Tallow Based Detergent Formulations: Mixtures of Alcohol Sulfates, Salts of *a*-Sulfo Acids and Esters, and Soap[1]

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Abstract

Saturated (I, $ROSO_3Na$) and unsaturated (II, $R'OSO_3Na$) tallow alcohol sulfates, the disodium salt of *a*-sulfonated saturated tallow fatty acids (III, $RCH(SO_3Na)CO_2Na$), the sodium salt of the methyl ester of *a*-sulfonated saturated tallow fatty acids (IV, $RCH(SO_3Na)CO_2CH_3$), and commercial tallow soap flakes (V) were compared, singly and in combinations, as built and unbuilt solutions in soft and hard water, with respect to foam height and detergency, using four different types of standard soiled cotton.

Built solutions of combinations of the two most soluble detergents, II and IV, at concentration 0.05% total active ingredient plus 0.20% builder in hard water of 300 ppm, remained perfectly clear on standing for several months. Built solutions containing I or II had the best foaming properties. The presence of soap decreased foam height.

Cloths A and B showed the detergency of built solutions to be in the order I = II > IV > III > V, and all combinations containing I or II were superior detergents. With cloth C, detergents ranked in the order I = II = IV > III > V, and many combinations containing I or II with IV were synergistic. Cloth D did not distinguish sharply between detergents in built solutions in hard water.

In general, detergent systems containing tallow alcohol sulfates with *a*-sulfo esters had the most desirable solubility, wetting, foaming, and detergent properties.

Introduction

THE PROPERTIES of saturated and unsaturated tallow alcohol sulfates (12) and salts of *a*-sulfo acids and esters (4,8,9) have been described, but their combinations with each other and with soap have been investigated only to a limited extent (4,10). Evidence that tallow alcohol sulfates and the *a*-sulfo esters have quite desirable properties as biodegradable detergents, liquid detergents, and lime soap dispersing agents (1,2,4,6,11) stimulated the present investigation of detergent combinations.

The saturated and unsaturated tallow alcohol sulfates were compared in combinations with disodium *a*-sulfotallowate, sodium methyl *a*-sulfotallowate, and soap, in the form of unbuilt and built solutions in soft and hard water. Properties examined were solubility (conveniently measured by the Krafft point) wetting, foam height, and detergency, using four different types of standard soiled cotton.

Experimental

Mixtures of pure compounds were prepared representing tallow alcohol sulfates (I, $ROSO_3Na$, 6% sodium tetradecyl sulfate, 28% sodium hexadecyl sulfate, and 66% sodium octadecyl sulfate) obtainable from tallow by nonselective catalytic hydrogenolysis followed by sulfation. Unsaturated tallow alcohol sulfates (II, $R'OSO_3Na$) obtainable by selective catalytic hydrogenolysis or sodium reduction were represented by a mixture containing 6% sodium tetradecyl sulfate, 28% sodium hexadecyl sulfate, 52% sodium oleyl sulfate and 14% sodium octadecyl sulfate. Disodium *a*-sulfotallowate (III, $RCH(SO_3Na)CO_2Na$) from the *a*-sulfonation of hydrogenated tallow fatty acids, was represented by a mixture containing 6% disodium *a*-sulfomyristate, 28% disodium *a*-sulfopalmitate and 66% disodium *a*-sulfostearate. Sodium methyl *a*-sulfotallowate (IV, $RCH(SO_3Na)CO_2CH_3$), also from hydrogenated tallow fatty acids, was represented by a mixture containing a like amount of the three methyl esters. Commercial tallow soap flakes (V) were the fifth component.

The five components were studied as 0.25% solutions in distilled water and hard water of 300 ppm; and as built solutions of 0.05% total active ingredient plus 0.20% builder in hard water of 300 ppm. The builder was composed of 55% $Na_5P_3O_{10}$, 24% Na_2SO_4, 10% $Na_4P_2O_7$, 10% Na metasilicate, and 1% carboxymethylcellulose.

Solubility and Krafft Point

Built and unbuilt solutions of the five components and their combinations in soft and hard water, prepared as hot clear solutions, became turbid or partially precipitated on standing for 24 hr. Built II-IV combinations in hard water (300 ppm) containing 0.01% II + 0.04% IV + 0.20% builder, and 0.02% II + 0.03% IV + 0.20% builder, remained clear even after standing for more than a year. All solutions containing soap were turbid or opalescent.

The solubility and wetting properties of the five components and of quaternary combinations of I or II with III, IV and V in different ratios is shown in Table I. The Krafft point, the temperature at which

TABLE I

Detergents	Krafft point, 1% solution, C	Wetting time (3), 0.25%, 25C, sec
I [$ROSO_3Na$]	46	>300
II [$R'OSO_3Na$]	34	27
III [$RCH(SO_3Na)CO_2Na$]	88	...[a]
IV [$RCH(SO_3Na)CO_2CH_3$]	29	31
V [Soap]	36	14
Ratios of I-III-IV-V combinations		
2:1:1:1	38	34
1:2:1:1	33	60
1:1:2:1	31	29
1:1:1:2	35	30
Ratios of II-III-IV-V combinations		
2:1:1:1	30	26
1:2:1:1	33	32
1:1:2:1	29	20
1:1:1:2	30	20

[a] Not soluble enough for the test.

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TABLE II

Foaming Properties of Unbuilt Solutions in Soft and Hard Water

Detergent	Foam height (7), 0.25% solutions,	
	Distilled water	300 ppm
0.25 I [$ROSO_3Na$]	200	70
0.25 II [$R'OSO_3Na$]	210	210
0.25 III [$RCH(SO_3Na)CO_2NA$]	160[a]	210
0.25 IV [$RCH(SO_3Na)CO_2CH_3$]	190	195
0.25 V [Soap]	225	105[a]
0.05 I + 0.20 IV	205	205
0.20 I + 0.05 IV	215	90
0.05 II + 0.20 IV	200	210
0.20 II + 0.05 IV	210	210

[a] Unstable foam.

a 1% dispersion becomes a clear solution on gradual heating, is lower for detergent combinations, indicating less soluble detergents are solubilized by the more soluble. Both wetting time and Krafft point are lower for combinations showing they may be more effective than single detergents. Unsaturated tallow alcohol sulfate (II) and the α-sulfo ester (IV), the most soluble detergents, contribute most to solubility and wetting. Soap would be less effective in hard water.

Foam Height

The foam height by the Ross-Miles test (7) for 0.25% solutions of I, II, III, IV, V and for I-IV and II-V combinations at 60C is shown in Table II, in distilled water and hard water of 300 ppm. As unbuilt solutions II and IV have the best foaming properties in soft and hard water.

The foam height of binary, ternary, and quaternary combinations of I or II, with III, IV and V is shown in Table III for built solutions containing 0.05% total active ingredient plus 0.20% builder in hard water of 300 ppm. Single detergents had foam height values in the order II (205) > I (190 > IV (175 > III (60) > V (0). Binary mixtures containing I or II but not V were nearly equal and had the best foaming properties. I and II contribute most to foam and combinations containing I or II but not V may be partially substituted by III or IV without much change in foam height. The presence of soap (V) always decreases foam.

Detergency

Detergency was measured as the increase in reflectance, ΔR, after washing 10 swatches of standard soiled cotton in one liter of detergent solution in the Terg-O-Tometer for 20 min at 60C and 110 cycles/min. Four different kinds of standard soiled cotton, A, B, C, D,[3] were washed in soft and hard water as shown in Table IV. By analysis of variance (5) difference in ΔR of the value listed were significant with 95% probability.

From Table IV it is apparent that the order of detergent efficiency may depend upon the standard soiled cotton used. In soft water, soap (V) was always the best detergent or shared first position with others. In hard water, disodium α-sulfotallowate (III) was always the best, or shared first position with others.

In contrast to the other cloths, detergency data with cloth B showed all detergents, except soap, more efficient in hard than in soft water. Disodium α-sulfotallowate was the only detergent more efficient in hard water in every case. Synergism of II and IV was shown by cloth A in soft water. With cloth C combinations of I or II with IV were good detergents in soft or hard water.

Most of the detergency measurements were on built solutions (0.05% total active ingredient + 0.20% builder) in hard water. The results, quite different than with unbuilt solutions, gave a more realistic evaluation of tallow-based detergents in hard water. Only three cloths were used since cloth D was too easily washed by builder alone to distinguish sharply between built detergents. The ratios investigated in

[3] Testfabrics, U.S. Testing, Foster D. Snell, and ACH Fiber Service No. 115, respectively.

TABLE III

Foam Height (7), mm, 0.25% Built Solutions in Hard Water (0.05% total active ingredient + 0.20% builder,[a] 300 ppm, 60C)

Active ingredient	Ratio of components[c]			
Components,[b] binary system	4:1	3:2	2:3	1:4
I-III	195	195	190	185
II-III	185	195	195	190
I-IV	195	190	180	180
II-IV	195	190	195	195
I-V	150	140	145	120
II-V	180	165	145	95
III-IV	150	180	175	180
Components, ternary system	Ratio of components			
	3:1:1	1:3:1	1:2:2	1:1:3
I-III-IV	180	175	180	185
II-III-IV	190	200	190	185
I-III-V	155	175	155	155
II-III-V	155	180	165	145
I-IV-V	155	155	125	110
II-IV-V	140	135	120	105
III-IV-V	165	155[d]	140	110[d]
Components, quaternary system	Ratio of components			
	2:1:1:1	1:2:1:1	1:1:2:1	1:1:1:2
I-III-IV-V	140	140	160	155
II-III-IV-V	160	160	160	135

[a] 55% $Na_5P_3O_{10}$, 24% Na_2SO_4, 10% $Na_4P_2O_7$, 10% Na metasilicate, 1% CMC.

[b] Built detergents containing only one active ingredient had the following foam heights: I [$ROSO_3Na$] 190; II [$R'OSO_3Na$] 205; III [$RCH(SO_3Na)CO_2Na$] 60; IV [$RCH(SO_3Na)CO_2CH_3$] 175; V [Soap.] 0. Combinations III-IV had no measurable foam; IV-V combinations gave an unstable foam, initial values 70–115 mm.

[c] For example, when the active ingredient is 0.01% II + 0.04% V, foam height = 95 mm.

[d] Unstable foam. All other values of Table III are foam heights stable for 5 min.

TABLE IV

Detergency, ΔR,[a] of 0.25% Unbuilt Solutions in Soft and Hard Water, with Four Kinds of Standard Soiled Cotton (A,B,C,D).

Detergent	A		B		C		D	
	Distilled water	300 ppm	Distilled water	300 ppm	Distilled water	300 ppm	Distilled water	300 ppm
I [$ROSO_3Na$]	28.7	29.8	11.9	14.5	35.4	24.5	32.5	28.1
II [$R'OSO_3Na$]	26.7	17.5	11.0	12.6	35.1	23.2	31.1	22.1
III [$RCH(SO_3Na)CO_2Na$]	30.1	34.1	10.2	14.1	30.4	33.4	27.3	29.3
IV [$RCH(SO_3Na)CO_2CH_3$]	18.8	13.9	8.3	10.8	21.4	31.2	32.1	23.7
V [Soap]	37.9	29.8	13.2	6.2	35.2	2.2	32.7	23.9
.05 I + .20 IV	23.1	14.7	8.2	11.2	32.0	31.2	32.5	24.0
.20 I + .05 IV	26.6	24.1	10.1	14.8	33.7	26.7	33.4	26.6
.05 II + .20 IV	31.5[b]	13.0	8.0	9.8	30.8	31.4	31.5	22.7
.20 II + .05 IV	30.0	16.4	10.2	13.3	35.6	27.4	31.3	23.0
Na dodecyl sulfate	20.9	16.5	7.5	11.0	29.5	33.4	28.6	23.9
Significance level[c]	1.3	0.9	0.6	0.7	0.9	0.4	0.9	0.5

[a] Increase in reflectance after washing standard soiled cotton, 10 swatches per liter, in the Terg-O-Tometer for 20 min, at 60C and 110 cycles/min.

[b] Synergistic combination.

[c] Differences in ΔR of the value listed are significant with 95% probability.

TABLE V

Detergency,[a] ΔR, 0.25% Built Solutions in Hard Water (0.05% total active ingredient + 0.20% builder, 300 ppm, 60C)

Active ingredient components[b]	Cloth A				Cloth B				Cloth C			
Binary system	Ratio of components											
	4:1	3:2	2:3	1:4	4:1	3:2	2:3	1:4	4:1	3:2	2:3	1:4
II-III	28.3	28.3	28.1	20.3	11.9	11.0	10.8	10.3	30.4	24.5	23.2	18.7
II-IV	29.7	29.0	27.2	23.1	11.8	10.6	10.3	9.6	34.2[c]	33.3[c]	33.5[c]	32.8[c]
II-V	29.8	29.7	28.9	27.5	12.2	13.3[c]	12.4	10.5	28.5	23.8	20.7	15.7
III-IV	22.7[c]	21.4[c]	21.2[c]	19.7	10.6[c]	10.0[c]	10.6[c]	9.9[c]	26.6	30.8	29.8	29.0
III-V	14.0	14.2	15.0	13.2	7.0[c]	5.5	5.1	3.7	5.5	5.8	5.0	5.4
IV-V	19.2	19.6	18.8	18.7	9.4[c]	9.3[c]	9.5[c]	10.4[c]	4.5	3.7	4.1	4.3
Ternary system	Ratio of components											
	3:1:1	2:1:2	1:3:1	1:1:3	3:1:1	2:1:2	1:3:1	1:1:3	3:1:1	2:1:2	1:3:1	1:1:3
II-III-IV	27.6	26.1	27.4	25.3	12.7[c]	11.0	10.2	10.3	31.3	31.8	24.5	31.2
II-III-V	29.4	28.5	27.0	25.1	13.5[c]	12.8[c]	12.3	11.5	26.4	25.7	21.5	17.0
II-IV-V	27.4	24.9	23.7	24.1	12.2	11.8	10.5	10.5	34.5[c]	32.1	36.0[c]	29.2
III-IV-V	20.9[c]	22.1[c]	22.6[c]	20.9[c]	11.3[c]	6.3	10.4[c]	10.1[c]	30.1	29.7	31.4	23.2
Quaternary system	Ratio of components											
	2:1:1:1	1:2:1:1	1:1:2:1	1:1:1:2	2:1:1:1	1:2:1:1	1:1:2:1	1:1:1:2	2:1:1:1	1:2:1:1	1:1:2:1	1:1:1:2
II-III-IV-V	28.7	28.2	25.0	25.6	12.2	11.2	10.4	11.4	35.3[c]	33.2[c]	36.3[c]	29.1

[a] Significance levels: A, 1.5; B, 0.7; C, 1.1.
[b] Built solutions containing only one active ingredient, and built Na dodecyl sulfate used as control, gave the following ΔR values with the 3 cloths resp.: II ($R'OSO_3Na$) 29.8, 11.8, 30.7; III [$RCH(SO_3Na)CO_2Na$] 15.6, 5.1, 7.6; IV [$RCH(SO_3Na)CO_2CH_3$] 18.8, 8.3, 31.7; V [Soap] 14.0, 1.5, 3.0; $C_{12}H_{25}OSO_3Na$ 16.5, 7.1, 11.4.
[c] Synergistic combinations.

binary combinations were 4:1, 3:2, 2:3, 1:4; in ternary combinations 3:1:1, 2:2:1, 2:1:2, 1:3:1, 1:2:2, 1:1:3. Since the saturated (I) and unsaturated (II) tallow alcohol sulfates were nearly equal in detergency and gave similar results in detergent combinations, the data for combinations containing I are omitted in Table V. Further in the direction of simplicity, Table V presents only four of the six ternary combinations.

With cloth A built detergents containing only one active ingredient (footnote b, Table V) ranked as follows: II (29.8) > IV (18.8) > Control (16.5) = III (15.6) > V (14.0). In compositions containing II, the most important active ingredient, the presence of III, IV or V could be tolerated without much loss in detergency. The best binary combination, II-V, was slightly superior to II-III and II-IV combinations. Synergism was shown only for combinations of inferior detergents.

The results with cloth B were quite similar but synergism was shown in a greater number of cases. Detergents ranked in the order II (11.8) > IV (8.3) > Control (7.1) > III (5.1) > V (1.5). Maximum detergency, superior to II alone, was shown by some synergistic II-V, II-III-IV, and II-III-V combinations.

Although cloth C differed from A and B there were some similarities. Detergents ranked in the order IV (31.7) = II (30.7) > Control (11.4) > III 7.6 > V (3.0), not greatly different from cloths A or B except that the α-sulfo ester (IV) and the unsaturated tallow alcohol sulfate (II) were equally good and were the best detergents. Synergism was shown in II-IV, II-IV-V, and II-III-IV-V combinations. This synergism was shown also with I in the place of II.

The results of Table V are presented also in triangular coordinate systems, Figure 1, 2, and 3. The irregular lines, with the detergency value shown, help to define the composition of the better detergent combinations.

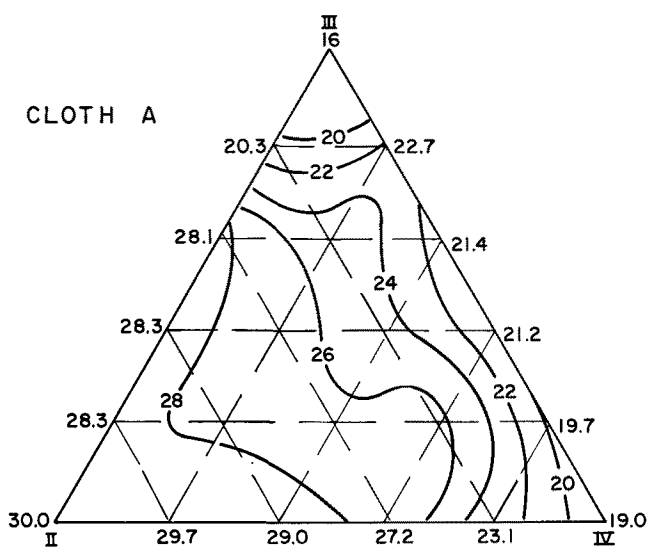

FIG. 1. Detergency, ΔR, of built solutions of II-III-IV in hard water using cloth A.

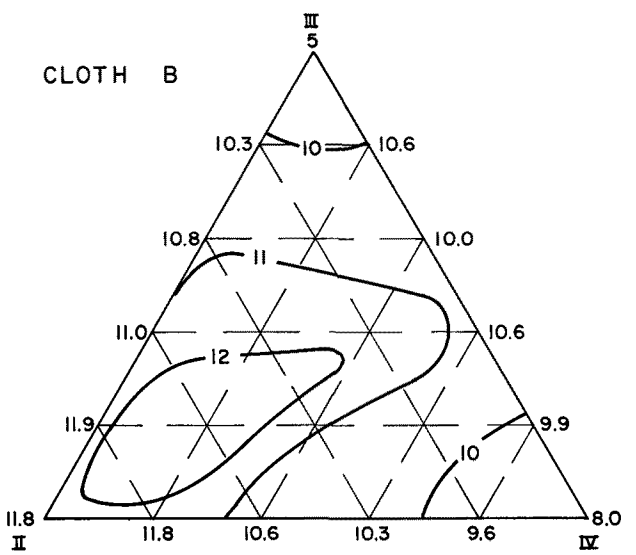

FIG. 2. Detergency, ΔR, of built solutions of II-III-IV in hard water, using cloth B.

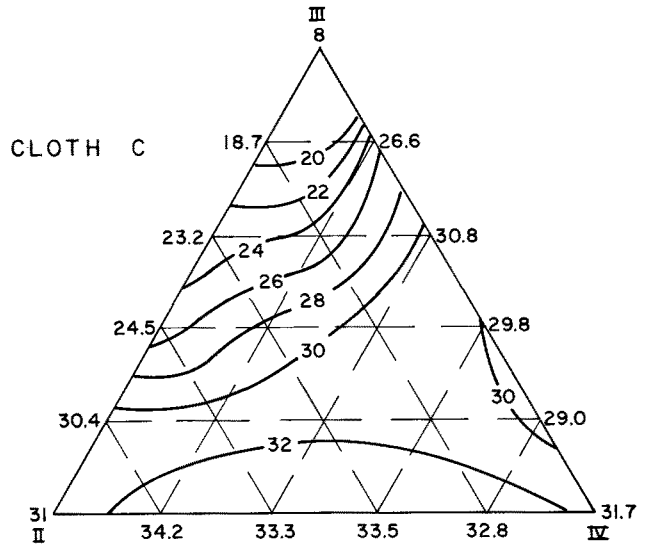

FIG. 3. Detergency, ΔR, of built solutions of II-III-IV in hard water, using cloth C.

Results and Discussion

Examination of unbuilt solutions using four different kinds of standard soiled cotton showed that soap (V) was the best detergent in soft water and disodium α-sulfotallowate (III) the best in hard water. Unsaturated tallow alcohol sulfate (II) and sodium methyl α-sulfotallowate (IV), the two most soluble detergents, had the best foaming properties in soft and hard water.

Examination of combinations of built solutions of I or II with III, IV and V, in hard water, with three different kinds of standard soiled cotton showed that detergent performance depended upon the particular soil removal problem. With cloths A and B the saturated and unsaturated tallow alcohol sulfates (I and II) were the most important detergents which could enter into combinations with III, IV or V without much loss in detergency. Maximum detergency with cloth B was shown by some synergistic II-V, II-III-IV, and II-III-V combinations.

Cloth C showed the α-sulfo ester (IV) and the tallow alcohol sulfates (I and II) were equally good and were the best detergents. Marked synergism was shown in combinations of I or II with IV.

The tallow alcohol sulfates contributed most to good foaming properties in built solutions in hard water. The presence of III or IV could be accepted without much loss in foam height. The presence of soap always decreased foam.

Since different kinds of standard soiled cotton gave somewhat different results with the five detergents it was difficult to decide upon the best detergent composition. Based on solubility, wetting, foam, and detergency, combinations of the tallow alcohol sulfates (I or II) with α-sulfo ester (IV) appear to have the most desirable properties.

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