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Synthesis, Physicochemical Properties, and Detergency of Disodium 2-Alkyl-1,3-propanediyl Bissulfates

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ABSTRACT: In this paper we describe the synthesis and the physicochemical properties of a series of highly calcium-tolerant anionic surfactants. Detergency tests for one of the surfactants, disodium 2-*n*-hexadecyl-1,3-propanediyl bissulfate **3d**, in formulations with and without builder are reported. These tests were performed using a robot-Terg-O-tometer. The results of these tests are compared to the results of detergency tests of standard surfactants: LAS 113, a linear alkylbenzenesulfonate, PAS 45, a linear alkylsulfate, and PAES 23-2S, an alkylethersulfate, representing standard commercial anionic surfactants of which the last is calcium-tolerant, i.e., it does not precipitate from its aqueous solution in the presence of calcium ions. The detergency performance of bissulfate **3d** was similar to that of PAES 23-2S, with and without builder. *JSD* 1, 23-28 (1998).

KEY WORDS: Anionic surfactants, bissulfates, calcium tolerance, detergency, Krafft temperature, physicochemical properties.

One of the problems of applying anionic surfactants in, for example, laundry detergents is the precipitation of calcium salts (1-4). Precipitation of anionic surfactants in laundry detergents decreases the detergency performance. Much effort has been directed toward avoiding this precipitation. There are at least three ways to tackle the problem. The first involves the use of a large quantity of surfactant to prevent precipitation of the calcium salt. A second approach uses additives to enhance tolerance toward calcium ions. The third option is the development of anionic surfactants which do not precipitate in the presence of calcium ions. The environmental advantage of the latter compounds in detergent formulations is that less or no additives such as either phosphates or zeolites (builders) are needed. The function of builders is to trap divalent cations such as calcium.

In a previous paper (5), we discussed the synthesis and the relevant physicochemical properties of aqueous solutions of some highly calcium-tolerant anionic surfactants,

the disodium 2-alkyl-1,3-propanediyl bissulfates. The goal of this research was to obtain calcium-tolerant surfactants with low critical micelle concentrations (CMC) and low Krafft temperatures and to establish guidelines for the development of calcium-tolerant anionic surfactants.

In this work we discuss the relation between the chain length of calcium-tolerant bissulfate surfactants and their physicochemical properties, such as CMC and counterion binding (β). We also report detergency tests for one of these surfactants in formulations with and without builder, and compare the results to those of commercial surfactants. The thermodynamics of micellization of bisulfate surfactants will be discussed in a future paper. The structure and synthesis of surfactants **3a-e** are depicted in Scheme 1: (i) (a) $\text{CH}_3\text{CH}_2\text{OH}/\text{CH}_3\text{CH}_2\text{ONa}$, (b) alkyl bromide; (ii) $\text{LiAlH}_4/\text{tetrahydrofuran}$ (THF); (iii) (a) $\text{C}_5\text{H}_5\text{N}:\text{SO}_3/\text{CHCl}_3$, (b) $\text{NaOH}/\text{H}_2\text{O}$. Compounds **1-3: a-e**, $\text{R} = n\text{-C}_{10}\text{H}_{21}$ to $n\text{-C}_{18}\text{H}_{37}$ (even number of carbon atoms). Of these, only compound **3b** has been reported in the literature (6), although no synthetic details or characterization of this material were discussed. Chain length of the surfactants with two sulfate head groups was varied from *n*-decyl (**3a**) to *n*-octadecyl (**3e**). The hypothesis was that an increase of the headgroup area by doubling the number of headgroups would lead to an increased solubility of the Ca^{2+} salt by providing the possibility of compensating for a loss of charge on binding of Ca^{2+} by the micelle. This should lead to a decreased Krafft temperature of the calcium salt.

EXPERIMENTAL PROCEDURES

General methods. All synthetic reaction mixtures were stirred magnetically and reactions were performed at ambient atmosphere unless stated otherwise. All solvents were freshly distilled. Ethanol was distilled from Mg; ether and chloroform (CHCl_3) were distilled from P_2O_5 . All commercially available chemicals were purchased from Merck (Darmstadt, Germany), Aldrich, Janssen, or Fluka and were used without further purification. Corrected melting points were determined on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope. The 200 MHz ^1H nuclear magnetic resonance (NMR) spectra

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SCHEME 1

were recorded on a Nicolet NT-200 spectrometer; the 300 MHz ^1H NMR spectra were recorded on a Varian VXR-300 spectrometer (Palo Alto, CA). The chemical shifts are reported in δ units (ppm) with the solvent as internal standard and converted to the tetramethylsilane (TMS)-scale, TMS as a standard at $\delta = 0.00$ ppm, using $\delta(\text{CHCl}_3) = 7.24$ ppm and $\delta(\text{DOH}) = 4.65$ ppm. All spectra were recorded in either CDCl_3 or D_2O as indicated. Splitting patterns are represented as: *s* (singlet), *bs* (broad singlet), *d* (doublet), *dd* (double doublet), *t* (triplet), *q* (quartet), *qi* (quintet), *m* (multiplet), and *c* (complex). ^{13}C NMR spectra were recorded on a Varian Gemini-200 NMR spectrometer (50.3 MHz) or a Varian VXR-300 spectrometer (75.43 MHz). Infrared (IR) spectra were recorded on a Perkin-Elmer 841 spectrophotometer (Norwalk, CT). Element analyses were performed in the Microanalytical Department of the University of Groningen, The Netherlands. Average values of duplicate or triplicate determinations are reported.

Synthesis of diethyl alkylmalonates (1a-e) (see Ref. 7). In a typical experiment, 11.6 g (0.5 mol) of Na was dissolved with stirring in 800 mL of absolute ethanol; 82.5 g (0.48 mol) of diethyl malonate was added to the solution. After 30 min, 116 g (0.47 mmol) of 1-bromododecane dissolved in 100 mL of ethanol was added carefully. After addition, the reaction mixture was refluxed for 2 h. A white precipitate of NaBr was obtained. The reaction mixture was cooled, and ethanol was removed under reduced pressure. The remaining slurry was suspended in diethyl ether (500 mL) and washed twice with water (150 mL). The combined aqueous layers were extracted with 100 mL of ether. The combined organic layers were dried with Na_2SO_4 . Ether was removed under reduced pressure to yield a yellow liquid. This liquid was distilled under reduced pressure to yield diethyl *n*-dodecylmalonate as a colorless liquid. The yields of **1a-e** varied with changing chain length: **1a** (70%, b.p. 39–41°C at 0.2 mm Hg); **1b** (80%); **1c** (87%); **1d** (65%); **1e** (57%). A typical 200 MHz ^1H NMR spectrum (compound **1b**) exhibits the following signals: (CDCl_3) δ 4.19 (4H, *q*, OCH_2), 3.30 (1H, *t*, H-2), 1.88 (2H, *c*, H-3), 1.26 (28H, *c*, H's of the alkyl chain and CH_3 ethyl), 0.87 (3H, *t*, CH_3) ppm.

Synthesis of 2-alkyl-1,3-propanediols (2a-e). In a typical experiment, a solution of 82 g (0.25 mol) of diethyl *n*-dodecylmalonate **1b** in ether (200 mL) was added to a stirred 1 M solution of LiAlH_4 in THF (500 mL) following the method described by Alagui *et al.* (8) After 1 h, ethyl acetate (150 mL) was carefully added to the reaction mixture to quench the remaining LiAlH_4 . A large quantity of solid white aluminum salts precipitated, sometimes causing stir-

ring problems. To this slurry, sulfuric acid (7.5 N) was added until all precipitate had dissolved. The solution was extracted with ether (twice 250 mL). The organic layers were combined and washed with saturated NaCl (twice 50 mL), saturated NaHCO_3 (50 mL), and water (twice 50 mL), respectively. The organic layer was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The raw product was crystallized from *n*-hexane yielding white crystalline diol **2b** (49 g, 80%); m.p. **2b** = 71.0–71.5°C; 200 MHz ^1H NMR (**2b**) (CDCl_3) δ 3.80 (2H, *dd*, CH_2OH), 3.63 (2H, *dd*, CH_2OH), 1.29 (23H, *c*, CH_2 's of the chain), 0.87 (3H, *t*, CH_3) ppm; ^{13}C NMR (**2b**) (CDCl_3) δ 66.40 (CH_2OH), 41.92 (CH), 31.90–22.60 (C alkyl chain), 14.08 (CH_3). NMR spectra for **2a**, **2c**, **2d**, **2e** were similar. M.p. **2a** = 61.0–61.5°C; m.p. **2c** = 77.7–78.1°C; m.p. **2d** = 83.5–83.8°C; m.p. **2e** = 86.9–88.4°C.

Synthesis of disodium 2-alkyl-1,3-propanediyl bissulfates (3a-e). These were obtained using a method described by Tarras (9) [see also Gilbert (10)]. Milder conditions were required to avoid coloring of the product. Therefore, SO_3 complexes were used instead of the more aggressive SO_3 . In a typical experiment, 1 g (2.1 mmol) of diol **2b** was added to a stirred slurry of trimethylamine- SO_3 complex (3.1 g, 22.1 mmol) in 25 mL of dry CHCl_3 at 0°C. After 30 min, the solvent was evaporated under reduced pressure. The residue was dissolved in 5 mL of water and neutralized with a 2 M aqueous NaOH solution. The resulting solution was cooled in an ice-water bath. The crude crystalline product **3b** was recrystallized from methanol. For compound **3a** the procedure was slightly different. After neutralization, water was evaporated carefully. 1,4-Dioxane was added to reduce the foaming during evaporation. The residue was extracted with methanol. The white product **3a** crystallized from the filtrate upon standing at -20°C. The sodium bissulfates **3a-e** were dried under vacuum at 120°C. Chemical yields after crystallization were in the range of 50–95%. Typical spectra: ^1H NMR (**3b**) (D_2O) δ 4.83 (HOD), 4.07 (4H, *d*, $J_{1,3 \rightarrow 2} = 5.55$ Hz, $\text{CH}_2\text{OSO}_3\text{Na}$), 2.12 (1H, *m*, CH), 1.29 (22H, *c*, CH_2 's of the chain), 0.87 (3H, *t*, CH_3) ppm; IR (KBr) 3451 (crystal water) 2955 ($\nu_{\text{as}} \text{CH}_3$), 2924 ($\nu_{\text{as}} \text{CH}_2$), 2853 ($\nu_{\text{s}} \text{CH}_2/\text{CH}_3$), 1468 and 1457 ($\nu_{\text{as}} \text{CH}_2/\text{CH}_3$), 1262 and 1222 ($\nu_{\text{as}} \text{S=O}$, ROSO_3), 1073 and 1064 ($\nu_{\text{s}} \text{S=O}$, ROSO_3) cm^{-1} . Calcd. for **3a** C, 37.14; H, 6.25; S, 15.25; Na, 10.90; found: C, 36.82; H, 6.28; S, 15.32; Na, 11.01. Calcd. for **3b** C, 40.17; H, 6.74; S, 14.3; Na, 10.25; found: C, 40.23; H, 6.86; S, 13.74; Na, 10.16. Calcd. for **3c** C, 42.85; H, 7.19; S, 13.65; Na, 9.65; found: C, 42.75; H, 7.25; S, 13.57; Na, 9.70. Calcd. for **3d** C, 45.23; H, 7.59; S, 12.71; Na, 9.11; found: C, 45.60; H,

TABLE 1
Critical Micelle Concentration (CMC) and Counterion Binding^a

Compound	298 K		308 K		318 K		328 K	
	CMC (mM)	β (%)	CMC (mM)	β (%)	CMC (mM)	β (%)	CMC (mM)	β (%)
3b	24.0 $\pm$ 0.1	49 $\pm$ 1	27.7 $\pm$ 0.1	52 $\pm$ 1	28.6 $\pm$ 0.1	50 $\pm$ 1	30.6 $\pm$ 0.3	54 $\pm$ 1
3c	-	-	10.0 $\pm$ 0.1	53 $\pm$ 1	11.4 $\pm$ 0.1	55 $\pm$ 2	12.5 $\pm$ 0.6	54 $\pm$ 3
3d	-	-	-	-	4.68 $\pm$ 0.01	66 $\pm$ 1	4.95 $\pm$ 0.02	62 $\pm$ 3
3e	-	-	-	-	-	-	2.39 $\pm$ 0.02	66 $\pm$ 1

^a - = Temperature below T_{Krafft} .

7.54; S, 12.58; Na, 9.02. Calcd. for **3e** C, 47.35; H, 7.95; S, 12.04; Na, 8.63; found: C, 47.13; H, 7.94; S, 11.92; Na, 8.70.

Conductivity measurements. Conductivity measurements were performed using a Wayne-Kerr Autobalance Universal Bridge B642 fitted having a Philips electrode PW 95121/01 with a cell constant of 0.71 cm⁻¹. The water in the cell was thermostated at the appropriate temperature for at least 15 min before the experiment was started and stirred magnetically at a constant rate. Surfactant concentration was varied by titrating small (5-50 μ L) volumes of a concentrated stock solution, normally 20 times the CMC, into the cell. After each injection, conductivity was measured. CMC values were taken from the intersection of the tangents drawn before and beyond the break in the conductivity vs. surfactant concentration plot. Counterion binding was calculated (11) by dividing the slope of the tangent beyond the CMC by the slope below the CMC.

Krafft temperatures. Krafft temperatures were determined by monitoring the heat flow or turbidity during a slow temperature increase using a Perkin-Elmer DSC7 or a Philips PU 8740 ultraviolet-visible scanning spectrophotometer equipped with a Haake F3 water bath, respectively. In both cases a small amount of surfactant (3 and 50 mg, respectively) was heated in water (0.05 and 2 mL, respectively).

Detergency tests. The detergency tests were performed by J.T. Bouman at the Royal Dutch Shell Laboratories, Amsterdam. The tests were performed at 40°C using a formulation concentration of 2.5 g/L. The concentration of Ca²⁺ was 3 mM in the tests using hard water. The standard test procedure (24) was performed using a robot-Terg-O-tometer, except that the bisulfate surfactant **3d** was added to the washwater *via* a pipet. This was necessary because of the high Krafft temperature of this surfactant. Permanent press polyester-cotton swatches were soiled with radiolabeled multi sebum and cetane/squalane. Samples were taken after 2, 5, 10, and 20 min and analyzed for radioactivity.

RESULTS AND DISCUSSION

CMC and counterion binding from conductivity experiments. Surfactants **3b,c** showed an increase in CMC upon increasing temperature (Table 1) as has been found previously (12) for sodium *n*-alkylmonosulfates such as sodium *n*-dode-

cylsulfate (SDS). This effect is complex. The major driving force for micellization involves the hydrophobic interactions between alkyl chains of surfactant molecules (13) which originate from the limited capacity of water to accommodate the apolar solute and to maintain its original hydrogen-bond network (14). Accordingly, elongation of alkyl chains(s) decreased the CMC. An increase in temperature often leads to increased hydrophobic interactions and should lower CMC. This trend is only found, however, for nonionic surfactants (15,16). For ionic surfactants the situation is more complex due to coulombic headgroup repulsions and stabilizing effects from the binding of counterions (17-21).

Counterion binding appeared to be quite independent of temperature for the disodium bisulfate surfactants (Table 1). An increase in the chain length from C₁₂ (**3b**) to C₁₈ (**3e**) led to a higher counterion binding at 55°C. This increase may be caused by a tighter packing of the surfactant molecules in the micelle, forcing the headgroups closer together and therefore increasing the need for compensating the electrostatic repulsion between the head groups by more efficient counterion binding.

Krafft temperatures. The Krafft temperature is the temperature at which the solubility of the surfactant equals its CMC. Increasing the alkyl chain of a surfactant decreases CMC, but decreases solubility at the same time. Varying the alkyl chain length is a tool for fine-tuning the properties of surfactants. A balance must be struck between low CMC and low Krafft temperature to obtain micelles at low surfactant concentration and temperature for application in, for example, detergent formulations.

The Krafft temperatures of bisulfates **3b-e** were determined by monitoring the turbidity with increasing temperature (Fig. 1). Recently, another method was established for

TABLE 2
Krafft Temperatures and Enthalpies of Dissolution of Disodium 2-Alkyl-1,3-propanediyl Bisulfates^a

Compound	$T_{\text{Krafft}}^{\text{Turb}}$ (°C)	$T_{\text{Krafft}}^{\text{DSC}}$ (°C)	$\Delta_{\text{dissol}}H^\circ$ (kJ/mol)
3a	-	-	-
3b	-	23.8	56 $\pm$ 2
3c	29.8	29.5	65 $\pm$ 1
3d	39.8	39.6	80 $\pm$ 2
3e	47.3	52.5	84 $\pm$ 2

^a - = The Krafft temperature was too low to be measured by this method; DSC, differential scanning calorimetry; dissol, dissolution; Turb, turbidity.

TABLE 3
CMC and Precipitation Concentrations (PC) of the Bissulfate Surfactants **3b-e**, SDS, and LAS

Compound ^a	CMC	CMC	PC at 25°C	PC at 55°C
	at 25°C	at 55°C	(mM CaCl ₂)	(mM CaCl ₂)
3b	24.0	30.6	> 1000	> 1000
3c	^b	12.5	^b	> 1000
3d	^b	4.95	^b	17.3 ± 0.3
3e	^b	2.39	^b	8.6 ± 0.1
SDS	8.1 ^c	9.4 ^c	1.8 ± 0.1	^d
LAS	2 ^c	^d	3.5 ± 0.1	^d

^aInitial concentrations of surfactants **3b-d**, sodium *n*-dodecylsulfate (SDS), and linear alkylbenzene sulfonate (LAS) are 60.00 mM, 25.56 mM, 16.00 mM, 9.37 mM, 27.4 mM, and 10.1 mM, respectively.

^bTemperature below Krafft temperature.

^cTaken from Ref. 12.

^dNot measured. See Table 1 for other abbreviations.

nonionic alkyl glycosides. Van Doren and Wingert (22), as well as Galema (23), showed that differential scanning calorimetry (DSC) yields very similar results as the classical method in which the temperature dependence of turbidity is measured. In this study, both methods were used and compared. When DSC was used, the Krafft temperature was characterized by dissolution of the surfactant, and the heat effect accompanying that process was measured (Fig. 2). The DSC trace yielded the Krafft temperature and heat of dissolution. Since the peak caused by the heat of dissolution can be relatively broad, the temperature at which the heat effect emerges (the onset) was used to determine the Krafft temperature. Onset of the heat effect depended linearly on scanning rate. The Krafft temperature was obtained at the intersection of the straight line with the y-axis (Fig. 3). The enthalpy of dissolution was positive (endothermic) and increased with increasing chain length. Dissolution of bissulfates **3b-e** was an entropy-driven process. The classical method monitors the turbidity with increasing temperature. The Krafft temperature was obtained from the point at which the transmission at 550 nm was reduced to 50% (Fig. 1 and Table 2). The temperatures obtained by both methods were in satisfactory agreement.

Calcium tolerance. The degree of calcium tolerance of surfactants **3b-e** was determined by monitoring turbidity with increasing calcium concentration. The calcium concentration at which the aqueous surfactant started to precipitate was defined as the precipitation concentration

TABLE 4
Formulations in the Detergency Tests

Components	Composition		
	A (%)	B (%)	C (%)
Surfactant	20	20	20
Zeolite	35	0	0
Na ₂ CO ₃	15	0	0
SKS-6 (a disilicate builder)	0	55	0
Britesil H ₂ O	5	0	0
NaBO ₃	15	15	0
H ₂ O	10	10	80

TABLE 5
Detergency Tests for Bissulfate **3d**, LAS 113, PAS 45, and PAES 23-2S in Hard Water at 40°C; Removal of a Cetane/Squalene Mixture^a

Surfactant	Composition	Removed soil (%) after:			
		2 min	5 min	10 min	20 min
Bissulfate 3d	A	34	40	44	48
Bissulfate 3d	B	35	41	45	49
Bissulfate 3d	C	30	38	42	47
LAS 113	A	37	47	51	56
LAS 113	B	35	44	49	53
LAS 113	C	9	11	12	15
PAS 45	A	34	41	46	50
PAS 45	B	30	39	44	48
PAS 45	C	20	29	36	41
PAES 23-2S	A	35	41	44	46
PAES 23-2S	B	32	39	44	48
PAES 23-2S	C	32	41	46	52
None	A	9	11	14	17
None	B	9	11	13	14

^aCompositions are given in Table 4.

(PC). The results of the titrations for surfactants **3b-e**, SDS and LAS, the sodium salt of a linear alkylbenzenesulfonic acid, are summarized in Table 3. All experiments were performed at a surfactant concentration 2-4 times the CMC. The highly calcium-tolerant behavior of dodecyl and tetradecyl bissulfates **3b** and **3c** was striking. They did not precipitate, even in a 1 M aqueous solution of CaCl₂. Compared to SDS and LAS, **3d** and **3e** were highly calcium-tolerant. These surfactants precipitated at a molar ratio of surfactant/CaCl₂ of 1:1 while LAS and SDS already precipitate at a molar ratio of surfactant/CaCl₂ of 7.8:1 and 5.6:1, respectively. This observation confirms the hypothesis that a loss of charge at the micelle-water interface due to Ca²⁺-binding was compensated by the presence of a "second headgroup."

Detergency tests. Detergency of bissulfate **3d** was tested (24) and compared with three reference surfactants: LAS 113, a mixture of LAS having chain lengths of 11 to 13 carbon atoms, PAS 45, a mixture of primary alkylsulfates having chain lengths of 14 and 15 carbon atoms, and PAES 23-2S, a mixture of primary alkylethersulfates having chain lengths of 12 and 13 carbons and 2 ethylene oxide units between the headgroup and the alkyl chain. In a standard procedure, two kinds of soil were used. The first was an oil-like stain consisting of squalene and cetane. The second was a fatty stain (sebum), representing dirt produced by the skin, consisting

TABLE 6
Detergency Tests for Bissulfate **3d** at 40°C in Demineralized Water; Removal of Cetane/Squalene^a

Surfactant	Composition	Removed soil (%) after:			
		2 min	5 min	10 min	20 min
Bissulfate 3d	A	34	39	43	49
Bissulfate 3d	B	34	40	45	49
Bissulfate 3d	C	25	30	35	40

^aCompositions are given in Table 4.

FIG. 1. Optical transmission vs. temperature for a bissulfate surfactant **3e**-water mixture.

of mono-, di- and triglycerides, fatty acids, cholesterol, esters from fatty from fatty acids and cholesterol, esters of fatty acids and aliphatic alkanols, squalene, and aliphatic alkanes. In Table 4 the detergent formulations are given; Tables 5-8 show the results of the detergency tests.

According to the results in Table 5, the less calcium-tolerant LAS 113 showed a dramatic decrease in detergency performance if used without builder (composition C); the detergency performance resembled that of formulations without any surfactant. PAS 45 without builder was a less efficient detergent than PAES 23-2S and bissulfate **3d** in both performance and in the kinetics of the removal of cetane/squalene soil. In the absence of builder, PAES 23-2S and bissulfate **3d** did not differ significantly in efficiency, although the commercial surfactant was slightly better. In compositions including a builder (A and B), all surfactants showed similar performances, with LAS 113 having the best efficiency.

When the same test was performed in demineralized water, the detergency of bissulfate **3d** without builder dropped from 49 to 40% removal of cetane/squalene soil (Table 6). Clearly, the presence of electrolytes was essential for the performance of laundry detergents. In compositions with builder, the same performance level as in hard water was obtained, which is most likely due to the presence of Na_2CO_3 (formulation A) and NaBO_3 (formulations

FIG. 2. Heat flow vs. temperature for a bissulfate surfactant **3e**-water mixture monitored by differential scanning calorimetry (DSC).

TABLE 7

Detergency Tests for Bissulfate **3d**, LAS 113, PAS 45, and PAES 23-2S at 40°C in Hard Water; Removal of Sebum^a

Surfactant	Composition	Removed soil (%) after:			
		2 min	5 min	10 min	20 min
Bissulfate 3d	A	66	79	83	85
Bissulfate 3d	B	70	79	84	86
Bissulfate 3d	C	28	45	64	77
LAS 113	A	37	48	62	76
LAS 113	B	64	71	75	86
LAS 113	C	3	6	8	12
PAS 45	A	56	71	78	83
PAS 45	B	62	73	79	84
PAS 45	C	7	13	19	31
PAES 23-2S	A	58	70	75	79
PAES 23-2S	B	62	72	78	83
PAES 23-2S	C	25	42	60	76
none	A	46	53	53	53
none	B	41	40	38	37

^aCompositions are given in Table 4. Sebum consists of mono-, di-, and triglycerides, fatty acids, cholesterol, esters of fatty acids and cholesterol, esters of fatty acids and aliphatic alkanols, squalene, and aliphatic alkanes.

A and B). Added salt decreased CMC and affected detergency performance. Similar tests were carried out using sebum soil. As for the previous test, bissulfate surfactant **3d** and PAES 23-2S maintained a good level of detergency even without builder (Table 7). Both surfactants exhibited a slightly decreased performance in detergency when no builder was present; the rate of soil removal was also affected. Decrease in performance of LAS 113 and PAS 45 in the absence of builder was dramatic, as was expected on the basis of the previous results. When testing was performed using demineralized water (Table 8), a significant decrease in performance was found for bissulfate **3d** without builder, again showing the importance of electrolytes.

In both series of tests i.e., removal of cetane/squalene and removal of sebum, performance of the calcium-tolerant anionic surfactant **3d** was similar to that of the commercial surfactant PAES 23-2S. In both series of tests, performance of all tested surfactants in the presence of a builder showed only minor differences.

We conclude that in hard water, the detergency of bissulfate surfactant **3d** was similar to that of LAS 113, PAS 45, and PAES 23-2S in formulations with builder. Detergency was better compared to LAS 113 and PAS 45 and was similar to that of PAES 23-2S in formulations without

TABLE 8

Detergency Tests for Bissulfate **3d** at 40°C in Demineralized Water; Removal of Sebum^a

Surfactant	Composition	Removed soil (%) after:			
		2 min	5 min	10 min	20 min
Bissulfate 3d	A	75	83	86	86
Bissulfate 3d	B	81	85	87	90
Bissulfate 3d	C	16	25	33	42

^aCompositions are given in Table 4.

FIG. 3. Linear dependence of the onsets of DSC peaks on the scanning rate for bisulfates **3b** (-▲-), **3c** (-●-), **3d** (-◆-), and **3e** (-■-). See Figure 2 for abbreviation.

builder. Demineralized water decreased the detergency performance of bisulfate **3d** in formulations without builder, stressing the importance of electrolytes in the laundry process.

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