α-Sulfonated Fatty Acid Esters: I. Structural Effects of Sodium α-Sulfonated Fatty Acid Higher Alcohol Esters on Surface-Active Properties and Emulsification Ability

T. Okano, J. Tanabe, M. Fukuda* and M. Tanaka
Lion Corporation, Applied Research Laboratories 8, Tokyo 132, Japan

The surface-active properties and emulsification ability of sodium α-sulfonated fatty acid esters, $C_mH_{2m+1}CH(SO_3Na)COOC_nH_{2n+1}$, were studied as a function of the hydrophobic alkyl chainlength in the fatty acid (m = 8–16) and the alcohol (n = 8–18). As a result, it was discovered that sodium α-sulfonated fatty acid esters have a structural effect on the Krafft point different from that of amphiphiles with short alkyl chains. Moreover, some of the α-sulfonated fatty acid esters have quite low interfacial tensions, as well as non-foaming properties, which depend upon the total (m+n) number of carbon atoms in the alkyl chains.

KEY WORDS: α-Sulfonated fatty acid, critical micelle concentration, emulsification ability, foam property, higher alcohol esters, Krafft point, non-foaming emulsifier, structural effects, surface active properties, two hydrophobic alkyl chains.

The structural effects on the fundamental interfacial properties of surface-active compounds with two lipophilic alkyl chains is of current interest (1–3). To make these effects clear, many types of amphiphiles have been studied, such as branched alkane sulfates (4), Guerbet alcohol sulfates (5), amphiphatic compounds with plural lipophilic groups and plural hydrophilic groups (6) and so on, and several results of interest have been reported. Stirton *et al.* (7) reported the surface-active properties of a series of α-sulfonated fatty acid esters, $C_mH_{2m+1}CH(SO_3Na)COOC_nH_{2n+1}$, in relation to their structure. Similar to the other studies, however, their attention was focused only on the amphiphiles that had good hydrophilic affinity and spontaneously formed micelles in water. That is, α-sulfonated fatty acid chainlengths examined were varied from m = 1–16, and the alcohol chainlength from n = 1–16, and the total carbon number, m + n, was limited to less than 17. The higher alcohol esters of sodium α-sulfonated fatty acids are to be regarded as double-chain amphiphiles, much like lecithin or dialkyl dimethyl ammonium halide, because of the close similarity of their structural elements. Therefore, these α-sulfonated fatty acid esters can be expected to form bilayer membranes, like vesicles or lamellar liquid crystals, rather than micelles in water. Nevertheless, little is known about the properties of α-sulfonated fatty acid esters with long alkyl chains in both fatty acid residue and alcohol. We report here the structural effects of sodium α-sulfonated fatty acid higher alcohol esters on the surface-active properties and emulsification ability.

EXPERIMENTAL PROCEDURES

Preparation of α-sulfonated fatty acids. The α-sulfonated fatty acids were conveniently prepared from the saturated long-chain fatty acids by means of liquid sulfur trioxide in the presence of carbon tetrachloride, and they were used in the following process after recrystallizing twice from carbon tetrachloride.

Preparation of sodium α-sulfonated fatty acid esters. A mixture of the given alcohol, the α-sulfonated fatty acid, and toluene as a solvent was heated at reflux temperature with azeotropic removal of water. After evaporating the solvent, the esterification mixture was poured into a large excess of ethanol and neutralized with aqueous sodium hydroxide. Recrystallizing twice from ethanol gave the corresponding sodium α-sulfonated fatty acid ester in a good yield. Their purity was ascertained by high-performance liquid chromatography (HPLC) and H-nuclear magnetic resonance (NMR) techniques.

Measurement of surface-active properties. The Drafft point was determined as the coagel to liquid-crystal phase transition temperature (Tc) of 20 wt% surfactant solution by differential scanning calorimetry (DSC) (8,9). No dependency of Tc on the concentration was observed, at least at water contents above 50 wt%. Critical micelle concentration (CMC) was measured by a conductivity method (10) at 70°C. Interfacial tension of 0.01 wt% surfactant solution was measured by the drop weight method (11) at 70°C. Wetting ability was determined as the time in seconds to sink a piece of felt (AW-8020; 10 × 10 mm) in 100 mL of 0.01 wt% surfactant solution at 70°C. Foam height was measured instantly after constant shaking a 100-mL Epton tube containing 10 mL of a 1 wt% surfactant solution for 30 seconds at 70°C. For emulsification ability, we measured the type of emulsion and the separated phase volume after 30 min for stability. Calcium stability was measured by titration to a turbidimetric end point with calcium acetate at 70°C, and was expressed in terms of stability at the indicated value of water hardness (12).

RESULTS AND DISCUSSION

All the data obtained are summarized in Table 1. Almost all of the sodium α-sulfonated fatty acid esters prepared for this study had relatively high Krafft points and did not dissolve in water at room temperature. As a rule, the Krafft point became higher with the increasing total carbon number, m + n. It is well known that for numerous surfactants Krafft points shift to lower temperatures by branching in the hydrocarbon chain (4). Therefore, it is noteworthy that the Krafft points were highest at m = n in a series of homologues with the same total carbon number. This suggests strongly that the packing of α-sulfonated fatty acid ester molecules becomes close and tight when the hydrophobic alkyl chainlengths in the α-sulfonated fatty acid and the alcohol are fairly long and equal to each other. This may be the reason why double-chain amphiphiles show a propensity to form bilayer membranes or lamellar liquid crystals.

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*To whom correspondence should be addressed at Lion Corp., Applied Research Lab 8, 7-13-12, Hirai, Edogawa-ku, Tokyo 132, Japan.

TABLE 1

Structure and Properties of $C_mH_{2m+1}CH(SO_3Na)COOC_nH_{2n+1}$

	Number of carbon atoms			Krafft point (°C)	CMC (mmol/kg)	Interfacial tension (mN/m)		Wetting ability (sec)	Foam volume (mL)	Emulsification ability/type of emulsion and the separated phase volume (vol%)				Calcium stability[a] (ppm)
No.	m	n	m + n			Octane	Xylene			Octane	Xylene	Liq. paraffin	Soybean oil	
1	8	8	16	23	3.00	23	16	1	>100	O/W 70	O/W 20	O/W 80	O/W 80	110
2	10	8	18	28	2.15	15	8	2	80	O/W 80	O/W 22	O/W 80	O/W 75	130
3	8	10	18	35	1.92	12	5	2	85	O/W 80	O/W 22	O/W 80	O/W 80	150
4	12	8	20	22	0.41	7	3	4	55	O/W 80	O/W 24	O/W 80	O/W 60	210
5	10	10	20	42	0.51	6	2	5	70	O/W 75	O/W 26	O/W 70	O/W 50	190
6	8	12	20	30	0.73	6	4	5	55	O/W 80	O/W 39	O/W 80	O/W 80	260
7	14	8	22	29	0.24	4	3	12	25	O/W 80	W/O 10	O/W 70	O/W 50	230
8	12	10	22	44	0.19	5	3	13	15	O/W 70	W/O 40	O/W 45	O/W 45	210
9	10	12	22	45	0.22	3	3	13	17	O/W 30	O/W 12	O/W 50	O/W 50	220
10	8	14	22	29	0.23	4	3	12	10	O/W 20	O/W 2	O/W 70	O/W 60	250
11	16	8	24	37	0.20	4	4	19	1	O/W 75	W/O 20	O/W 65	O/W 45	210
12	14	10	24	39	0.17	5	4	22	1	O/W 50	W/O 55	O/W 40	O/W 30	210
13	12	12	24	52	0.17	5	3	22	1	W/O 75	W/O 80	O/W 45	O/W 20	170
14	10	14	24	45	0.18	4	5	21	2	W/O 80	W/O 60	O/W 40	O/W 35	190
15	8	16	24	29	0.18	5	4		2	W/O 90	W/O 20	O/W 70	O/W 40	200
16	16	10	26	43	0.15	13	12	23	0	W/O 85	W/O 75	O/W 60	O/W 40	230
17	14	12	26	55	0.16	16	9	24	0	W/O 80	W/O 90	O/W 40	O/W 20	230
18	12	14	26	56	0.16	12	6	23	0	W/O 80	W/O 90	O/W 40	O/W 10	210
19	10	16	26	43	0.11	10	12	[c]	0	W/O 95	W/O 90	O/W 25	O/W 40	230
20	8	18	26	34	0.12	14	14	[c]	0	W/O 90	W/O 75	O/W 0	O/W 5	190
21	16	12	28	51	0.13	23	16	24	0	W/O 95	W/O 95	O/W 50	O/W 20	260
22	14	14	28	62	0.11	23	16	25	0	W/O 95	W/O 95	O/W 35	O/W 10	290
23	12	16	28	55	[b]	24	19	[c]	0	W/O 95	W/O 90	O/W 20	O/W 40	230
24	10	18	28	46	[b]	28	18	[c]	0	W/O 95	W/O 90	O/W 10	O/W 30	250
25	16	14	30	64	[b]	29	22	26	0	W/O 95	W/O 95	O/W 40	O/W 20	250
26	14	16	30	63	[b]	31	21	[c]	0	W/O 95	W/O 95	O/W 25	O/W 20	270
27	12	18	30	53	[b]	30	21	[c]	0	W/O 95	W/O 95	O/W 20	O/W 40	320
28	16	16	32	68	[b]	19	10	[c]	0	W/O 95	W/O 95	O/W 40	O/W 30	320
29	14	18	32	63	[b]	19	13	[c]	0	W/O 95	W/O 95	O/W 20	O/W 25	320
30	16	18	34	69	[b]	30	24	[c]	0	W/O 95	W/O 95	O/W 15	O/W 30	200

[a] Esters of methanol (m = 8–16, n = 1) exhibited excellent calcium stability, >1800 ppm.

[b] Critical micelle concentration too small to be determined.

[c] Wetting time greater than 30 seconds.

The Krafft points of surfactants are known to depend greatly on the type of counter ion (13). The potassium salt of Compound no. 4 had a relatively higher Krafft point than the sodium salt or the ammonium salt. The triethanolammonium salt could reduce the Krafft point slightly, and all bivalent cations, *e.g.*, calcium and magnesium, raised the Krafft point. The formation of eutectics by blending two or three adjacent homologous surfactants was effective in lowering the Krafft point. For example, blends of 20 wt% solutions of Compound numbers 2, 4, and 7 gave a Krafft point of 14°C, and the mixture existed as liquid crystals at room temperature.

The CMC values were small compared with common anionic surfactants, and evidently they are governed by the total carbon number. On the other hand, their values may be considered to be about three or six orders of magnitude larger than expected for double-chain amphiphiles that can spontaneously form vesicles in water (14). The solutions of α-sulfonated fatty acid esters were optically isotropic, and distinct bends were observed in the conductivity-concentration curve. These results indicate, therefore, that they do not form vesicles in the concentration range near the CMC. However, solutions of α-sulfonated fatty acid esters in the vicinity of the CMC appeared slightly turbid, even above the Krafft point, and the solubilization capacity for Oil Yellow OB dye was about five to ten times larger than with the corresponding methyl ester (data not shown). These results imply that the possibility of the existence of so-called spherical micelles is excluded. It seems reasonable at this time to assume that a solution of α-sulfonated fatty acid esters above the Krafft point is composed of monomers and large aggregates equilibrated with monomers. The exact model will be clarified in the near future with the aid of light scattering and other measurements.

The interfacial tensions between 0.01 wt% aqueous solutions and octane clearly depended on the total carbon number of m + n, rather than on the balance in length between m and n. The same tendency was observed with xylene, and the minimum was observed at m + n equal to 22. To attain the same magnitude in the interfacial tension between a solution of LAS and octane, the required concentration of LAS was 0.1 wt%. This is ten times the concentration required for α-sulfonated fatty acid esters. Thus, α-sulfonated fatty acid esters with m + n equal to 20–24 are indicative of excellent interfacial activity at temperatures above the Krafft point.

In many technical processes such as flotation, washing, rinsing and cleaning, it is most important to control foaming behavior. Foam volumes were also evidently dependent on the total carbon number, m + n. It is noteworthy that the foam volumes become nearly zero when m + n is 24 or greater. As mentioned above, since the α-sulfonated fatty acid esters with m + n equal to 20–24 have excellent interfacial activities, those esters with m + n equal to 24 are especially promising as non-foaming emulsifiers.

Emulsion type is apparently governed by the total carbon number of the α-sulfonated fatty acid esters when oils are octane and xylene. That is, with the larger values of m + n, W/O (water-in-oil) emulsions were formed, and O/W (oil-in-water) emulsions were formed with the smaller values. This agrees with the rule that more lipophilic emulsifiers form W/O emulsions or *vice versa* (15). It is interesting that the interfacial tension showed a minimum where the emulsion type was altered from O/W to W/O. Using a LAS solution as emulsifier under the same conditions, the drained (separated) phase volume was about 80%. Therefore, a value of less than 50% can be considered fairly stable. In the system with xylene, when the total carbon number of the emulsifier was less than 24, stable O/W emulsions were formed. On the contrary, emulsions obtained from liquid paraffin or soybean oil were all of the O/W type and had good stabilities, especially when the total carbon number of the emulsifiers was more than 24. These phenomena cannot be explained with the concept of oil specificity (16) as well as with HLB.

In O/W emulsions, the hydrophilic part of the emulsifier molecule has a high affinity toward the water phase. If the hydrophobic part, *i.e.,* the fatty acid chain and the alcohol chain, does not solely adsorb on the oil-water interface but invades the core of the oil droplet, the emulsifier molecules form a so-called two-dimensional monolayer film (17) on the surface of the oil droplet. Hence, it seems important that the properties of such two-dimensional monolayer films, to which oil molecules have contributed, should be investigated to interpret the differences in type and stability of the emulsions.

Calcium stabilities of α-sulfonated fatty acid esters were not superior to their methyl esters. In other words, almost all of the esters examined in this work had an extremely high sensitivity to calcium ions. If these esters are used as emulsifiers for O/W emulsions, addition of calcium ions can easily alter the properties of two-dimensional monolayer films on the surface of oil droplets and cause de-emulsification.

This study has shown that sodium α-sulfonated fatty acid higher alcohol esters have several characteristic features and have promising possibilities for usage as non-foaming emulsifiers in the toiletry and chemical industries.

REFERENCES

1. Rosen, M.J., *Surfactants and Interfacial Phenomena,* Wiley-Interscience, New York, 1978.
2. Lindman, B., and H. Wennerstrom, *Topics in Current Chemistry,* Vol. 87, Springer-Verlag, New York, 1980, p. 1.
3. Rosen, M.J., Z.H. Zhu, B. Gu and D.S. Murphy, *Langmuir 4*:1273 (1988).
4. Gotte, E., and M.J. Schwuger, *Tenside 6*:131 (1969).
5. Varadaraj, R., J. Bock, P. Valint, Jr., S. Zushma and R. Thomas, *J. Phys. Chem. 95*:1671 (1991).
6. Okahara, M., A. Masuyama, Y. Sumida and Y.P. Zhu, *J. Jpn. Oil Chem. Soc. 37*:746 (1988).
7. Stirton, A.J., R.G. Bistline, Jr., J.K. Weil, W.C. Ault and E.W. Maurer, *J. Am. Oil Chem. Soc. 39*:128 (1962).
8. Kodama, M., and S. Seki, *Hyoumen 22*:61 (1984).
9. Kodama, M., and S. Seiki, *J. Jpn. Oil Chem. Soc. 30*:749 (1981).
10. Ralston, A.W., D.N. Eggenberger and P.L. Dubrow, *J. Am. Chem. Soc. 70*:977 (1948).
11. Harkins, W.D., and F.E. Brown, *Ibid. 41*:499 (1919).
12. Wilkes, B.G., and J.N. Wickert, *Ind. Eng. Chem. 29*:1234 (1937).
13. Matsumura, R., Y. Moroi and N. Ikeda, *Surfactants in Solution,* Vol. 4, edited by K.L. Mittal and P. Bothorel, Plenum, 1986, p. 289.
14. Inoue, K., and S. Nojima, *Pharmacia 20*:869 (1984).
15. Shinoda, K., and H. Sagitani, *J. Colloid Interface Sci. 64*:68 (1978).
16. Cayias, J.L., R.S. Schechter and W.H. Wade, *Ibid. 59*:31 (1977).
17. Kajiyama, T., K. Uemura, M. Uchida, Y. Oishi and R. Takei, *Bull. Chem. Soc. Jpn. 62*:3004 (1989).

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