,000 ohms with an error of 0.1% or less. Measurements were made at 25.00 ± 0.05° in a cell with a constant of 2.26 ± 0.02. Variations in conductance due to temperature were thus found to be less than one part in five thousand. Surfactants were dissolved in a redistilled water with a specific conductance of 2.53 × 10⁻⁶ mho and correction made for the conductance of the solvent in all cases.

Dye Titration.—Determinations of c.m.c. by the pinacyanole method were carried out as described by Corrin, Klevens and Harkins.⁹ A solution of surfactant in 10⁻⁵ M pinacyanole chloride (0.0005%) solution was made up at a concentration well above the c.m.c. of the surfactant and diluted with 10⁻⁵ M dye solution. Critical micelle concentrations were determined both by visual observation of the color change and from a plot of the light absorbance at the maxima: 480, 557 and 608 m μ , as measured in a Beckman model DU spectrophotometer.

Solubility.—The solubility of the more readily soluble surfactants was determined by filtering insoluble matter from an equilibrated mixture of solid and water.⁵ Lower solubilities were determined by a trial and error method to determine the limiting concentration capable of producing a clear solution.

Discussion of Results

Table I lists the c.m.c. values determined by the surface tension, conductance and dye titration methods for α -sulfo-myristic, α -sulfo-palmitic and α -sulfo-stearic acids and some of their esters. The conductance method has an advantage over the other methods in that it is not affected either by small amounts of impurities, as is the surface tension method, or by the presence of dye particles, as is the dye titration method.⁶ The conductance values reported have been found to have a normal Onsager slope below the c.m.c. Figure 1 shows the conductance curve for α -sulfo-myristic acid, in the upper part; and the conductance curves for disodium 2-sulfoethyl α -sulfo-palmitate (A) and disodium 2-sulfoethyl α -sulfo-stearate (B), in the lower part.

Figure 2 shows surface tension curves for solutions of disodium 2-sulfoethyl α -sulfo-stearate after ether extraction as the only purification, and after foam fractionation of the same material. Ether extraction of the ester resulted in a surface tension curve with a broad minimum but foam fractiona-

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TABLE I
CRITICAL MICELLE CONCENTRATION
Per Cent. at Room Temperature

	Surface tension method	Dye Method		Conductance method (25°)
		Spectrophotometer	Visual	
α -Sulfomyristic acid	0.07	0.075	0.08	0.13
α -Sulfopalmitic acid	.02	.023	.017	
α -Sulfostearic acid	.005	.004	.005	
Sodium methyl α -sulfopalmitate	.012	.014	.015	
Sodium ethyl α -sulfopalmitate	.009	.013		
Sodium propyl α -sulfopalmitate	.004			
Sodium methyl α -sulfostearate	.004	.004	.003	
Sodium ethyl α -sulfostearate	.005	.002	.002	
Sodium propyl α -sulfostearate	.0005			
Sodium isopropyl α -sulfostearate	.001			
Disodium 2-sulfoethyl α -sulfopalmitate		.3	.4	.53
Disodium 2-sulfoethyl α -sulfostearate	.13	.10		.16

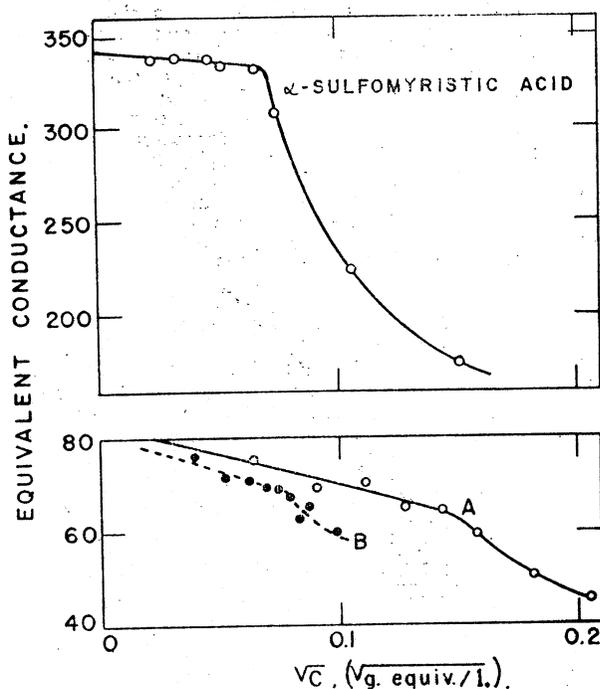


Fig. 1.—Variation of equivalent conductance with concentration for α -sulfonated fatty acids and esters, 25.00 \pm 0.05°: A, disodium 2-sulfoethyl α -sulfopalmitate; B, disodium 2-sulfoethyl α -sulfostearate.

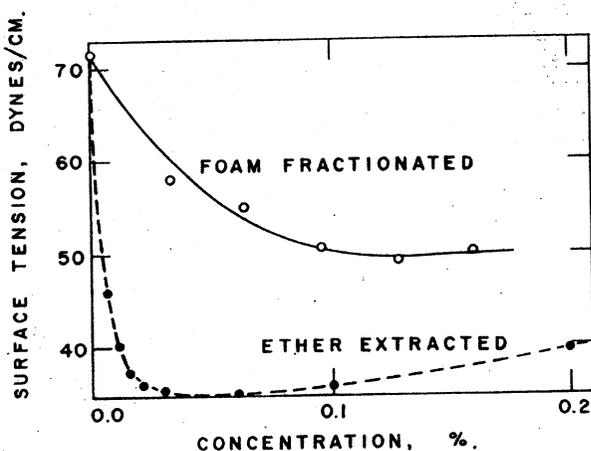


Fig. 2.—Variation of surface tension with concentration for disodium 2-sulfoethyl α -sulfostearate, 23°.

tion was able to remove it completely. Miles and Shedlovsky¹⁰ have illustrated the effect of adding a material of lower c.m.c. such as sodium cetyl sulfate to sodium lauryl sulfate. Their curves were similar to those shown here. Small amounts of suspected ether-insoluble impurities such as sodium ethyl α -sulfostearate and sodium 2-sulfoethyl stearate, which have lower c.m.c. values, may be expected to be responsible for this effect. Critical micelle concentrations of foam fractionated and non-foam fractionated disodium 2-sulfoethyl α -sulfostearate by the dye titration method were in agreement with c.m.c. values shown in Fig. 2.

Table II lists the solubility of some mono- and disodium salts of α -sulfonated fatty acids. When pinacyanole chloride was added to solutions of these surfactants at the concentrations shown in Table II, micelles were found to be absent in all cases. The c.m.c., accordingly, is not less than the concentration of a saturated solution. Little difference is observed in comparing the solubility of sodium α -sulfostearic acid, sodium α -sulfopalmitic acid and sodium α -sulfomyristic acid (Table II) with the c.m.c. values of α -sulfostearic acid, α -sulfopalmitic acid and α -sulfomyristic acid (Table I), respectively.

TABLE II
SOLUBILITY OF SODIUM SALTS OF α -SULFONATED FATTY ACIDS IN PER CENT. AT 25°

Disodium α -sulfomyristate	1.50
Disodium α -sulfopalmitate	0.25
Disodium α -sulfostearate	0.10
Sodium α -sulfolauric acid	0.42
Sodium α -sulfomyristic acid	0.11
Sodium α -sulfopalmitic acid	0.02
Sodium α -sulfostearic acid	<0.01

Increase in the length of the fatty acid chain of these compounds results in a decrease in c.m.c. in the usual logarithmic relationship shown for other homologous series.^{11,12} There is also a general decrease in the c.m.c. with increase in number of carbon atoms in the alcohol portion of the esters but no consistent relationship is shown over this limited range. Only a slight decrease in c.m.c. is observed on esterifying the diacid or monosodium salt with methyl alcohol.

(10) G. D. Miles and L. Shedlovsky, *THIS JOURNAL*, **48**, 57 (1944).

(11) S. H. Herzfeld, *ibid.*, **56**, 953 (1952).

(12) P. Debye, *J. Colloid Sci.*, **3**, 407 (1948).

Some interesting observations may be made on the effect of adding a second hydrophilic group to a long hydrophobic chain. The solubility of disodium α -sulfostearate and the c.m.c. of disodium 2-sulfoethyl α -sulfostearate are not what one might expect from half the number of carbon atoms attached to one hydrophilic group but rather their ion solubilities are about midway between those reported¹³ for sodium dodecyl sulfate and sodium tetradecyl sulfate. Likewise, disodium α -sulfopalmitate and disodium 2-sulfoethyl α -sulfopalmitate have a little higher ion solubility than sodium dodecyl sulfate. Disodium 2-sulfoethyl α -sulfostearate has been found to have good detergency and shows a response to building⁴ similar to that of surfactants with twelve and fourteen carbon atoms. The c.m.c. values given here are only slightly lower than those reported by Shinoda¹⁴ for corresponding alkyl malonates: $C_{12}H_{25}CH(COOK)_2$, 1.7%; $C_{14}H_{29}CH(COOK)_2$, 0.7%; $C_{16}H_{33}CH(COOK)_2$, 0.2–0.4%.

(13) J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937).

(14) K. Shinoda, *This Journal*, **59**, 432 (1955).

Conclusions

The conductance method is preferred for measurement of critical micelle concentrations of α -sulfonated acids and esters when the value obtained is above 0.05% (0.001 *M*). The surface tension and dye titration methods were used for those having lower c.m.c. values.

α -Sulfonated acids and their alkyl esters have c.m.c. values in the same region as other surfactants of equal carbon chain length. Disodium 2-sulfoethyl α -sulfostearate has a c.m.c. between that of sodium dodecyl sulfate and sodium tetradecyl sulfate. Simple monosodium and disodium salts of α -sulfonated acids do not form micelles at room temperature but have solubilities which are very close to the c.m.c. values of other materials having the same length of alkyl chain and the same number of hydrophilic groups.

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