Soap-Based Detergent Formulations: VII. Sodium Methyl Alkylbenzoylsulfopropionates as Lime Soap Dispersing Agents[1]

WILLIAM N. MARMER, DAVID E. VAN HORN, and **WARNER M. LINFIELD,** Eastern Regional Research Center[2], Philadelphia, Pennsylvania 19118

ABSTRACT

Research was performed on the development of lime soap dispersing agents derived from alkylbenzenes. The sulfonation with sodium bisulfite of a variety of methyl β-*p*-alkylbenzoylacrylates (III) produced adducts (I) whose detergent properties were studied. Yields were optimized, model compounds were synthesized, and products characterized by NMR spectroscopy. The sulfonated adduct (I-A) derived from a commercial mixture of alkylbenzenes can be formulated with tallow soap, sodium silicate, and sodium carboxymethylcellulose to give a product that is competitive with a standard linear alkylbenzenesulfonate-phosphate household detergent.

INTRODUCTION

A study was undertaken of the synthesis of a variety of sodium methyl alkylbenzoylsulfopropionates (I) to determine their effectiveness as lime soap dispersing agents in tallow soap-based laundry detergents. These compounds first were reported by Hedrick, et al. (1), who described their synthesis (Fig. 1) and their versatility as surfactants. Linfield, et al., (2) found them to be excellent detergents by themselves, as well as when formulated with nonphosphate builders.

In view of this and the structural similarity to α-sulfofatty esters, which are excellent lime soap dispersing agents, it seemed likely that the sulfopropionates also would be good lime soap dispersing agents.

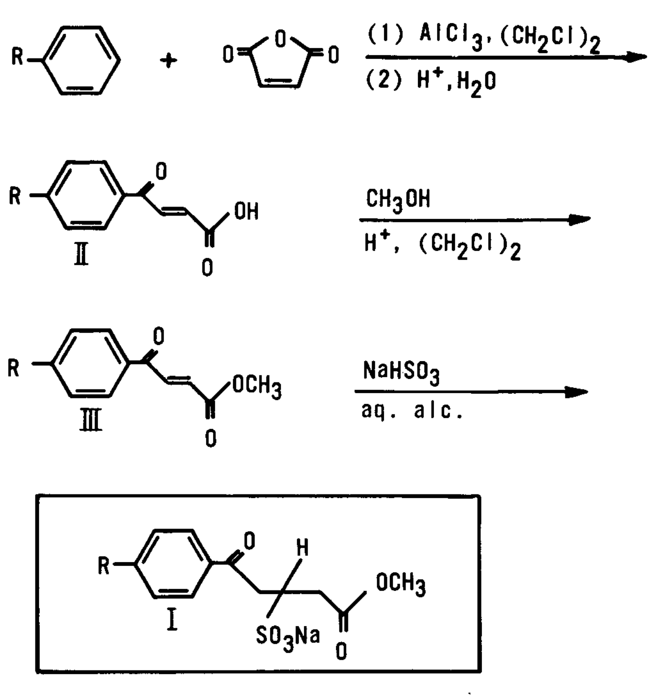

FIG. 1. Synthesis. R = long chain alkyl group.

EXPERIMENTAL PROCEDURES

Synthesis of the Surfactants and Intermediates

Data pertaining to the synthesis of model compounds are given in Table I. The model alkylbenzenes used as starting materials were at least 97% pure (by gas liquid chromatography [GLC] DEGS column).

Aroylacrylic acid (II-A) from Nalkylene 500 (alkylbenzene mixture, average mol wt 236, Continental Oil Co., Ponca City, Okla.): The product (II-A) was prepared by the reaction of the alkylbenzene mixture in 1,2-dichloroethane with an equimolar amount of maleic anhydride and 80% excess anhydrous aluminum chloride (2). The apparatus was rendered anhydrous by the removal of a small amount of the solvent by distillation, along with azeotroped water, prior to the addition of the reagents.

Methyl aroylacrylate from Nalkylene 500 (III-A): The literature procedure was followed explicitly (1, 2). The crude aroylacrylic acid (II-A) in 1,2-dichloroethane was esterified without prior purification.

Sulfonated methyl aroylacrylates (I): Sulfonations were carried out using sodium bisulfite, according to modified literature procedures (2). Best yields were obtained when the reactions proceeded in a closed container. Larger runs, thus, were carried out in hydrogenation bottles wrapped with heating tape and thermally controlled (100-110 C) by an external thermocouple setup. To agitate the mixture, the bottle was placed in a rocker-shaker. Small runs were carried out in sealed glass ampoules, which were rotated tor agitation by attaching to the shaft of a rotary motor; heating was accomplished in a steam bath. The extent of sulfonation was determined by cationic titration (7).

The Nalkylene 500 derived sulfonated product (I-A) was obtained at 100-110 C from the crude, but solvent-free, methyl aroylacrylate (III-A). Best results were obtained from reactions run in sealed containers. This obviated frothing and loss of sulfur dioxide and allowed the use of aqueous ethanol or isopropanol as solvent to diminish viscosity. Yields suffered from dilution beyond the concentration called for in the literature (2).

NMR Studies

NMR analyses were performed routinely to elucidate structure and especially to observe the extent of degradation of the double bond in compounds II and III. Spectra were obtained on a Jeolco C60H instrument. Data are listed in Table II.

Surface Active Properties

The lime soap dispersant requirements were determined by the Borghetty-Bergman procedure (8), and the data are recorded in Table III.

Calcium ion stability (9): It was determined that >5.0 ml of an 0.05% solution of the model sulfonated compounds will not form a precipitate with a 2.5% solution of

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[2] ARS, USDA.

TABLE I

Syntheses of Model Compounds

							Analysis			
							Calculated		Found	
		Para substituent	Recrystallization solvent	Yield (%)	Melting point (C) (literature MP)	Equivalent wt (theoretical)	C%	H%	C%	H%
Aroyl-acrylic acids	II-B	CH_3	$(CH_2Cl)_2$	66	136-7 (137-8)[a]	—	—	—	—	—
	II-C	n-C_8H_{17}	$(CH_2Cl)_2$	78	76.0-6.5	287[b] (288)	74.97	8.39	75.26	8.15
	II-D	n-$C_{10}H_{21}$	$(CH_2Cl)_2$	75	81.5-2.5	311[b] (316)	75.91	8.92	75.73	8.79
	II-E	n-$C_{12}H_{25}$	$(CH_2Cl)_2$	70	81.5-2.5	339[b] (344)	76.70	9.36	76.88	9.29
Methyl aroylacrylates	III-B	CH_3	(distilled at 138 C$_{0.30}$)	89	42-5 (45.5-6.0)[c]	206.6[d] (204.2)	—	—	—	—
	III-C	n-C_8H_{17}	ligroin	64	24-5	—	75.46	8.67	75.61	8.38
	III-D	n-$C_{10}H_{21}$	ligroin	61	33.5-4.0	—	76.33	9.15	76.22	8.93
	III-E	n-$C_{12}H_{25}$	ligroin	89	43.5-4.0	—	77.05	9.56	76.88	9.24
							Sulfate ash (% Na)			
							Calculated		Found	
Sulfonated methyl aroylacrylates	I-B	CH_3	—	—	154-6 (dec)[f]	—	—		—	
	I-C	n-C_8H_{17}	Absolute EtOH	100[e]	182.5-4.5 (dec)	—	5.66		5.71	
	I-D	n-$C_{10}H_{21}$	EtOAc	86[e]	187.5-9.0 (dec)	—	5.29		5.12	
	I-E	n-$C_{12}H_{25}$	EtOAc	75[e]	188.5-190.5 (dec)	—	4.97		4.80	

[a] See ref. 3.

[b] Titration with NaOH.

[c] See ref. 4.

[d] Hydrogenation (5, 6).

[e] Cationic titration (7) of crude product.

[f] Crude product.

TABLE II

NMR Data of Alkylbenzoylacrylic Acids (II), Their Methyl (III), and Their Sulfonated Methyl Esters (I)[a]

Assignment	(II-A) in CF_3CO_2H	(III-A) in $CDCl_3$	(III-B) in $CDCl_3$	(I-B) in CF_3CO_2H	(I-A) in CF_3CO_2H
Aromatic, downfield (doublet) (para pattern)	δ8.05,1.7H	8.05,1.9H	7.96,2.1H	8.02,2.0H	8.01,2.0H
Aromatic, upfield (doublet)	δ7.44,2.0H	7.38,2.0H	7.45,2.0H	7.42,2.0H	7.41,2.0H
Aromatic, J = (in Hz)	8.06	8.25	8.25	8.25	8.25
Vinyl, downfield (doublet)	δ8.18,0.9H	8.04,0.9H	7.98,1.0H		
Vinyl, upfield (doublet)	δ6.94,0.9H	6.97,0.9H	6.91,1.0H		
Vinyl, J = (in Hz)	15.4 (trans)	15 (trans)	15 (trans)		
Benzylic	M,2.8δ	M,3.6,1.1H	S,2.45,3.1H	S,2.44,3.0H	M,2.75,0.94H
$CH-SO_3$ (triplet)				4.91,0.88H	4.89,0.88H
CH_2 (doublet)				4.12,1.83H	4.12,1.78H
J = (in Hz)				6.75	6.75
OCH_3 (singlet)		δ3.9,2.8H	3.88,3.1H	3.94,3.0H	3.93,3.0H
R group (not including benzylic)[b]	δ0.5-2.1	0.6-2.0			0.5-2.1,19H

[a] δ values are given in ppm downfield from internal tetramethylsilane.

[b] R = Nalkylene 500 alkyl group mixture.

calcium acetate. This is equivalent to a toleration of hard water containing >1755 ppm calcium ion. Results are given in Table III.

Surface tension (γ): Measurements on a du Noüy tensiometer were made of solutions above the critical micelle concentration. Results are given in Table III in dynes/cm.

Krafft point (10): Results are given in Table III.

Detergency evaluations: Detergencies were obtained with the aid of a Terg-O-Tometer. All washings were run for 20 min at 120 F in 1 liter water of 300 ppm hardness with an agitation speed of 100 cpm. Five circular swatches each (4 in. diameter) of EMPA 101 cotton, U.S. Testing cotton (UST), and Testfabric cotton-polyester with permanent press finish (TF) were washed together in each beaker. Detergency was measured in terms of increased reflectance ΔR of the washed cloth over the soiled cloth. Results are shown in Figure 2. Sodium carboxymethylcellulose was added to all formulations as a standard antiredeposition agent.

RESULTS AND DISCUSSION

Syntheses

The alkylbenzoylacrylic acids (II) were synthesized from a commercial detergent alkylate Nalkylene 500 (Conoco), whose average mol wt of 236 corresponds to the formula $C_{11.3}H_{23.6}$-C_6H_5. Also used were the Monsanto detergent alkylates Alkylate 215 ($C_{11.3}H_{23.6}C_6H_5$), Alkylate 225 ($C_{11.8}H_{24.6}C_6H_5$), and Alkylate 230L ($C_{13.1}H_{27.2}C_6H_5$). The toluene derivative was synthesized as a model compound for NMR work; comparison of NMR data (Table II) demonstrated that this and all other derivatives had *trans*-double bonds and para substitution on the aromatic ring. Finally, derivatives of 1-phenyloctane, 1-phenyldecane, and 1-phenyldodecane were prepared as model surfactants, since these materials could be purified by recrystallization and the surface active properties of the pure compounds, thus, obtained.

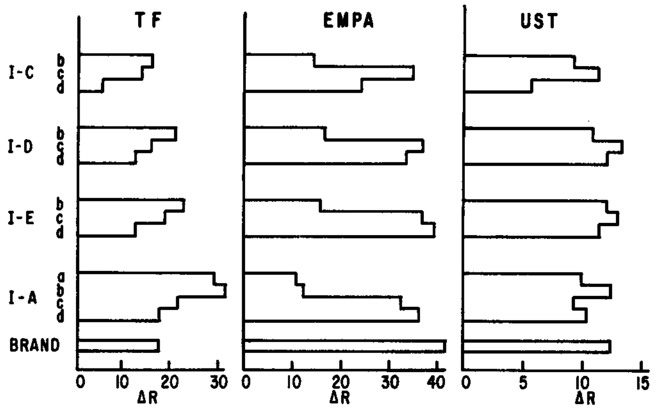


FIG. 2. Detergency (ΔR) at 300 ppm water hardness and 120 F. All solutions contain 0.002% CMC. Formulations: a = 0.04% lime soap dispersing agent (LSDA); b = 0.2% LSDA; c = 0.05% LSDA and 0.15% tallow soap; d = 0.04% LSDA, 0.13% soap, and 0.03% sodium silicate (SiO_2: Na_2O = 1.6 : 1.0). BRAND = a commercial phosphate-built detergent. Fabrics: TF = Testfabric cotton-polyester with permanent press finish, EMPA = EMPA 101 cotton, and UST = U.S. Testing cotton.

Each of the three synthetic steps (Fig. 1) was found to be replete with problems affecting the yields. The Friedel-Crafts acylation step was found to be sensitive to heat and to strong acid. Best results were obtained by regulating the reaction temperature (<25 C) and by minimizing the number of sulfuric acid washings called for in the literature procedure (2). NMR analysis showed that the crude unsaturated acid (II-A) derived from Nalkylene 500 retained 90-95% of its double bond content. Unsaturated acids (II) derived from Monsanto's detergent alkylate mixtures (Alkylates 215, 225, or 230L) were extremely prone to side-reactions, though 90% double bond content could be obtained by following the precautions mentioned above.

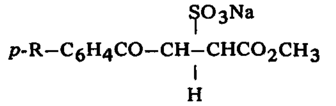
NMR analysis showed that the esterification of the Nalkylene 500 derived unsaturated acid proceeded fairly smoothly; the spectrum of the crude product (III-A) showed that 90% of the unsaturation still remained. A lack of extraneous NMR absorptions suggested the absence of significant amounts of side-products. On the other hand, esterification of the unsaturated acids (II) derived from the Monsanto Alkylate series was unsuccessful. NMR analysis of the crude esters (III) showed the absence of 40% of the vinyl group. Instead of a clean baseline, the spectral pattern was interrupted by a triplet (δ4.4), a singlet (δ3.7), and other extraneous signals, which suggested that methanol had added across the double bond to a large extent (30%).

The replacement of sulfuric acid in the esterification reaction by para-toluenesulfonic acid, fluoboric acid, or boron trifluoride had no advantageous effect upon the esterification of the unsaturated acids derived from the Alkylates. The use of anhydrous hydrogen chloride affected a 90% loss of the double bond of the aroylacrylic acid (II). The advantageous use of this side reaction currently is being explored, and results will appear in a later report.

Particular attention was given the sulfonation step. The extent of sulfonation could be analyzed by observing the

TABLE III

Some Properties of Sodium Methyl Alkylbenzoylsulfopropionates

Compound I  $p\text{-R-C}_6\text{H}_4\text{CO-}\underset{\text{H}}{\overset{\text{SO}_3\text{Na}}{\text{CH}}}\text{-CHCO}_2\text{CH}_3$		Properties			
		LSDR[a]	Ca^{++} stability	γ[b]	Krafft point
R[c]					
n-C_8H_{17}	(I-C)	7	>1755 ppm	39.0	8.25 C
n-$C_{10}H_{21}$	(I-D)	7	>1755 ppm	38.1	23.0 C
n-$C_{12}H_{25}$	(I-E)	7	>1755 ppm	37.2	30.5 C
$C_{11.3}H_{23.6}$ (from Nalkylene 500)	(I-A)	8	1724 ppm		

[a] Lime soap dispersing requirement.

[b] Surface tension (dynes/cm).

[c] R = Nalkylene 500 alkyl group mixture.

disappearance of the NMR signals of the vinyl protons of the unsaturated ester (III). Furthermore, the sulfonated ester (I) could be titrated against a cationic surfactant Hyamine 1622, according to a standard procedure.

The literature procedure of sulfonation (1, 2) suffers from problems due to frothing, loss of sulfur dioxide from the reaction mixture, and difficulty in mixing due to a two phase system and increasing viscosity. Results of the current project show that the procedure is not modified effectively by dilution or the addition of preformed product. However, yields are increased by replacement of some or all of the water with ethanol or isopropanol and operation in a sealed system. Although cationic titration showed that the maximum yield was 88% sulfonation, NMR analysis of the crude products showed the complete disappearance of the vinyl proton signals. Sulfonation was, therefore, as complete as possible; the remaining 12% of the vinyl groups presumably had disappeared in side-reactions in the earlier Friedel-Crafts and esterification steps.

Surface Activity

The data in Table III demonstrate that the sulfonated esters I are good lime soap dispersing agents per se and are not precipitated in hard water.

The results of preliminary detergency screening tests are depicted graphically in Figure 2. The lime soap dispersing agent/soap/silicate formulation (d) formulated with the Nalkylene 500 derived sulfonated ester (I-A) is an effective detergent. The performance is somewhat less effective than that of the control detergent on the two types of cotton test cloth (UST and EMPA) and a trace better than the control performance on the permanent press cotton-polyester material (TF). I-A's performance on TF without soap and silicate (formulation a) is surprisingly superior to that of the ternary formulation (d) and of the control. The replacement of 75% of the test surfactant by tallow soap (formulation c) and, in turn, the replacement of 15% of this binary mixture by sodium silicate (formulation d) show a synergistic effect, however, with respect to the laundering of the EMPA test swatches.

Among the model compounds studied, the performance of the octylbenzene derived sulfonated ester (I-C) is always inferior to the performance of the compounds derived from decylbenzene (I-D) and dodecylbenzene (I-E). Finally, better detergency results are obtained for the TF blended fabric with the Nalkylene 500 derived I-A than with any of the model compounds (I-C, D, E). This suggests that a branched alkyl group on the aromatic ring is more desirable for detergency than a straight chain alkyl group.

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