Long Chain Alkanesulfonates and 1-Hydroxy-2-Alkanesulfonates: Structure and Property Relations[1]

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Abstract

Even chain sodium alkanesulfonates from the Strecker reaction, odd chain sodium alkanesulfonates from the alkaline decarboxylation of α-sulfo acids, and sodium 1-hydroxy-2-alkanesulfonates from the reduction of esters of α-sulfo acids were compared with respect to Krafft point, critical micelle concentration, detergency and foam height. Sodium alkanesulfonates and crude fusion products from the α-sulfo acids (mixtures of alkanesulfonates of one less carbon atom with a lesser amount of a soap of two less carbon atoms) are more soluble and have better detergent and foaming properties. Sodium 1-hydroxy-2-alkanesulfonates resemble monosodium salts of α-sulfo acids.

Alkanesulfonic acids and 1-hydroxy-2-alkanesulfonic acids obtained from the sodium salts by ion exchange have lower Krafft points and are more readily soluble. The critical micelle concentrations of 1-hydroxy-2-alkanesulfonic acids and α-sulfo acids are nearly the same and about equal to those of alkanesulfonic acids of one less carbon atom.

Introduction

A continued investigation of the use of long-chain α-sulfo acids as chemical intermediates, has shown (15) that alkanesulfonates are formed by decarboxylation and 1-hydroxy-2-alkanesulfonates by metal borohydride reduction, represented as follows:

$$\text{I. } RCH_2CH(SO_3Na)CO_2Na \xrightarrow[300C]{NaOH} RCH_2CH_2SO_3Na + Na_2CO_3$$

$$\text{II. } RCH_2CH(SO_3Na)CO_2CH_3 \xrightarrow[(CH_3)_2CHOH]{NaBH_4} RCH_2CH(SO_3Na)CH_2OH$$

Decarboxylation

Desulfonation rather than decarboxylation occurred when α-sulfostearic acid was heated in o-dichlorobenzene at the reflux temperature, and stearic acid was recovered quantitatively. Similarly, a decarboxylation method (2) for sodium α-sulfostearic acid, heating the monosodium salt at 265C under nitrogen, gave in our case, a lower yield of desulfonation product with no evidence for decarboxylation.

Decarboxylation of disodium salts of α-sulfomyristic, palmitic, and stearic acids to sodium tridecane-, pentadecane-, and heptadecanesulfonate, according to equation I, was accomplished in yields of 35–50% by fusion of the disodium salt under nitrogen in an excess of sodium hydroxide at 300–320C. A lesser amount of sodium laurate, myristate, and palmitate (15–25%) was also formed by desulfonation and the Varrentrapp reaction (1):

$$RCH_2CH(SO_3Na)CO_2Na + NaOH \longrightarrow RCH{=}CHCO_2Na + Na_2SO_3 + H_2O;$$

$$RCH{=}CHCO_2Na + NaOH + H_2O \longrightarrow RCO_2Na + CH_3CO_2Na + H_2.$$

The crude fusion product from disodium α-sulfopalmitate was found to consist of 60% sodium pentadecanesulfonate, 25% sodium myristate, and 15% inorganic salts; from disodium α-sulfostearate. 45% sodium heptadecanesulfonate, 17% sodium palmitate, and 38% inorganic salts. The ratio of alkanesulfonate to soap was 18:7. Removal of soap and inorganic salts and final crystallization from aqueous ethanol gave the sodium alkanesulfonates of 13,15 and 17 carbon atoms in a pure state. Sodium alkanesulfonates of 12,14,16 and 18 carbon atoms were made by the Strecker reaction (11). Alkanesulfonic acids were prepared from the sodium salts by ion exchange.

Reduction

Sodium or lithium salts of methyl α-sulfolaurate, myristate, palmitate or stearate were reduced to the corresponding primary alcohol in yields of 60–75% by means of sodium or lithium borohydride in isopropyl alcohol, as shown by equation II. With correction for unreduced ester recovered as the hydrolysis product (the neutral salt of the α-sulfo acid) the yield was nearly 100%. By ion exchange the reduction product was isolated as the 1-hydroxy-2-alkanesulfonic acid or the sodium salt.

Discussion

Sodium Alkanesulfonates and 1-Hydroxy-2-Alkanesulfonates

Properties of aqueous solutions of sodium alkanesulfonates, sodium 1-hydroxy-2-alkanesulfonates, and related compounds of 12-18 carbon atoms are shown in Tables I and II.

Krafft Point. The Krafft point, a convenient indication of relative solubility was measured as the temperature at which a 1% aqueous dispersion becomes clear on gradual heating (4). Sodium alkanesulfonates show a decrease in Krafft point from even to odd members, with increasing chain length (15) similar to alternation in melting points in the fatty acid series (10).

Decarboxylation reduces the Krafft point and improves solubility. The monosodium salts of the α-sulfo acids and sodium 1-hydroxy-2-alkanesulfonates have the highest Krafft points. Low solubility in both cases may be due to hydrogen bonding of the type

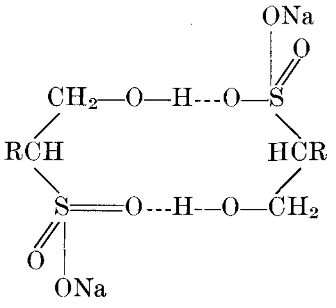

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TABLE I
Properties of Sodium Alkanesulfonates, Fusion Products, and Sodium 1-Hydroxy-2-Alkanesulfonates

	Krafft point[a] 1%, C	cmc[b] Millimoles per liter	Detergency 0.25% 60C ΔR[c]		Foam height[d] 0.25%, 60C mm	
			Dist. water	300 ppm	Dist. water	300 ppm
Sodium alkanesulfonates						
Dodecane	38	6.9	21.0	24.0	210	240
Tridecane	35.5	3.52	24.5	28.8	230	240
Tetradecane	48	2.03	25.0	27.6	220	240
Pentadecane	48	0.66	27.9	29.3	245	250
Hexadecane	57	0.45	26.6	30.8	230	165
Heptadecane	62	0.21	27.7	29.2	230	45
Octadecane	70	....[e]	30.1	14.7	230	45
Fusion products						
From disodium α-sulfopalmitate[f]	....	....	26.0	28.8	250	230
From disodium α-sulfopalmitate[g]	....	....	24.4	29.0	240	240
From disodium α-sulfostearate[h]	....	....	31.2	19.7	240	25
From disodium α-sulfostearate[g]	....	....	32.6	28.5	220	65
Sodium 1-hydroxy-2-alkanesulfonates						
Dodecane	59	....[e]	14.8	....[e]	....[i]	....[e]
Tetradecane	73	....[e]	25.0	....[e]	....[i]	....[e]
Hexadecane	84	....[e]	26.2	....[e]	....[i]	....[e]
Octadecane	93	....[e]	24.8	....[e]	....[i]	....[e]

[a] Temperature at which a 1% dispersion became a clear solution on gradual heating (4).

[b] Critical micelle concentration visual, Pinacyanole Chloride method (3).

[c] Increase in reflectance after washing GDC No. 26 standard soiled cotton (5), Terg-O-Tometer, 10 swatches/l., 20 min, 110 cycles/min. For comparison ΔR values for sodium dodecyl sulfate are 25.7, 21.5; for sodium octadecyl sulfate 32.6, 31.0 resp.

[d] Ross-Miles test (12); except as noted the foam was stable for at least 5 min.

[e] Not sufficiently soluble.

[f] 60% $C_{15}H_{31}SO_3Na$, 25% $C_{13}H_{27}CO_2Na$, 15% inorganic salts.

[g] Inorganic salts removed.

[h] 45% $C_{17}H_{35}SO_3Na$, 17% $C_{15}H_{31}CO_2Na$, 38% inorganic salts

[i] Foam collapsed very rapidly.

or the similar intramolecular compound. Either structure would facilitate the separation of an insoluble crystalline phase.

The sodium alkyl sulfates (17), isomeric with sodium 1-hydroxy-2-alkanesulfonates, and with one more oxygen atom than the sodium alkanesulfonates, have the lowest Krafft points.

Critical Micelle Concentration. Because of the limited solubility of the higher members the cmc of the compounds of Tables I and II were based on solubility at 25C or measured by the visual dye titration method (3) at an elevated temperature, approximately 50C. The sodium alkanesulfonates of 12–17 carbon atoms, show the expected linear relation between log cmc and chain length.

It might be expected that sulfates would have lower cmc values than sulfonates of the same number of carbon atoms (7), but under our conditions of measurement we found little difference. Disodium salts of α-sulfo acids (16) have the highest critical micelle concentration.

Detergency and Foam. Detergency was measured as the increase in reflectance after washing GDC No. 26 standard soiled cotton (5) in the Terg-O-Tometer at 0.25% concentration, 10 swatches/l., 20 min at 60C, 110 cycles/min. The detergency of sodium alkanesulfonates, crude fusion products, and sodium 1-hydroxy-2-alkanesulfonates were compared with sodium dodecyl sulfate and sodium octadecyl sulfates as controls. The sodium alkanesulfonates of 13–17 carbon atoms and fusion products from disodium α-sulfopalmitate or disodium α-sulfostearate, free of inorganic salts, were the best detergents in hard water with ΔR values of about 28–31 compared to 21.5 and 31.0 for sodium dodecyl and octadecyl sulfate, respectively.

The sodium alkanesulfonates of 12–15 carbon atoms and the fusion product from disodium α-sulfopalmitate formed turbid solutions in hard water with excellent foaming properties (12), recorded in Table I.

Alkanesulfonic and 1-Hydroxy-2-Alkanesulfonic Acids

Since solubility limited the measurements which could be made on the sodium salts they were converted to the more soluble free acids by ion exchange with Dowex 50W-X8 in the acid form (15).

A solution of the sodium salt in 50% ethanol was heated with a portion of the ion exchange resin to facilitate solution and passed through a one foot column of the resin with a bed volume of 300 ml. The aqueous ethanol solution after ion exchange was evaporated to dryness and twice crystallized from dry chloroform to give the alkanesulfonic and 1-hydroxy-2-alkanesulfonic acids in a pure state, as listed in Table III.

Melting Point and Krafft Point. Because of the relation of the Krafft point of soaps to the melting point of the fatty acids (4), alternation in the Krafft point of sodium alkanesulfonates would suggest an alternation in the melting point of corresponding alkanesulfonic acids. Although alternation in the melting point of alkanesulfonic acids, by decrease from odd to even, has been demonstrated for alkanesulfonic acids of 1–6 carbon atoms (13,14), the data of Table III shows there is neither alternation in melting point nor in Krafft point for alkanesulfonic acids of 12–18 carbon atoms. The melting points are higher than previous literature values (9,13).

The alkanesulfonic acids, and the 1-hydroxy-2-alkanesulfonic acids in particular, have low Krafft points and are easily soluble, in marked contrast to the corresponding sodium salts. Like the α-sulfo fatty

TABLE II
Krafft Point and Critical Micelle Concentration of Sodium Alkanesulfonates, Sodium 1-Hydroxy-2-Alkanesulfonates and Related Compounds

	Krafft point 1%, C				cmc Millimoles per liter			
	Total number of C atoms				Total number of C atoms			
	12	14	16	18	12	14	16	18
$RCH_2CH_2SO_3Na$	38C	48C	57C	70C	6.9[a]	2.03[a]	0.45[a]	....
$RCH(SO_3Na)CO_2Na$	....	....	76C[b]	91C[b]	....	42.6[c]	6.6[c]	2.5[c]
$RCH(SO_3Na)CO_2H$	52C	68C	83C	94C	13.9[c]	3.3[c]	0.6[c]	0.3[c]
$RCH(SO_3Na)CH_2OH$	59C	73C	84C	93C	15.0[c]	3.4[c]	0.3[c]	0.1[c]
$RCH_2CH_2OSO_3Na$	16C	30C	45C	56C	6.8[a]	1.32[a]	0.42[a]	0.11[a]

[a] Critical micelle concentration by visual Pinacyanole Chloride method.

[b] Decarboxylation reduces the Krafft point to 48C and 62C, resp.

[c] Based on solubility at 25C (16).

TABLE III

Alkanesulfonic and 1-Hydroxy-2-Alkanesulfonic Acids

	Neutralization equivalent		Melting point C	Krafft point 1%, C	cmc Millimoles per liter	
	Found	Theory			Surface tension method [a]	Visual dye titration method
Alkanesulfonic acids						
Dodecane	253.3	250.4	56 –7.5C	....[b]	4.39 (.11)	5.55
Tridecane	264.4	264.4	63.7–5C	....[b]	2.53 (.068)	2.60
Tetradecane	277.8	278.4	67.5–8.6C	12.5C	1.36 (.038)	1.32
Pentadecane	293.4	292.5	70.6–1.6C	27.0C	0.79 (.023)	0.48
Hexadecane	306.3	306.5	75 –6C	34.0C	0.42 (.013)	0.28
Heptadecane	319.8	320.5	78.4–9.6C	42.5C	0.18 (.0057)	0.14
Octadecane	334.6	334.6	81.4–2.6C	50.0C	0.10 (.0035)	0.10
1-Hydroxy-2-alkanesulfonic acids						
Dodecane	265.9	266.4	108C	....[b]	13.1 (.35)	16.1
Tetradecane	294.0	294.4	111.5C	....[b]	1.94 (.057)	2.61
Hexadecane	322.9	322.5	114.6C	....[b]	0.65 (.021)	0.58
Octadecane	350.0	350.6	115C	28.5C	0.22 (.0078)	0.21 [c]

[a] Values in parentheses are critical micelle concentration in %.
[b] Krafft points too low for measurement.
[c] For comparison the value for the isomeric octadecylsulfuric acid is 0.039 millimoles/l. (8).

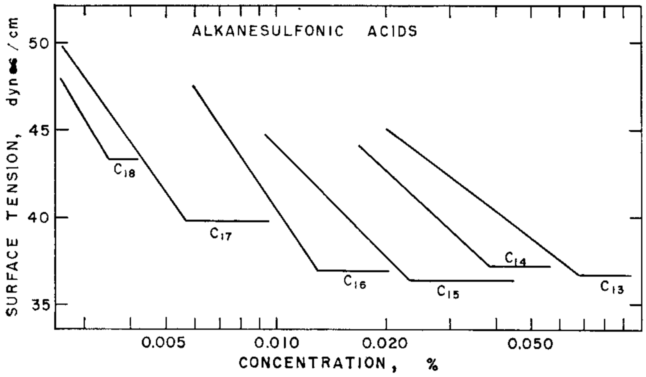

FIG. 1. Surface tension vs. log concentration for alkanesulfonic acids.

acids, the presence of a hydrogen ion appears to break the hydrogen bond responsible for the low solubility of sodium 1-hydroxy-2-alkanesulfonates and the monosodium salt of α-sulfo fatty acids.

Critical Micelle Concentration. Surface tension was measured with the duNoüy tensiometer, values were corrected according to Harkins and Jordan (6) and plotted against log concentration in Figures 1 and 2 for alkanesulfonic and 1-hydroxy-2-alkanesulfonic acids, respectively. All curves were minimum free, except for 1-hydroxy-2-octadecanesulfonic acid. Critical micelle concentration values taken as the inflection point are recorded in Table III and plotted as a function of chain length in Figure 3. Values by the dye titration method are recorded for comparison. Sodium alkanesulfonates have a higher cmc than the free acids, probably because of greater ionization.

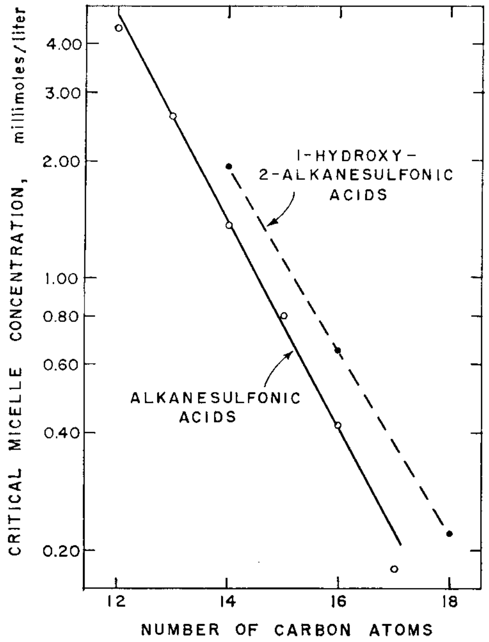

FIG. 3. Relation of critical micelle concentration to chain length for alkanesulfonic and 1-hydroxy-2-alkanesulfonic acids.

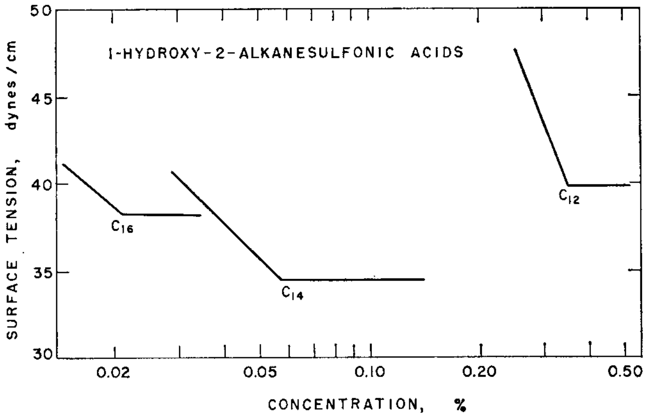

FIG. 2. Surface tension vs. log concentration for 1-hydroxy-2-alkanesulfonic acids.

The cmc of 1-hydroxy-2-alkanesulfonic acids are about equal to those for alkanesulfonic acids of one less carbon atom (Table III and Fig. 3), and about equal to the cmc of α-sulfo fatty acids of the same number of carbon atoms (16). In each case the long hydrophobic chain attached to the sulfonic acid group has the same number of carbon atoms.

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N,N-Bis(2-Acyloxyethyl) Amides of Long Chain Fatty Acids as Plasticizers[1]

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Abstract

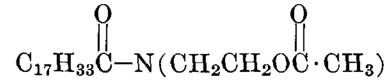
A series of N,N-bis-(2-acyloxyethyl)amides and a few related derivatives have been prepared wherein a long chain fatty acid or fatty acid mixture comprises 33 mole percent of the total acyl groups present; the other 66 mole percent being either a short chain aliphatic or aromatic acyl group. Both ordered and random diesteramides have been prepared. All have been tested as plasticizers for vinyl chloride copolymers. Some are acceptable as nitrile rubber softeners and cellulose acetate plasticizers. The ordered diesteramides give the best overall performance as plasticizers, but it is possible to achieve acceptable performance levels in semi-ordered diesteramides.

Introduction

It was apparent from previous work on N,N-disubstituted amides of long chain fatty acids as polyvinyl chloride plasticizers (1), that an amide group, while superior to an ester group as a compatibilizer, did not insure adequate compatibility of the product. The superiority of the fatty acid morpholides over other amides in compatibility can be attributed to the presence of a second compatibilizing group, namely the ether group of the morpholine moiety. It might therefore be expected that diesteramides of diethanolamine, having two ester groups in addition to the amide group, would have compatibilities comparable to the morpholides.

Esteramides and diesteramides, obtained by condensing certain alkanolamines with a fatty acid, are compatible polyvinyl chloride plasticizers, provided the fatty acid moiety is restricted to chain lengths of 3–10 carbon atoms (2,3). This restriction clearly precludes the employment of a long chain fatty acid, such as oleic acid as the exclusive fatty acid moiety in such compounds but not necessarily as one of the fatty acid moieties in an internally mixed diesteramide: e.g., a diesteramide containing only one long chain acyl group.

Such internally mixed diesteramides can be synthesized from the methyl ester of the long chain acid by catalytic amidation with diethanolamine (4,5) and subsequent esterification with the short chain acid anhydride. The diesteramides prepared by this method, which will be referred to as the "directed" method, are specific internally mixed diesteramides of known chemical configuration, in contrast to the mixtures of diesteramides obtained by the "random" method, in which the diethanolamine and the two acids are mixed and amidation and esterification are carried out simultaneously. Thus a preparation involving a 1:1:2 molar ratio of diethanolamine, oleic acid, and acetic acid yields

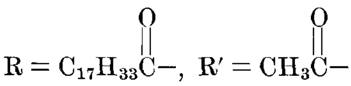


$$C_{17}H_{33}\overset{\overset{O}{\|}}{C}-N(CH_2CH_2O\overset{\overset{O}{\|}}{C}\cdot CH_3)_2$$

by the directed method while the random method would result in a mixture which theoretically might contain as many as six diesteramides; namely,

$$R-NX-R'_2,\ R-NX-R_2,\ R-NX-RR',$$
$$R'-NX-R_2,\ R'-NX-RR',\ R'-NX-R'_2,$$

where



$$R = C_{17}H_{33}\overset{\overset{O}{\|}}{C}-,\quad R' = CH_3\overset{\overset{O}{\|}}{C}-,$$

and $NX = -N(CH_2CH_2O-)_2$. By using the directed method the effect of different short chain esterifying groups on the plasticizing properties can be studied.

This paper is concerned with the preparation and plasticizer evaluation of a number of diesteramides prepared by the directed method and a comparison of some of these with diesteramides involving the same two acid moieties but prepared by the random method.

Materials

All reagents with the exception of the long chain fatty acids, cottonseed fatty acids or other natural acid mixtures were white label Eastman organic chemicals. The methyl oleate and oleoyl chloride were prepared from Emery Industries' best grade of oleic acid, Elaine 233LL, and the methyl linoleate from a 93%-pure sample of linoleic acid. The methyl esters of the cottonseed acids were prepared from cottonseed oil fatty acids having an iodine value (I.V.) of 113 and a neutralization equivalent of 273. The methyl esters of the hydrogenated cottonseed acids were derived from a cottonseed oil selectively hydrogenated to an I.V. of 69.8 and a thiocyanogen value of 65.0. The methyl ester of rapeseed fatty acids, predominantly erucic acid, were prepared from a rapeseed oil which had an I.V. of 101.5 and whose acids had a neutralization equivalent of 303.9.

Experimental

N,N-bis(2-acetoxyethyl)oleamide (I). 296 g (1 mole) of methyl oleate was slowly added to a vigorously stirred mixture of 105 g (1 mole) of diethanolamine and 3.6 g (0.15 mole) of metallic sodium dissolved in absolute methanol. The reaction was carried out with continued stirring at 65–75C at 60 mm pressure. It was necessary to add the methyl oleate slowly so as to control frothing of the reaction mixture. The reaction was complete after all the methyl oleate had been added and the evolution of methanol had ceased. The product of this reaction was N,N-bis(2-hydroxyethyl)-

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[1] Presented at the AOCS meeting in New Orleans, La., 1962.
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