Soap-Based Detergent Formulations. XVI. Surface Active Sulfosuccinimides[1]

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ABSTRACT

A series of sodium N-alkylsulfosuccinimides and N-acyloxymethylsulfosuccinimides were prepared by reaction of the corresponding N-alkylmaleimides and N-acyloxymethylmaleimides with sodium bisulfite in aqueous ethanol. The N-alkylmaleimides were prepared by dehydration of N-alkylmaleamic acids with acetic anhydride and fused sodium acetate. The N-acyloxymethylmaleimides were obtained by reaction of an acyl chloride with N-methylolmaleimide in a pyridine-acetone solvent. The surface active properties of the sulfonated derivatives showed them to be efficient lime soap dispersing agents with good calcium ion stability but relatively high Krafft points. The 2 types of compounds exhibited similar detergency characteristics under the conditions employed and were generally comparable to the control on a cotton-polyester blend when used alone and in a ternary formulation with soap and silicate builder on cotton test cloths.
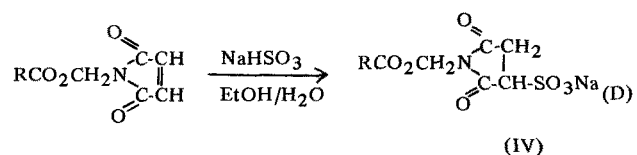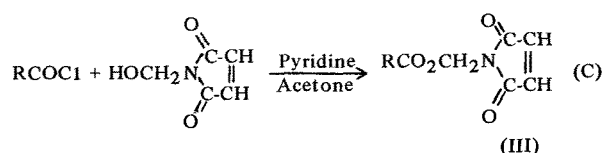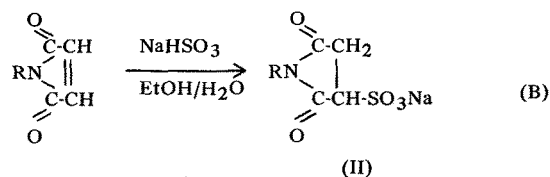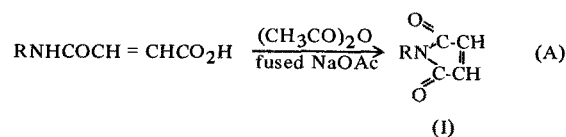
INTRODUCTION

Various types of anionic lime soap dispersing agents (LSDA) have been synthesized and evaluated in this laboratory. Recent publications (1,2) have shown that tallow soap based detergent formulations containing soap LSDA builder combinations were effective detergents in hard water with washing ability comparable to that of a standard phosphate built heavy duty household detergent. Sodium silicate ($Na_2O:SiO_2$, 1:1.6) was found to be an efficient builder in ternary systems containing 80% soap, 10% LSDA, and 10% silicate with lime soap curd remaining in colloidal suspension during and after washing (1).

In a recent study (3) property-structure relationships were developed for disodium N-alkylsulfosuccinamates and sodium methyl N-alkylsulfosuccinamates. Relative to the disodium salts, the sodium methyl N-alkylsulfosuccinamates exhibited better water solubility, lower lime soap dispersant requirement, and superior calcium ion stability. They generally showed better detergency than the disodium salts when used alone, in combination with soap, and in a soap-LSDA-silicate formulation. Unfortunately, they were found to have poor hydrolytic stability in the presence of strong base. In view of the versatile reactivity of N-alkylmaleamic acids, it was of interest to determine if similar structure-property relationships existed between sodium N-alkylsulfosuccinimides and sodium N-acyloxymethylsulfosuccinimides. The surface active properties and detergency of sulfosuccinimide derivatives are not available in the literature. A patent issued to A.O. Jaeger (4) describes the synthesis of several surface active amides, including sodium N-dodecylsulfosuccinimide.

Among the literature references for the preparation of N-aryl and N-alkylmaleimides, most of the procedures were based on Searle's method (5) involving cyclization of N-arylmaleamic acids with acetic anhydride, and were cited in a previous paper (3). A recent publication involving the synthesis of such compounds used the reaction of silver or mercury maleimide with alkyl and aralkyl halides in solvents such as benzene or toluene (6). In these investiga-

tions, the yields of N-substituted maleimides generally ranged from 20 to 60% and were similar to the results found by us. Maleimide derivatives are known to undergo polymerization across the double bond in the presence of free radical catalysts (7). Furthermore, E.L. Coleman, et al., (8) found that N-alkylmaleamic acids partially polymerize at high temperatures to yield nondistillable condensation products ($-\overset{R}{N}COCH = CHCO-)_x$ with retention of the double bond. The crude N-alkylmaleimides and N-acyloxymethylmaleimides in this study contained 20-45% nondistillable residue, presumably a telomeric polymer.

N-Alkylmaleamic acids were dehydrated with acetic anhydride in the presence of fused sodium acetate to give N-alkylmaleimides (I). A variation of the Schotten-Baumann procedure was used to obtain the N-acyloxymethylmaleimides (III) by reaction between a fatty acyl chloride and N-methylolmaleimide in a pyridine-acetone solvent. Sodium N-alkylsulfosuccinimides (II) and sodium N-acyloxymethylsulfosuccinimides (IV) were obtained by addition of sodium bisulfite in aqueous ethanol to the respective maleimide derivatives. The synthesis of these compounds is shown in equations A to D.

$$RNHCOCH = CHCO_2H \xrightarrow[\text{fused NaOAc}]{(CH_3CO)_2O} RN\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH\\ \| \\ C\text{-}CH\end{smallmatrix} \quad (A)$$

(I)

$$RN\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH\\ \| \\ C\text{-}CH\end{smallmatrix} \xrightarrow[\text{EtOH/H}_2\text{O}]{NaHSO_3} RN\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH_2\\ | \\ C\text{-}CH\text{-}SO_3Na\end{smallmatrix} \quad (B)$$

(II)

$$RCOCl + HOCH_2N\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH\\ \| \\ C\text{-}CH\end{smallmatrix} \xrightarrow[\text{Acetone}]{\text{Pyridine}} RCO_2CH_2N\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH\\ \| \\ C\text{-}CH\end{smallmatrix} \quad (C)$$

(III)

$$RCO_2CH_2N\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH\\ \| \\ C\text{-}CH\end{smallmatrix} \xrightarrow[\text{EtOH/H}_2\text{O}]{NaHSO_3} RCO_2CH_2N\underset{O}{\overset{O}{\underset{\diagdown}{\diagup}}}\begin{smallmatrix}C\text{-}CH_2\\ | \\ C\text{-}CH\text{-}SO_3Na\end{smallmatrix} \quad (D)$$

(IV)

We also attempted to synthesize sodium N-acylsulfosuccinimides by addition of busulfite to the corresponding N-acylmaleimide. The addition reaction in aqueous ethanol and dioxane water led to cleavage of the acyl group with isolation of the starting fatty acid as the only identifiable product.

EXPERIMENTAL PROCEDURES

Materials

Primary fatty alkyl amines (Eastman Organic Chemicals, Rochester, NY, and Matheson Scientific Co., Joliet, IL) were distilled at reduced pressure through a 2-ft column of

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TABLE I

Elemental Analysis of Sodium N-Alkylsulfosuccinimides

N-Alkyl substituent	% Carbon		% Hydrogen		% Nitrogen		% Sulfur		% Sodium		Saponification equivalent	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$C_{12}H_{25}$-	52.02	51.67	7.64	7.88	3.78	3.64	8.68	8.71	6.22	6.13	370	369
$C_{14}H_{29}$-	54.39	54.52	8.12	8.14	3.52	3.39	8.07	7.96	5.78	5.63	398	393
$C_{16}H_{33}$-	56.44	56.79	8.53	8.95	3.29	3.18	7.54	7.68	5.40	5.32	426	428
$C_{18}H_{37}$-	58.25	57.44	8.89	8.80	3.09	3.00	7.07	7.16	5.07	5.02	454	461

Elemental Analysis of Sodium N-Acyloxymethylsulfosuccinimides

Acyl substituent	% Carbon		% Hydrogen		% Nitrogen		% Sulfur		% Sodium		Saponification equivalent	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$C_{11}H_{23}CO$	49.38	49.49	6.83	6.85	3.39	3.32	7.75	8.09	5.56	5.45	207	210
$C_{13}H_{27}CO$	51.68	51.77	7.31	7.40	3.17	3.13	7.26	7.49	5.21	5.32	222	225
$C_{15}H_{31}CO$	53.71	54.24	7.73	8.05	2.98	2.90	6.83	6.80	4.90	4.81	235	237
$C_{17}H_{35}CO$	55.51	55.03	8.10	8.08	2.82	2.57	6.44	6.42	4.62	4.48	249	256

protruded packing under a nitrogen atmosphere. Gas liquid chromatography (GLC) of the center cuts showed them to be > 98% pure. Acetic anhydride, anhydrous sodium acetate, pyridine, acetone, and formaldehyde (37% solution) were reagent grade. Maleimide, sodium bisulfite, and the acid chlorides were practical grade chemicals (Eastman Organic Chemicals, Rochester, NY). Those acid chlorides which were discolored were purified by vacuum distillation to give colorless products. N-alkylmaleamic acids were prepared by a previously described method (3). N-methylolmaleimide was obtained according to the procedure given by P.O. Tawney, et al., (7).

Synthesis of N-alkylmaleimide (I)

The method used here is based on procedures described by N.E. Searle for the synthesis of N-arylmaleimides (5). To a liter flask equipped with a stirrer, 4.0 g anhydrous sodium acetate which was fused at 0.1 mm was added. After the flask cooled to room temperature, 110 g (0.32 mole) N-hexadecylmaleamic acid was added and dried at 95 C/0.1 mm for 45 min. After this drying period, 190 ml acetic anhydride was added, and the flask was equipped with a condenser, thermometer, and drying tube. The mixture was heated 5 hr at 100 C and poured into 1500 ml of ice water. The suspension of brown solid was stirred for an hour and then neutralized with solid sodium carbonate. The mixture was treated with 500 ml ether to yield an upper emulsified ether layer and a lower water layer. The ether layer was filtered to break the emulsion, and the layers were separated. The combined water layers were extracted 4 times with 100-ml portions of ether. All ether solutions and extracts were combined and washed 4 times with 100-ml portions of water, filtered, and decolorized with active carbon black. Evaporation of the solvent yielded 96.4 g crude N-hexa-decylmaleimide. The crude product was distilled at 0.2 mm to give 56 g of distillate (bp, 158-175 C) and a pot residue of nondistillable material. Repeated crystallizations of the distillate from absolute ethanol gave 25.2 g (24% yield) N-hexadecylmaleimide (mp 66.5-67.5 C). The other N-alkylmaleimides were prepared in an analogous manner with reaction times of 4-6 hr and with similar molar ratios of reactants. We observed the following yields and mp respectively for these derivatives: N-dodecyl (45%) 56-57 C; N-tetradecyl (29%) 61-62 C: and N-octadecyl (28%) 72.5-73.5 C.

Synthesis of N-acyloxymethylmaleimide (III)

This procedure is based on the approach employed by P.O. Tawney (7) to prepare N-benzoyloxymethylmaleimide. To a 500-ml flask equipped with a mechanical stirrer and reflux condenser was added 54.9 g (0.22 mole) myris-

toyl chloride, 50 ml acetone, and 18.2 g (0.23 mole) pyridine. To the stirred suspension of solid was added a hot solution of N-methylolmaleimide in 50 ml acetone. After 2 hr the reaction mixture had cooled to room temperature and was filtered. The pyridine hydrochloride precipitate was washed with 200 ml hot acetone, and the wash liquid was added to the original filtrate. The acetone solution was added to 600 ml of ice water and filtered. The crude product was washed twice again with 700 ml portions of water to yield after drying 70 g tan amorphous solid. Two successive simple distillations at 0.15 mm (bp, 150-190 C) gave 55 g white crystalline solid. Repeated crystallizations of the distillate from absolute ethanol yielded 42 g (56% yield) N-myristoyloxymethylmaleimide (mp, 67-68 C). The other compounds of this series were prepared in essentially the same manner. The following yields and mp, were found for these compounds, respectively: lauroyl (30%) 59.5-60.5 C; palmitoyl (51%) 72-73 C; and stearoyl (36%) 75-76 C.

Sulfonation of Succinimide Derivatives (I) and (III)

The addition of sodium bisulfite to N-alkylmaleimides (I) and N-acyloxymethylmaleimides (III) in aqueous ethanol is so similar that the procedure for the synthesis of sodium N-hexadecylsulfosuccinimide should suffice to illustrate the preparation of both types of compounds. To a 250-ml flask equipped with a condenser was added 30 ml water and 5.1 g (0.049 mole) sodium bisulfite. After the salt had dissolved, 15 g (0.047 mole) N-hexadecylmaleimide was added along with 70 ml ethanol. The mixture was refluxed 2 hr on a steam bath and filtered hot. The filtrate was treated with 60 ml aqueous ethanol (1:1) and cooled to 25 C. After filtration and drying, 19.3 g crude product was obtained. Recrystallization from aqueous ethanol gave 18.5 g (90% yield) sodium N-hexadecylsulfosuccinimide. The other analogs of this series were prepared in the same manner with the following yields being observed: dodecyl, 75%; tetradecyl, 76%, and octadecyl, 95%.

Similarly, the reaction of sodium bisulfite with N-acyloxymethylmaleimides required reflux periods of 4-5 hr. Shorter reaction times led to lower yields of sodium N-acyloxymethylsulfosuccinimides. These derivatives frequently required two or more crystallizations from aqueous thanol to obtain a purified sample. The following yields were observed where the acyl group was: lauroyl, 61%; myristoyl, 80%; palmitoyl, 67%; and stearoyl, 83%.

Saponification equivalents for both types of compounds were determined by a standard method using 0.2 N alcoholic potassium hydroxide at 100 C for 1 hr. Saponification equivalents and elemental analyses are shown in Table I.

Stability to Hydrolysis

The alkaline hydrolysis of sodium N-tetradecylsulfosuc-

TABLE II

Surface Active Properties of Sodium N-Alkylsulfosuccinimides

N-Alkyl substituent	LSDR[a]	Krafft point (C)	Calcium ion[b] stability	CMC[c] (mmoles/liter)
$C_{12}H_{25}$-	9	36	>1800	4.71
$C_{14}H_{29}$-	8	46	1660	1.23
$C_{16}H_{33}$-	9	59	1270	0.31
$C_{18}H_{37}$-	9	68	1170	0.16

Surface Active Properties of Sodium N-Acyloxymethylsulfosuccinimides

Acyl substituent				
$C_{11}H_{23}CO$	7	47	>1800	3.82
$C_{13}H_{27}CO$	6	54	1800	1.06
$C_{15}H_{31}CO$	8	62	.[d]	0.48
$C_{17}H_{35}CO$	7	-[d]	1500	0.17

[a]LSDR = Lime soap dispersing requirement.

[b]Calcium ion stability as ppm $CaCO_3$.

[c]CMC = Critical micelle concentration.

[d]This sample formed a clear gel at 55 C with solution appearing to occur at 65 C.

TABLE III

Detergency of Sodium N-Alkylsulfosuccinimides

N-Alkyl substituent	Detergency[a] (ΔR)											
	0.05% Compound			0.2% Compound			0.2% Binary[b]			0.2% Ternary[c]		
	TF[d]	EMPA[d]	UST[d]	TF	EMPA	UST	TF	EMPA	UST	TF	EMPA	UST
$C_{12}H_{25}$	20	9	9	27	12	11	5	14	5	2	20	4
$C_{14}H_{29}$	26	8	11	30	9	11	23	27	13	19	35	12
$C_{16}H_{33}$	27	5	12	33	7	11	24	25	12	19	34	13
$C_{18}H_{37}$	6	6	4	16	6	9	20	17	10	16	28	10
Control[d]				28	34	12						

Detergency of Sodium N-Acyloxymethylsulfosuccinimides

Acyl substituent												
$C_{11}H_{23}CO$	16	11	6	25	10	10	-4	6	1	-6	7	2
$C_{13}H_{27}CO$	24	11	10	30	9	12	10	15	7	2	19	4
$C_{15}H_{31}CO$	28	6	10	35	9	12	15	16	9	12	30	9
$C_{17}H_{35}CO$	16	8	9	28	5	11	14	14	8	12	30	9
Control[d]				28	34	12						

[a]Detergency values shown as ΔR, the increase in reflectance after washing. The values were obtained using 1 liter hard water 300 ppm, calculated as $CaCO_3$, containing 1% carboxymethylcellulose based on total solids.

[b]0.05% compound plus 0.15% sodium tallowate.

[c]0.04% compound plus 0.13% sodium tallowate plus 0.03% sodium silicate (1:1.6).

[d]TF = Testfabrics cotton-polyester; EMPA = EMPA 101 cotton; UST = US Testing cotton.

[e]Control was a commercial phosphate built detergent used at 0.2% concentration.

cinimide was measured by heating 0.005 mole compound in 100 ml 0.05 N NaOH, pH 11.8, at 80 C. The degree of hydrolysis was measured by pipetting aliquots of solution into neutralized ethanol and titrating the samples with 0.1 N HCl. This same procedure was applied to a sample of sodium N-myristoyloxymethylsulfosuccinimide at the same concentration of base but only 0.0025 mole of sample was used, because it consumed base by both ester hydrolysis and opening of the sulfosuccinimide ring.

A solution containing 0.3% sodium silicate (Na_2):SiO_2, 1:1.6; (pH 11.2) and 0.5% sodium N-octadecylsulfosuccinimide was prepared in a liter of water. An aliquot of solution was titrated with 0.1 N HCl initially and after stirring the solution for 60 min at 90 C. An analogous hydrolysis study was undertaken with an 0.03% solution of sodium silicate and 0.05% of test surfactant at 50 C for 25 min to simulate conditions obtained during detergency evaluation studies.

Surface Active Properties

Lime soap dispersant requirement (LSDR) was deter-

mined by the Borghetty-Bergman method (9). The values indicate the grams of compound required to prevent precipitation of 100 g sodium oleate in 333 ppm hard water. Krafft point is the temperature at which a 1% suspension of compound becomes a clear solution. Calcium ion stability (10) values were obtained with heated solutions which were quickly cooled and immediately titrated with calcium acetate. Critical micelle concentration was determined by the pinacyanole dye titration method (11). Surface active properties of the sodium N-alkylsulfosuccinimides and sodium N-acyloxymethylsulfosuccinimides are shown in Table II. Detergency values for these compounds were measured in terms of difference in reflectance (ΔR) before and after washing in a Tergotometer operated at 120 F, 110 cpm for 20 min in 1 liter of water 300 ppm hardness, calculated as $CaCO_3$. Five circular swatches, 4 in. in diameter, of EMPA 101 cotton, US Testing cotton, and Testfabrics cotton-polyester blend with a permanent press finish were washed in each beaker. Four washing formulations were used: a) 0.05% test compound; b) 0.2% test com-

pound; c) a binary mixture of 0.05% test compound, and 0.15% sodium tallowate, and d) a ternary mixture of 0.04% test compound, 0.13% sodium tallowate, and 0.03% sodium silicate ($Na_2O:SiO_2$, 1:1.6). Each formulation also contained 1% carboxymethylcellulose based on total solids. Detergency date are listed in Table III for sodium N-alkyl-sulfosuccinimides and sodium N-acyloxymethylsulfosuccinimides.

RESULTS AND DISCUSSION

The overall yields of the desired surfactants were generally poor because of the side reactions occurring in the cyclization step discussed above. However, other side reactions occurred, because the distillable fraction from both types of compounds required repeated crystallizations from ethanol to obtain the pure intermediates.

In the presence of sodium hydroxide at 80 C, both types of compounds were > 90% hydrolyzed after 20 min. When solutions of 0.5% test compound and 0.3% sodium silicate were heated 60 min at 90 C, ca. 50-60% hydrolysis was observed. No hydrolysis occurred under conditions of detergency testing where solutions containing 0.05% test compound and 0.03% sodium silicate were heated at 50 C for 25 min. Thus, the instability of these compounds to hydrolysis under conditions of high alkalinity restricted their use to mildly alkaline formulations.

The surface active properties of these salts are shown in Table II. The sodium N-alkylsulfosuccinimides exhibited good LSDR with values of 8-9. The Krafft points are somewhat high ranging from 36-68 C, respectively, for the dodecyl and octadecyl derivatives, thereby indicating rather low water solubility. The calcium ion stability values decrease from >1800 ppm for the dodecyl compound to 1170 ppm for the octadecyl derivative, thus showing good stability in hard water. Critical micelle concentrations decrease from 4.71 to 0.16 mmols/liter with increasing chain length of the N-alkyl substituent. In comparison to the N-alkylsulfosuccinimides the sodium N-acyloxymethylsulfosuccinimides show slightly better LSDR values of 6-8 and similar calcium ion stability values, which show a smaller decrease from the lauroyl to the stearoyl compounds. Krafft points and cricial micelle concentration values are essentially equivalent to those of the N-alkylsulfosuccinimides. As is evident, the surface active properties of both types of compounds are comparable in every respect. Thus, insertion of the ester function did not give the anticipated

improved water solubility with positive changes in the surface active properties.

Fairly good detergency values (Table III) were found for the N-alkylsulfosuccinimides and the N-acyloxymethylsulfosuccinimides. The values for the compounds are comparable to each other in the formulations used. For the N-alkyl derivatives, the C_{14} and C_{16} compounds gave the best detergency performance, while the C_{12} and C_{18} derivatives were less effective. Similar washing ability was observed in the ester series with the lauroyl and stearoyl compounds being deficient, while the palmitoyl compound gave the best results. At 0.05% and 0.2% concentration, the compounds generally were equal to the control on Testfabrics (TF) and US Testing cloth (UST), but poorer on the EMPA cloth. In the binary system at 0.2% concentration, the combination with soap resulted in marked improvement in washing ability of EMPA cloth, no change on UST, and a decrease in detergency for TF cloth. In the ternary system containing test compound-soap-silicate, the values for EMPA cloth were comparable to the control. No change was found with UST, but a still further decrease was observed with TF cloth. This type of detergency behavior also was noted for other types of anionic lime soap dispersants (3,12,13).

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