Synthesis and Characterization of Single-Chain Second Generation Cleavable Surfactants

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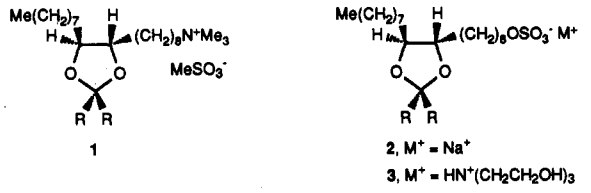
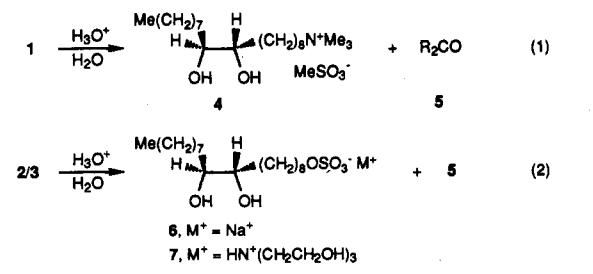
Three series of single-chain, second generation cleavable surfactants, *trans*-[8-(2,2-dialkyl-5-octyl-1,3-dioxolan-4-yl)octyl]trimethylammonium methanesulfonate (**1**) and sodium (**2**) and triethanolammonium *trans*-8-(2,2-dialkyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (**3**) (**a**, R = Me; **b**, R = Et; **c**, R = Pr; **d**, R = Bu), were prepared. They were characterized by critical micelle concentration, Krafft temperature, and dynamic laser light scattering measurements. Acid-catalyzed hydrolysis of surfactants **1**, **2**, and **3** gives (*threo*-9,10-dihydroxyoctadecyl)trimethylammonium methanesulfonate (**4**) and sodium (**6**) and triethanolammonium *threo*-9,10-dihydroxyoctadecane-1-sulfate (**7**), respectively, and a dialkyl ketone **5** (**a**, Me_2CO; **b**, Et_2CO; **c**, Pr_2CO; **d**, Bu_2CO). Cleavage of these surfactants thus gives another surfactant, with a higher critical micelle concentration, and a water-soluble neutral compound. Surfactants **3** were about 20 times more reactive than **1**.

Surfactants have many beneficial applications. But sometimes the presence of an intact surfactant after its use can lead to complications like the formation of persistent emulsions. Cleavable (destructible) surfactants[1] present the potential for elimination of some of these problems. In most of the cleavable surfactants reported previously,[1] functional groups separate the major lipophilic and hydrophilic portions. Cleavage at the functional group gives two nonsurfactant products: an ionic, water-soluble compound and a neutral, water-insoluble compound. In some applications of cleavable surfactants the water-insoluble fragment might present problems. And in others, conversion of the cleavable surfactant into another surfactant with different properties could be advantageous. Thus, we have prepared single-chain examples of what we term *second generation* cleavable surfactants, represented by the series **1**–**3**.[2] On acid-catalyzed hydrolysis (eqs 1 and 2), each of these surfactants is converted into two fragments: another surfactant (**4**, **6**, and **7**, respectively) and a water-soluble, neutral compound (**5**). Ringsdorf and co-workers[3] have reported disulfide-based, double-chain and bolaform cleavable surfactants that can be cleaved into two single-chain surfactants.





Results

Syntheses. Surfactants **1** were prepared as illustrated in Scheme I. Methyl (*Z*)-9-octadecenoate, obtained from **8**, was reduced to (*Z*)-9-octadecen-1-ol, which gave **9**. Then **9** was converted into surfactant **10**, which on antihydroxylation, followed by ion exchange, yielded **4**; subsequent ketalization of **4** gave **1**. An alternative synthetic route to surfactant **1a** is outlined in Scheme II. Reduction of dihydroxy acid **11** gave triol **12**, which was converted into ketal alcohol **13a**. Then **13a** was transformed into **1a** through the corresponding methanesulfonate. Saturated surfactant **14** was prepared by the treatment of octadecyl methanesulfonate with Me_3N in MeOH.

$$\text{Me}(CH_2)_{17}N^+Me_3\ MeSO_3^-$$

14

The syntheses of surfactants **2** and **3** are illustrated in Scheme III. The former were prepared by sulfation[4] of ketal alcohols **13** with SO_3·Me_3N and added Et_3N, followed by the addition of NaOH and ion exchange. The latter were prepared by sulfation of **13** with SO_3·pyridine and added pyridine, followed by the addition of triethanolamine and the removal of pyridine. Dihydroxy surfactants **6** and **7** were obtained by hydrolysis of **2a** and **3a**, respectively. Unsaturated surfactants **15**[5] and **16** were prepared by sulfation of (*Z*)-9-octadecen-1-ol using the procedures for **2** and **3**, respectively. Saturated surfactants **17** and **18** are known compounds.[5]

Surfactant Characterization. Surfactant series **1**–**3** were characterized by critical micelle concentration (cmc), Krafft temperature (T_k), and dynamic laser light scattering (DLLS) measurements and by their hydrolytic reactivities.

(1) For examples, see: Jaeger, D. A.; Jamrozik, J.; Golich, T. G.; Clennan, M. W.; Mohebalian, J. *J. Am. Chem. Soc.* **1989**, *111*, 3001 and references cited therein.

(2) Some of these results have been communicated (Jaeger, D. A.; Sayed, Y. M.; Dutta, A. K. *Tetrahedron Lett.* **1990**, *31*, 449).

(3) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113.

(4) Gilbert, E. E. *Sulfonation and Related Reactions*; Krieger: Huntington, NY, 1977; Chapter 6.

(5) Weil, J. K.; Stirton, R. J.; Bistline, R. G., Jr.; Maurer, E. W. *J. Am. Oil Chem. Soc.* **1959**, *36*, 241.

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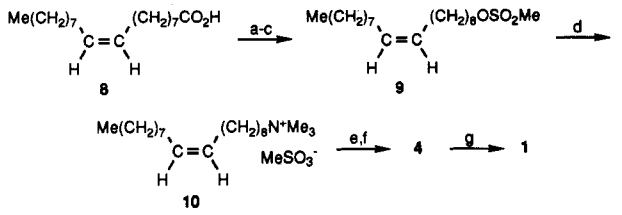
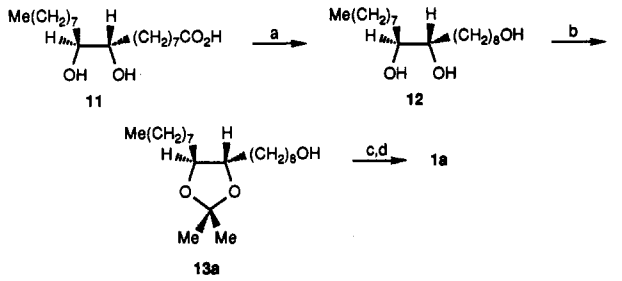
Scheme I[a]



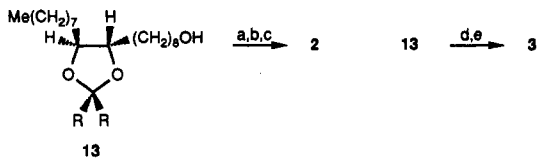
[a] Key: (a) MeOH, H_2SO_4; (b) $LiAlH_4$, Et_2O; (c) $MeSO_2Cl$, Et_3N, CH_2Cl_2; (d) Me_3N, MeOH; (e) H_2O_2, HCO_2H; (f) Biorad AG 1-X8, $MeSO_3^-$ form; (g) **1a**, Me_2CO, $MeSO_3H$; **1b–d**, R_2CO, $MeSO_3H$, C_6H_6 (Dean-Stark).

Scheme II[a]

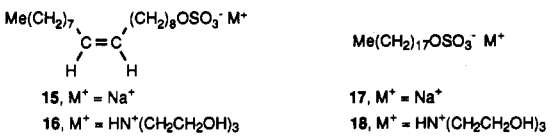


[a] Key: (a) $LiAlH_4$, THF; (b) Me_2CO, PPTS; (c) $MeSO_2Cl$, Et_3N, CH_2Cl_2; (d) Me_3N, MeOH.

Scheme III[a]



[a] Key: (a) SO_3·Me_3N, Et_3N; (b) NaOH, H_2O; (c) Biorad AG 50W-X4, Na^+ form; (d) SO_3·pyridine, pyridine; (e) $N(CH_2CH_2OH)_3$.



Some differential scanning calorimetry (DSC) measurements were also made.

Critical Micelle Concentrations and Krafft Temperatures. The cmc and T_k values of ketal surfactants 1–3, dihydroxy surfactants 4, 6, and 7, and their saturated and unsaturated analogues are given in Table I. Most of the cmc values were determined by the du Noüy ring method and the remainder by a light scattering procedure (see Experimental Section).

The T_k's of all the cationic surfactants are <25 °C, and their cmc's were obtained at 25 °C. Except for **2a** and **15**, the T_k's of the sodium sulfate surfactants are greater than 25 °C. The cmc's of **2a** and **15** were obtained at 25 °C and that of **6** at 75 °C. The T_k's of the triethanolammonium sulfate surfactants **3**, **7**, and **16** are <25 °C, and their cmc's were measured at 25 °C.

Dynamic Laser Light Scattering. DLLS measurements (90° scattering angle) for surfactants **1** and **3** at 23 °C are summarized in Table II. Measurements for **1a** were made in H_2O containing 0.010 M $NaHCO_3$ and 0.090 M NaBr and those for **1b–d** in H_2O containing 0.010 M $NaHCO_3$ and 0.010 M NaBr. Measurements for **3** were made in the pH 8.5 triethanolamine buffer. Distribution

Table I. Critical Micelle Concentrations[a–c] and Krafft Temperatures

surfactant	10^5 cmc, M, in 0.010 M $NaHCO_3$	10^5 cmc, M, in 0.0010 M Na_2CO_3	10^5 cmc, M, in pH 8.5 triethanolamine buffer	T_k, °C, in H_2O
1a	110			<25
1b	29			<25
1c	13			<25
1d	1.6			<25
4	160			<25
10	12			<25
14	4.2			<25
2a		32; 36;[d] 66[d,e]		<25
2b				>25
2c				>88
2d				>88
6		320[e,f]		72
15		25; 29[g,h]		<0[g]
17		11[g,h]		56[g]
3a			22	<25
3b			4.1	<25
3c			3.4	<25
3d			3.2	<25
7			162	<25
16			3.2	<25
18			7[g,h]	26[g]

[a] Averages of ≥2 determinations that differed by ≤10%. [b] By the du Noüy ring method unless noted otherwise. [c] At 25 °C in the indicated solvents unless noted otherwise. [d] In H_2O. [e] By the light scattering method (see Experimental Section). [f] At 75 °C. [g] Reference 5. [h] By the dye method (pinacyanole chloride) in H_2O at 50 °C.

analysis of the autocorrelation function disclosed the presence of one population each for **1a**/**3a** and **1b**/**3b** at the indicated hydrodynamic diameters and three populations each for **1c**/**3c** and **1d**/**3d**. No physical significance can be attributed to minor population 3. It probably corresponds to a few large particles that were grouped together as part of the trimodal distribution by the mathematical analysis of the light scattering data. Measurements for **4** in H_2O containing 0.010 M $NaHCO_3$ and 0.090 M NaBr and for **7** in the pH 8.5 triethanolamine buffer indicated that these surfactants form very small particles (hydrodynamic diameter <3 nm) or do not aggregate at all. The observation of cmc's for **4** and **7** strongly suggests the former.

Differential Scanning Calorimetry. DSC measurements were performed with surfactants **1c** and **1d**. Scans were made from 5 to 70 °C in H_2O containing 0.010 M $NaHCO_3$ and 0.010 M NaBr and from −25 to 50 °C in 1:1 (w/w) H_2O–$HOCH_2CH_2OH$. No phase transition was detected.

Hydrolytic Reactivities. Ketal surfactants **1** and **3** were hydrolyzed at concentrations above their cmc's at 25 °C in 5.5 M HCl and 0.010 M HCl, respectively. The extent of hydrolysis of **1** was determined by ^1H NMR analysis of isolated mixtures of unreacted **1** and **4** and that of **3** by reversed-phase HPLC analysis of reaction mixtures (see Experimental Section). The times required for ≥95% hydrolysis of **1** to dihydroxy surfactant **4** and ketones **5** (eq 1) are given in Table III. Pseudo-first-order rate constants, k_ψ, for the hydrolysis of **3** to dihydroxy surfactant **7** and **5** (eq 2) are given in Table IV. Ketones **5** have the following solubility limits in H_2O at 30 °C: **5a**, miscible; **5b**, 0.567 m; **5c**, 0.0335 m; and **5d**, 0.00255 m.[6]

The cmc values of Table I and the solubility limits of **5** indicate that it should be possible to convert a solution of **1**/**3**, above its cmc, into a solution of **4**/**7**, below its cmc,

(6) Gross, P.; Rintelen, J. C.; Saylor, J. H. *J. Phys. Chem.* **1939**, *43*, 197.

Table II. DLLS Measurements of Surfactants 1 and 3 at 23 °C[a,b]

surfactant		population 1		population 2		population 3	
nature	10^3 concn, M	diameter, nm	vol %	diameter, nm	vol %	diameter, nm	vol %
1a	5.7	5 ± 1	100				
1b	4.2	5 ± 1	100				
1c	1.6	12 ± 1	81 ± 3	74 ± 5	14 ± 2	298 ± 150	3 ± 2
1d	0.7	15 ± 3	73 ± 8	89 ± 8	19 ± 7	380 ± 30	8 ± 2
3a	4.1	4 ± 1	100				
3b	1.9	6 ± 1	100				
3c	1.6	11 ± 1	84 ± 1	55 ± 5	14 ± 1	160 ± 13	2 ± 1
3d	1.7	13 ± 2	82 ± 5	106 ± 8	10 ± 1	535 ± 42	8 ± 2

[a] The following solvents were used: **1a**, H_2O containing 0.010 M $NaHCO_3$ and 0.090 M NaBr; **1b–d**, H_2O containing 0.010 M $NaHCO_3$ and 0.010 M NaBr; **3a–d**, the pH 8.5 triethanolamine buffer. [b] The values are averages of three runs with different samples, and the limits of error are average deviations.

Table III. Hydrolytic Reactivities of Ketal Surfactants 1 in 5.5 M HCl at 25 °C

surfactant		time, min, for
nature	10^3 concn, M	≥95% hydrolysis[a]
1a	11	<5
1b	5.9	10
1c	2.5	60
1d	4.0	200

[a] Determined by ^1H NMR analysis of three runs that differed by ≤5%.

Table IV. Hydrolytic Reactivities of Ketal Surfactants 3 in 0.010 M HCl at 25 °C

surfactant		
nature	10^3 concn, M	10^4 k_ψ,[a,b] s^{-1}
3a	11	5.2 ± 0.5
3b	8.0	1.3 ± 0.1
3c	8.0	0.21 ± 0.02
3d	8.0	0.11 ± 0.01

[a] The values are averages of three runs, and the limits of error are average deviations. [b] For each run, four points were taken over 2–3 half-lives.

and **5**, below its solubility limit. This was demonstrated with **1d** and **3a**. The surface tension (γ) of a 4.0×10^{-5} M solution of **1d** in 5.5 M HCl at 25 °C was monitored over time. Within 1 min after the solution was prepared, γ = 32 dyn/cm, which is indicative of aggregated surfactant. After 200 min, γ increased to 49 dyn/cm, which is close to the value (53 dyn/cm) for a 4.0×10^{-5} M solution of **4** in 5.5 M HCl. Thus, after 200 min, the hydrolysis of **1d** was almost, if not entirely, complete to give a solution containing **4** at a concentration below its cmc, which is 4.2×10^{-4} M in 5.5 M HCl. The ketone hydrolysis product **5d** should be completely soluble in the reaction mixture. A control demonstrated that **4** is stable in 5.5 M HCl at 25 °C for 300 min. Similarly, the surface tension of a 4.1×10^{-4} M solution of **3a** in 0.010 M HCl at 25 °C was followed over time. Within 2 min after the solution was prepared, γ = 29 dyn/cm, which is indicative of aggregated surfactant. After 120 min, γ increased to 44 dyn/cm, which is close to the value (45 dyn/cm) for a 4.1×10^{-4} M solution of **7** in 0.010 M HCl. Thus, after 120 min, the hydrolysis of **3a** was almost complete to give a solution containing **7** at a concentration below its cmc, which is 1.55×10^{-3} M in 0.010 M HCl. A control demonstrated that **7** is stable in 0.010 M HCl at 25 °C for 200 h.

Discussion

The cmc's of dihydroxy surfactants **4**, **6**, and **7**, the hydrolysis products of eqs 1 and 2, are greater than those of ketal surfactants **1**, **2a**, and **3**, respectively. The comparison for **6** and **2a** involves measurements at different temperatures, but cmc values do not change much with temperature.[7] Surfactants **4** and **1d** gave the maximum difference, a factor of 100. The cmc's of surfactants **1** and **3** decreased in the order **a** > **b** > **c** > **d**, consistent with the increasing size of the alkyl substituent R.

In each of the cationic and anionic surfactant series, the dihydroxy surfactant and the unsaturated surfactant, except for **16**, have greater cmc's than the saturated parent compound. The lack of conformance of **16** with this pattern may reflect the fact that the literature[5] cmc of saturated surfactant **18**, reported in Table I, was obtained at a higher temperature, in a different solvent, and by a different method than used for **16**.

In general, but not always,[8] a surfactant containing a carbon–carbon double bond in its hydrophobic portion has a greater cmc than its saturated counterpart.[5,9] Also, a surfactant bearing a polar substituent on its hydrophobic portion typically has a greater cmc than the corresponding unsubstituted surfactant.[9c,10] The lesser T_k values of the triethanolammonium sulfate surfactants compared to the sodium sulfate analogues reflect the greater solubilities of the former.[5,11] Overall, the greater cmc's of the dihydroxy surfactants **4**, **6**, and **7** compared to all other surfactants of Table I reflect their larger hydrophile–lipophile balances.

Similar DLLS results were obtained for surfactant series **1** and **3** (Table II). Single aggregate populations with hydrodynamic diameters of 4–6 nm were observed for **1a**, **1b**, **3a**, and **3b**. These sizes are consistent with spherical micelles.[12] Three populations were observed for **1c**, **1d**, **3c**, and **3d**, but as noted above, no physical significance can be attributed to minor populations 3. Given the nature of the multimodal algorithm used in the data analysis, populations 1 and 2 most likely represent the extremes of a broad, asymmetric particle size distribution. Populations 1, with diameters of 11–15 nm, probably correspond to rod-shaped micelles. Populations 2, with diameters of 55–106 nm, are large enough to be vesicles. However, as noted above, no phase transitions were observed in DSC scans

(7) For examples, see: Jaeger, D. A.; Mohebalian, J.; Rose, P. L. *Langmuir* **1990**, *6*, 547.
(8) Escoula, B.; de Castro Danta, T. N.; Rico, I.; Lattes, A. *New J. Chem.* **1984**, *8*, 499.
(9) For examples, see: (a) Sprague, E. D.; Duecker, C. E.; Larrabee, C. E., Jr. *J. Colloid Interfac. Sci.* **1983**, *92*, 416. (b) Malliaris, A.; Paleos, C. M.; Dais, P. J. *J. Phys. Chem.* **1987**, *91*, 1149. (c) Klevins, H. B. *J. Am. Oil Chem. Soc.* **1953**, *30*, 74.
(10) For examples, see: (a) Brown, J. M.; Schofield, J. D. *J. Chem. Soc., Chem. Commun.* **1975**, 434. (b) Menger, F. M.; Jerkunica, J. M.; Johnston, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4676.
(11) Kashiwagi, M.; Ezaki, H. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 624.
(12) For examples, see: Briggs, J.; Dorshow, R. B.; Bunton, C. A.; Nicoli, D. F. *J. Chem. Phys.* **1982**, *76*, 775.

of aggregated **1c** and **1d** from 5 to 70 °C and from −25 to 50 °C in H_2O containing 0.010 M $NaHCO_3$ and 0.010 M NaBr and in 1:1 (w/w) H_2O–$HOCH_2CH_2OH$, respectively. The lack of phase transitions is consistent with the absence of bilayer structures, suggesting the absence of vesicles. However, bilayers with phase transitions of <−25 °C, or of low calorimetric enthalpies, cannot not be discounted. Populations 2 of **1c**, **1d**, **3c**, and **3d** could be rod-shaped micelles. The analysis of the DLLS data, obtained at a single angle, includes the assumption that all aggregates are spherical. Thus, the sizes of rod-shaped micelles would not be reported accurately.[13]

The shape of a surfactant monomer largely determines the morphology of its aggregates (spherical micelle, rod-shaped micelle, bilayer/vesicle).[14,15] A packing parameter, P, defined by eq 3, relates monomer shape to morphology.[14] In eq 3, v = the volume of the hydrophobic portion of the

$$P = v/(a_o l_c) \tag{3}$$

surfactant, a_o = the head group area, and l_c = the length of the alkyl chain. The transition from spherical micelles for the methyl (**1a** and **3a**) and ethyl-substituted ketal surfactants (**1b** and **3b**) to rod-shaped micelles for the propyl (**1c** and **3c**) and butyl-substituted surfactants (**1d** and **3d**) is consistent with an increase in P and the results of Engberts and co-workers.[15] The value of P increases since v increases going from R = Me to Et to Pr to Bu in surfactant series **1** and **3**.

As noted above, on the basis of the DLLS results dihydroxy surfactants **4** and **7** form very small aggregates (hydrodynamic diameter <3 nm) or do not aggregate at all. Since **4** and **7** exhibit cmc's, the latter possibility is unlikely. Perhaps the surfactant chain folds,[10b] as illustrated for **4** in Figure 1, to place the *vic*-diol group at the micelle–H_2O interface. As a result, the effective surfactant chain length is reduced. The significantly greater cmc's of **4** and **7** compared to the parent compounds **14** and **18** (Table I) are consistent with this possibility. However, it is noteworthy that surfactants **19** and **20**, each with one hydroxyl group on the surfactant chain, do not fold as proposed for **4** and **7**.[10a]

$Me(CH_2)_{10}CHOH(CH_2)_6N^+Me_3I^-$
19

$Me(CH_2)_5CHOH(CH_2)_{11}N^+Me_3Cl^-/I^-$
20

On the basis of literature analogy,[16] the hydrolyses of **1–3** are expected to proceed with specific acid catalysis and a rate-determining step involving cleavage of the protonated ketal group. For each compound there are two possible protonated species, e.g., **3′** and **3″** for **3**, whose relative involvement in hydrolysis is unknown. The k_ψ values of Table IV represent weighted averages of rate constants for aggregated and unaggregated surfactant according to eq 4, wherein k_m and k_o are the rate constants for the former and latter, respectively, and n is the mole

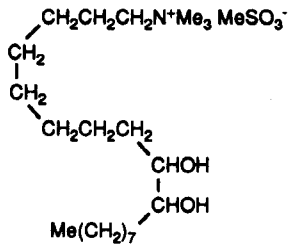
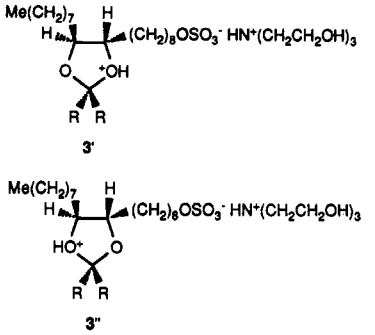


Figure 1. Folded conformation of surfactant 4.



fraction of aggregated surfactant. Furthermore, each k_m and k_o represents a composite value, including the rate constant for the rate determining step and the dissociation constant of the ketal.[17]

$$k_\psi = nk_m + (1-n)k_o \tag{4}$$

Since a negatively charged Stern layer electrostatically attracts H_3O^+,[18] the $[H_3O^+]$ experienced by micellar **3** will be greater than that experienced by unaggregated **3** in the aqueous phase. This effect will tend to increase the reactivity of micellar relative to unaggregated **3**, but opposing it is a medium effect. In general, the rate constant for hydrolysis of an acetal/ketal in water–organic solvent mixtures decreases with an increase in the relative amount of the latter.[19] The Stern layer of a micelle has an effective dielectric constant less than that of water and about that of methanol/ethanol.[20] Overall, it is likely that the former effect dominates, resulting in $k_m > k_o$, as found in the acid-catalyzed hydrolysis of sodium dodecyl sulfate.[21]

Under the conditions of the kinetic experiments summarized in Table IV, >90% of unreacted **3** remained in aggregated form at the end of each run. This fact and the greater reactivity of micellar relative to unaggregated surfactant allow neglect of the second term of eq 4. Thus, pseudo-first-order behavior is expected throughout the course of each kinetic run. Indeed, such behavior was observed even though the aggregates changed during the hydrolysis reactions due to the probable incorporation of dihydroxy surfactant **7** and ketone **5**.

In surfactant series **1** and **3** the hydrolytic reactivity decreased in the order **a** > **b** > **c** > **d**. For both aggregated and unaggregated surfactant, this trend perhaps reflects increasing hydrophobic shielding of the ketal linkage with an increasing length of the alkyl group R. As noted above,

(13) For a discussion, see: (a) Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075. (b) Young, C. Y.; Missel, P. J.; Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1978**, *82*, 1375.
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(19) (a) Cordes, E. H. *Progr. Phys. Org. Chem.* **1967**, *4*, 1. (b) Wolford, R. K. *J. Phys. Chem.* **1963**, *67*, 632.
(20) (a) Mukerjee, P.; Cardinal, J. R.; Desai, N. R. In *Micellization, Solubilization, and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1, p 241. (b) Sudholter, E. J. R.; van de Langkrius, G. B.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 73.
(21) Kurz, J. L. *J. Phys. Chem.* **1962**, *66*, 2239.

the rate constant for hydrolysis of an acetal/ketal in water–organic solvent mixtures decreases with an increase in the relative amount of the latter.[19]

Tables III and IV suggest that anionic surfactants **3** are more reactive than cationic surfactants **1**. Each anionic surfactant is estimated to be about 20 times more reactive than its cationic counterpart. The differences derive from the oppositely charged substituents on the dioxolane rings. On an aggregate basis, electrostatic depletion and accumulation of H_3O^+ exist at the aggregate–H_2O interfaces of **1** and **3**, respectively, relative to the bulk aqueous phase.[18,22] Thus, the $[H_3O^+]$ experienced by the anionic micelles will be greater than that experienced by the cationic micelles. On an intramolecular basis, the cationic substituent of **1** electrostatically hinders, whereas the anionic substituent of **3** electrostatically facilitates, protonation. Overall, the greater reactivity of **3** results from both of these related effects.

Second generation cleavable surfactants such as **1** and **3** should have several useful applications. For example, a water-insoluble compound could be solubilized in a micellar solution of **1**/**3**, and then desolubilized as desired by hydrolysis of **1**/**3**. The desolubilization process would not be complicated by the formation of a water-insoluble compound derived from the surfactant, as would be the case with the previously reported cleavable surfactants.[1]

Summary

Second generation cleavable surfactant series **1–3** were prepared and characterized by critical micelle concentration, Krafft temperature, and dynamic laser light scattering measurements. They undergo acid-catalyzed hydrolysis to give dihydroxy surfactants **4**, **6**, and **7**, respectively, and ketones **5**. The dihydroxy surfactant has a higher cmc than each of the corresponding ketal surfactants. Thus, **1–3** represent a new class of cleavable surfactants that can be converted into another surfactant with a higher cmc and a water-soluble, neutral fragment. Anionic surfactants **3** were more reactive than cationic surfactants **1**.

Experimental Section

General Procedures and Materials. ^1H (270 and 400 MHz) NMR spectra were recorded in $CDCl_3$, CD_3OD, and D_2O with Me_4Si, residual CD_2HOD (3.30 ppm relative to Me_4Si), and residual HOD (4.65 ppm) as internal standards, respectively. ^{13}C (67.9 and 100.6 MHz) NMR spectra were recorded in $CDCl_3$ and CD_3OD with $CDCl_3$ (center line at 77.00 ppm relative to Me_4Si) and CD_3OD (center line at 49.00 ppm relative to Me_4Si) as internal standards, respectively. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (Grant No. DIR 9017262). Silica gel (Merck 9385, 60 Å, 230–400 mesh) was used for flash chromatography. For open column chromatography silica gel (J. T. Baker 3405) and neutral aluminium oxide (J. T. Baker 0537) were used. TLC analyses of cationic surfactants were performed on 0.25-mm aluminum oxide plates (Merck 5731-3) with absolute EtOH as eluant and I_2 for visualization and those of anionic surfactants with Na^+ as counterion, on 0.25-mm silica gel plates (Merck 5714-3) with 4:1 Et_2O–MeOH as eluant and 5% (w/v) phosphomolybdic acid in EtOH for visualization. The solvents used for recrystallization of the cationic and anionic surfactants were reagent-grade (stored over Na_2CO_3) and spectral-grade, respectively. The pH 8.5 triethanolamine buffer contained 14.9 g (0.100 mol) of $(HOCH_2CH_2)_3N$ (Aldrich), 50.7 mL of 0.100 M HCl, and 949 mL of H_2O. Sonication was performed with Branson 2200 (125-W) and 3200 (150-W) ultrasonic cleaners. Extracts were dried over Na_2SO_4 or $MgSO_4$. Uncorrected melting points of the cationic surfactants were measured with sealed capillary tubes, and those of the anionic surfactants were determined in a drybox under N_2 with a Fisher-Johns melting point apparatus. The cmc's were measured by two methods. In the first, they were obtained from plots of surface tension (du Noüy ring) vs log [surfactant] using a Fisher Model 20 tensiometer and in the second from plots of relative light scattering vs log [surfactant]. The light scattering data were obtained using a Perkin-Elmer LS-5 fluorescence spectrometer with both excitation and emission set at 400 nm. The T_k values were determined according to a literature procedure.[23] Reversed-phase HPLC analyses were performed with RI detection on a 25-cm × 4.6-mm (i.d.) 10-μm C18 column (Alltech 60086) with a 3-cm × 4.6-mm (i.d.) 10-μm C18 guard column (Rainin 18-GU). Unless noted otherwise, the ratios describing the compositions of solvent mixtures represent relative volumes. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Octadecyltrimethylammonium Methanesulfonate (14). By a literature procedure,[24] 1-octadecanol was converted into octadecyl methanesulfonate. A mixture of 5.05 g (14.5 mmol) of this material and 150 mL of 25% (w/v) Me_3N–MeOH (37.5 g (0.64 mol) of Me_3N) was stirred at 25 °C for 3.5 days and then refluxed under a dry ice–Me_2CO condenser for 8 h. The residue after rotary evaporation was recrystallized from 6:1 Me_2CO–MeOH to give 4.49 g (76%) of **14**: mp 200–201 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.49 (m, 2 H, CH_2N), 3.34 (s, 9 H, $N(CH_3)_3$), 2.74 (s, 3 H, $CH_3SO_3^-$), 1.73 (m, 2 H, CH_2CH_2N), 1.20–1.46 (m, 30 H, $(CH_2)_{15}$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (270 MHz, $CDCl_3$) δ 66.64 (CH_2N), 52.87 ($N(CH_3)_3$), 39.67 ($CH_3SO_3^-$), 31.85, 29.63, 29.52, 29.43, 29.30, 29.17, 26.16, 23.10, 22.62, 14.05. Anal. Calcd for $C_{22}H_{49}NO_3S$: C, 64.81; H, 12.11. Found: C, 64.75; H, 12.12. The cmc of **14** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

Methyl (*Z*)-9-Octadecenoate.[25] By Fischer esterification with MeOH and concentrated H_2SO_4, 5.00 g (17.7 mmol) of oleic acid (**8**) (Aldrich, 99+%) was converted into 5.03 g (96%) of the title compound.

(*Z*)-9-Octadecen-1-ol.[26] In standard fashion, 5.54 g (18.7 mmol) of methyl (*Z*)-9-octadecenoate was reduced with $LiAlH_4$ in Et_2O to give 4.53 g (90%) of the title compound.

(*Z*)-9-Octadecenyl Methanesulfonate (9). With a literature procedure,[24] 5.80 g (21.6 mmol) of (*Z*)-9-octadecen-1-ol was converted into 6.81 g (91%) of **9** that was used without further purification: ^1H NMR (270 MHz, $CDCl_3$) δ 5.35 (m, 2 H, CH=CH), 4.22 (t, J = 6.6 Hz, 2 H, CH_2O), 3.00 (s, 3 H, $CH_3SO_3^-$), 2.01 (m, 4 H, CH_2CH=CHCH_2), 1.75 (m, 2 H, CH_2CH_2O), 1.27 and 1.30 (2 s, 22 H total, $(CH_2)_6$ and $(CH_2)_5$), 0.88 (t, 3 H, CH_3).

[(*Z*)-9-Octadecenyl]trimethylammonium Methanesulfonate (10). A mixture of 6.81 g (19.6 mmol) of **9** in 207 mL of 25% (w/v) Me_3N–MeOH (51.7 g (0.88 mol) of Me_3N) was stirred at 25 °C for 14 h and then refluxed under N_2 for 2 h. The residue after rotary evaporation was dried (25 °C, 0.01 mmHg) to give 7.90 g (99%) of **10** as a hygroscopic solid. This material was recrystallized twice from 3:1 EtOAc–Me_2CO (5 °C). Each time the surfactant was collected by filtration in a drybox under N_2, washed with anhydrous Et_2O, and dried (110 °C, 0.02 mmHg). A total of 6.80 g of **10** was obtained: mp 180–182 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 5.35 (m, 2 H, CH=CH), 3.47 (m, 2 H, CH_2N), 3.35 (s, 9 H, $N(CH_3)_3$), 2.75 (s, 3 H, $CH_3SO_3^-$), 2.00 (m, 4 H, CH_2CH=CHCH_2), 1.71 (m, 2 H, CH_2CH_2N), 1.30 (m, 22 H, $(CH_2)_6$, $(CH_2)_5$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 130.06 (CH), 129.60 (CH), 66.83 (CH_2N), 53.08 ($N(CH_3)_3$), 39.70 ($CH_3SO_3^-$), 31.88, 29.76, 29.67, 29.51, 29.29, 29.18, 27.23, 27.15, 26.22, 23.18, 22.66, 14.07. Anal. Calcd for $C_{22}H_{47}NO_3S$: C, 65.14; H, 11.68. Found: C, 65.04; H, 11.81. The cmc of **10** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

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(*threo*-9,10-Dihydroxyoctadecyl)trimethylammonium Methanesulfonate (4). A modified literature procedure[27] was used. A solution of 6.20 g (15.3 mmol) of **10**, 65 mL of 88% HCO_2H, and 13.9 mL of 30% H_2O_2 (0.209 mol) was stirred for 24 h at 40 °C and then rotary evaporated to near, but not complete, dryness. A solution of the residue in 100 mL of 3 M KOH was refluxed under N_2 for 2.5 h, acidified to pH 3 with $MeSO_3H$ (Aldrich, 99%), and lyophilized. The residue was extracted with two 100-mL portions of $CHCl_3$, and the combined extracts were dried and rotary evaporated. The resultant crude **4**, 3.50 g (52%) after drying (25 °C, 0.01 mmHg), was subjected to ^1H NMR analysis. If the $MeSO_3^-$ counterion and the quaternary ammonium ion were present in a 1:1 ratio, the crude material (1.20 g) was recrystallized from 3:1 EtOAc–$CHCl_3$ (25 °C), filtered through a 25- × 4-cm column of neutral aluminum oxide packed in absolute EtOH with EtOH as eluant, and recrystallized as above to give **4** (0.80 g).

If $MeSO_3^-$ was not present in the desired proportion an ion exchange was performed. To a fritted glass column was added 60 g (96 mequiv) of Biorad AG 1-X8 (Cl^- form, 39–45% (w/w) H_2O), and 1.0 M NaOH was passed through the column until the resin was completely converted to the ^-OH form as determined by analysis for residual Cl^- with $AgNO_3/HNO_3$. Then the resin was washed as follows until the pH of the eluate was as indicated: with H_2O to pH 7; with 1.0 M $MeSO_3H$ to pH 3; and with H_2O to pH 7. After air-drying, 31 g of resin was obtained. A mixture of 0.43 g of crude **4**, 15.5 g of the $MeSO_3^-$-form resin, and 50 mL of H_2O was held at 70 °C for 30 min and filtered. The filtrate was again treated with 15.5 g of the resin using the same procedure. The resultant filtrate was lyophilized to give material that was recrystallized twice and then chromatographed as above to yield 0.20 g of **4**: mp 80–82 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.51 (m, 2 H, CH_2N), 3.38 (m, 2 H, C*H*OH), 3.33 (s, 9 H, $N(CH_3)_3$), 2.75 (s, 3 H, $CH_3SO_3^-$), 1.75 (m, 2 H, C$H_2$$CH_2N$), 1.17–1.55 (m, 28 H, 2 OH, $(CH_2)_7$, $(CH_2)_6$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 74.50 (CHOH), 74.23 (CHOH), 66.62 (CH_2N), 53.08 ($N(CH_3)_3$), 39.73 ($CH_3SO_3^-$), 33.73, 33.48, 31.85, 29.76, 29.59, 29.27, 28.91, 28.67, 28.37, 25.79, 25.24, 22.85, 22.63, 14.04; FAB HRMS calcd for $C_{21}H_{46}NO_2$ (cation) 344.3528, found 344.3532. Anal. Calcd for $C_{22}H_{49}NO_5S$: C, 60.10; H, 11.23. Found: C, 60.20; H, 11.28. The cmc of **4** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

***trans*-[8-(2,2-Dimethyl-5-octyl-1,3-dioxolan-4-yl)octyl]trimethylammonium Methanesulfonate (1a).** A mixture of 0.812 g (1.85 mmol) of **4**, 25 g (0.43 mol) of Me_2CO, and 0.3 mL of $MeSO_3H$ was stirred for 36 h at 25 °C under N_2. After the addition of 3 mL of H_2O, the mixture was extracted with three 50-mL portions of $CHCl_3$. The combined extracts were dried and rotary evaporated to leave 0.48 g (54%) of crude material that was recrystallized from 3:1 Et_2O–$CHCl_3$ (5 °C). The surfactant was collected by filtration in a drybox under N_2 and washed with anhydrous Et_2O to give, after drying (110 °C, 0.02 mmHg), 0.38 g of **1a**: mp 180–182 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.58 (m, 2 H, CHO), 3.48 (m, 2 H, CH_2N), 3.35 (s, 9 H, $N(CH_3)_3$), 2.77 (s, 3 H, $CH_3SO_3^-$), 1.72 (m, 2 H, C$H_2$$CH_2N$), 1.18–1.52 (m with s at 1.38, 32 H, $(CH_2)_7$, $(CH_2)_6$, $(CH_3)_2CO_2$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 107.69 (CO_2), 81.00 (CHO), 66.75 (CH_2N), 53.02 ($N(CH_3)_3$), 39.70 ($CH_3SO_3^-$), 32.99, 31.82, 29.76, 29.59, 29.46, 29.21, 29.13, 27.34, 26.11, 23.15, 22.61, 14.04; FAB HRMS calcd for $C_{24}H_{50}NO_2$ (cation) 384.3841, found 384.3843. Anal. Calcd for $C_{25}H_{53}NO_5S$: C, 62.59; H, 11.14. Found: C, 62.37; H, 11.36. The cmc of **1a** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

***trans*-[8-(2,2-Diethyl-5-octyl-1,3-dioxolan-4-yl)octyl]trimethylammonium Methanesulfonate (1b).** Under N_2, a solution of 0.500 g (1.14 mmol) of **4**, 0.148 g (1.72 mmol) of 3-pentanone (Aldrich), 0.15 mL of $MeSO_3H$, and 10 mL of C_6H_6 was refluxed under a Dean-Stark trap for 44 h. Then 0.3 mL of H_2O was added, and the reaction mixture was rotary evaporated and extracted with three 25-mL portions of $CHCl_3$. The combined extracts were dried and rotary evaporated to give 0.47 g (81%) of crude surfactant that was chromatographed on a 12- × 5-cm column of neutral aluminum oxide packed in MeCN. After unreacted 3-pentanone was eluted with MeCN, **1b** was with eluted with 1:1 EtOH–MeCN and then recrystallized from 3:1 anhydrous Et_2O–$CHCl_3$ (5 °C). The surfactant was collected by filtration in a drybox under N_2 and washed with anhydrous Et_2O to give, after drying (110 °C, 0.02 mmHg), 0.33 g (57%) of hygroscopic **1b**: mp 147–149 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.55 (m, 2 H, CHO), 3.47 (m, 2 H, CH_2N), 3.34 (s, 9 H, $N(CH_3)_3$), 2.75 (s, 3 H, $CH_3SO_3^-$), 1.73 (m, 2 H, C$H_2$$CH_2N$), 1.62 (q, J = 7.5 Hz, 4 H, $(CH_3CH_2)_2CO_2$), 1.18–1.55 (m, 26 H, $(CH_2)_7$, $(CH_2)_6$), 0.89 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 111.39 (CO_2), 81.32 (CHO), 66.73 (CH_2N), 52.97 ($N(CH_3)_3$), 39.70 ($CH_3SO_3^-$), 32.94, 31.85, 30.79, 29.78, 29.65, 29.48, 29.27, 29.18, 26.17, 23.18, 22.66, 14.13, 8.09. Anal. Calcd for $C_{27}H_{57}NO_5S·0.5H_2O$: C, 62.75; H, 11.31. Found: C, 62.88; H, 11.39. The cmc of **1b** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

***trans*-[8-(2,2-Dipropyl-5-octyl-1,3-dioxolan-4-yl)octyl]trimethylammonium Methanesulfonate (1c).** With the procedure used for **1b**, the reaction of 0.500 g (1.14 mmol) of **4**, 0.195 g (1.71 mmol) of 5-heptanone (Aldrich), and 0.15 mL of $MeSO_3H$ in 10 mL of C_6H_6 gave 0.32 g (52%) of **1c**: mp 139–141 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.53 (m, 2 H, CHO), 3.48 (m, 2 H, CH_2N), 3.35 (s, 9 H, $N(CH_3)_3$), 2.76 (s, 3 H, $CH_3SO_3^-$), 1.73 (m, 2 H, C$H_2$$CH_2N$), 1.20–1.65 (m, 34 H, $(CH_3CH_2CH_2)_2CO_2$, $(CH_2)_7$, $(CH_2)_6$), 0.90 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 110.82 (CO_2), 81.20 (CHO), 67.67 (CH_2N), 52.92 ($N(CH_3)_3$), 40.93, 39.70 ($CH_3SO_3^-$), 32.91, 31.85, 29.78, 29.65, 29.46, 29.24, 26.19, 23.15, 22.63, 17.03, 14.40, 14.10. Anal. Calcd for $C_{29}H_{61}NO_5S·H_2O$: C, 62.89; H, 11.46. Found: C, 62.89; H, 11.31. The cmc of **1c** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

***trans*-[8-(2,2-Dibutyl-5-octyl-1,3-dioxolan-4-yl)octyl]trimethylammonium Methanesulfonate (1d).** With the procedure used for **1b**, the reaction of 0.750 g (1.71 mmol) of **4**, 0.364 g (2.56 mmol) of 5-nonanone (Aldrich), and 0.15 mL of $MeSO_3H$ in 15 mL of C_6H_6 gave 0.35 g (36%) of **1d**: mp 140–142 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.54 (m, 2 H, CHO), 3.48 (m, 2 H, CH_2N), 3.35 (s, 9 H, $N(CH_3)_3$), 2.75 (s, 3 H, $CH_3SO_3^-$), 1.72 (C$H_2$$CH_2N$), 1.20–1.65 (m, 38 H, $(CH_3CH_2CH_2CH_2)_2CO_2$, $(CH_2)_7$, $(CH_2)_6$), 0.90 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 110.95 (CO_2), 81.16 (CHO), 67.67 (CH_2N), 52.92 ($N(CH_3)_3$), 39.70 ($CH_3SO_3^-$), 38.26, 32.94, 31.82, 29.76, 29.65, 29.46, 29.27, 29.21, 26.17, 25.95, 23.15, 22.96, 22.63, 14.10; FAB HRMS calcd for $C_{30}H_{62}NO_2$ (cation) 468.4781, found 468.4782. Anal. Calcd for $C_{31}H_{65}NO_5S·0.25H_2O$: C, 65.50; H, 11.61. Found: C, 65.48; H, 11.49. The cmc of **1d** at 25 °C in 0.010 M $NaHCO_3$ is given in Table I.

Sodium (*Z*)-9-Octadecene-1-sulfate (15).[5] (*Z*)-9-Octadecen-1-ol was converted into surfactant **15** using a modified literature procedure.[28] A mixture of 1.00 g (3.72 mmol) of this alcohol and 0.57 g (4.1 mmol) of $SO_3·Me_3N$ (Aldrich) was stirred under N_2 at 125 °C for 6 h. Then 3 M NaOH was added to pH 10, and the resultant mixture was lyophilized and the residue extracted with 200 mL of 1-BuOH (75 °C). Rotary evaporation left 0.80 g of crude surfactant that by ^1H NMR analysis contained Me_3NH^+ as the counterion. A mixture of this material and 25 g (34 mequiv) of Biorad AG 50W-X4 (Na^+ form) ion-exchange resin in 100 mL of MeOH was stirred at 25 °C for 4 h and filtered. The resultant residue after rotary evaporation was recrystallized from 40 mL of MeOH (25 °C) to give 0.60 g of **15** that was chromatographed on a 20- × 5-cm column of silica gel packed in Et_2O with 1:3 MeOH–Et_2O as eluant. The purity of **15** was monitored by TLC (R_f = 0.4), and the column chromatography was performed a total of four times to give 0.40 g (29%) of **15**: mp 235–237 °C; ^1H NMR (270 MHz, CD_3OD) δ 5.33 (m, 2 H, CH=CH), 4.00 (t, J = 6.6 Hz, CH_2O), 2.01 (m, 4 H, CH_2CH=CHCH_2), 1.66 (m, 2 H, C$H_2$$CH_2O$), 1.29 and 1.31 (2 s, 22 H total, $(CH_2)_6$ and $(CH_2)_5$), 0.89 (t, 3 H, CH_3); ^{13}C NMR (67.9 MHz, CD_3OD) δ 130.81 (CH=CH), 69.18 (CH_2O), 33.03, 30.84, 30.58, 30.43, 30.37, 30.31, 28.14, 28.10, 26.88, 23.71, 14.45; FAB HRMS calcd for $C_{18}H_{35}SO_4$ (anion) 347.2256, found 347.2240. The cmc of **15** in 0.0010 M Na_2CO_3 at 25 °C is given in Table I.

Triethanolammonium (*Z*)-9-Octadecene-1-sulfate (16). A mixture of 1.00 g (3.72 mmol) of (*Z*)-9-octadecen-1-ol, 0.65 g (4.1 mmol) of SO_3·pyridine (Aldrich), and 1.0 mL of pyridine was

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stirred under N_2 at 115 °C for 4 h. Then 0.58 g (3.9 mmol) of $(HOCH_2CH_2)_3N$ was added, and the mixture was stirred for 3 h at 25 °C, followed by the removal of pyridine at 25 °C (0.01 mmHg). The resultant crude surfactant was recrystallized from 5:1 Et_2O–MeOH (−10 °C) with collection by filtration, in a drybox under N_2 using a jacketed filter funnel cooled with dry ice–Me_2CO, to give 0.75 g (41%) of **16**: mp 35–37 °C; ^1H NMR (270 MHz, CD_3OD) δ 5.34 (m, 2 H, CH=CH), 3.98 (t, J = 6.3 Hz, 2 H, $CH_2OSO_3^-$), 3.90 (t, J = 5.3 Hz, 6 H, CH_2OH), 3.45 (t, J = 5.3 Hz, 6 H, CH_2CH_2OH), 2.02 (m, 4 H, CH_2CH=$CHCH_2$), 1.65 (m, 2 H, $CH_2CH_2OSO_3^-$), 1.29 and 1.31 (2 s, 22 H total, $(CH_2)_6$ and $(CH_2)_5$), 0.89 (t, 3 H, CH_3); ^{13}C NMR (100.6 MHz, CD_3OD) δ 130.84, 69.13, 56.85, 56.47, 33.05, 30.86, 30.83, 30.59, 30.46, 30.43, 30.38, 30.32, 28.15, 28.11, 26.91, 23.72, 14.45. Anal. Calcd for $C_{24}H_{51}NO_7S·0.25H_2O$: C, 57.40; H, 10.34. Found: C, 57.27; H, 10.39. The cmc of **16** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

***threo*-1,9,10-Octadecanetriol (12).**[29] Methyl (*Z*)-9-octadecenoate was converted (63%) into *threo*-9,10-dihydroxyoctadecanoic acid (**11**), mp 90–91 °C (lit.[30] mp 95 °C), by a literature procedure.[27] This compound was reduced (76%) with $LiAlH_4$ in THF to give **12**, which was recrystallized from EtOAc: mp 81–82 °C (lit.[29] mp 82–82.5 °C).

***trans*-8-(2,2-Dimethyl-5-octyl-1,3-dioxolan-4-yl)octan-1-ol (13a).** A solution of 1.00 g (3.31 mmol) of **12**, 0.17 g (0.68 mmol) of pyridinium *p*-toluenesulfonate[31] (PPTS), and 35 mL of Me_2CO was refluxed under N_2 for 48 h and rotary evaporated. Then 60 mL of Et_2O was added to the residue, and the mixture was filtered and rotary evaporated. The resultant 1.40 g of crude product was flash chromatographed on a 12- × 5-cm column of silica gel with 1:1 Et_2O–hexane as eluant to give 1.04 g (92%) of **13a** as an oil: ^1H NMR (270 MHz, $CDCl_3$) δ 3.64 (t, J = 6.6 Hz, 2 H, CH_2OH), 3.60 (m, 2 H, CHO), 1.21–1.62 (m with s at 1.38, 35 H, OH, $(CH_3)_2CO_2$, 2 $(CH_2)_7$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 107.66 (CO_2), 80.96 (CHO), 62.85 (CH_2OH), 32.96, 32.69, 31.81, 29.74, 29.65, 29.43, 29.30, 29.21, 27.26, 26.11, 25.67, 22.61, 14.06; EI HRMS calcd for $C_{20}H_{39}O_3$ (M − CH_3) 327.2899, found 327.2906. Anal. Calcd for $C_{21}H_{42}O_3$: C, 73.63; H, 12.36. Found: C, 73.55; H, 12.32.

***trans*-8-(2,2-Diethyl-5-octyl-1,3-dioxolan-4-yl)octan-1-ol (13b).** A mixture of 1.00 g (3.31 mmol) of **12**, 0.328 g (3.81 mmol) of 3-pentanone (Aldrich), 0.17 g (0.68 mmol) of PPTS, and 20 mL of C_6H_5Me was refluxed for 48 h under a Dean-Stark trap and N_2 and then rotary evaporated. Thereafter, the same procedure as for **13a** gave 0.90 g (73%) of **13b** as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (t, J = 6.6 Hz, 2 H, CH_2OH), 3.58 (m, 2 H, CHO), 1.21–1.68 (m overlapping with q at 1.63, J = 7.3 Hz, 33 H, OH, 2 $(CH_2)_7$, $(CH_3CH_2)_2CO_2$), 0.89 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 111.32 (CO_2), 81.28 (CHO), 62.66 (CH_2OH), 32.87, 32.63, 31.77, 30.69, 29.71, 29.63, 29.38, 29.29, 29.17, 26.08, 25.66, 22.55, 13.98, 7.95. Anal. Calcd for $C_{23}H_{46}O_3$: C, 74.54; H, 12.51. Found: C, 74.26; H, 12.48.

***trans*-8-(2,2-Dipropyl-5-octyl-1,3-dioxolan-4-yl)octan-1-ol (13c).** With the same procedure as used for **13b** with the substitution of 4-heptanone (Aldrich) for 3-pentanone, **13c** was obtained (72%) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (t, J = 6.6 Hz, 2 H, CH_2OH), 3.57 (m, 2 H, CHO), 1.21–1.73 (m, 37 H, OH, 2 $(CH_2)_7$, $(CH_3CH_2CH_2)_2CO_2$), 0.91 (m, 9 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 110.95 (CO_2), 81.18 (CHO), 63.01 (CH_2OH), 38.30, 32.94, 32.75, 31.85, 29.78, 29.70, 29.46, 29.34, 29.25, 26.15, 25.94, 25.70, 22.99, 22.65, 14.12. Anal. Calcd for $C_{25}H_{50}O_3$: C, 75.32; H, 12.64. Found: C, 75.06; H, 12.54.

***trans*-8-(2,2-Dibutyl-5-octyl-1,3-dioxolan-4-yl)octan-1-ol (13d).** With the same procedure as used for **13b** with the substitution of 5-nonanone (Aldrich) for 3-pentanone, **13d** was obtained (71%) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (t, J = 6.6 Hz, 2 H, CH_2OH), 3.55 (m, 2 H, CHO), 1.21–1.66 (m, 41 H, OH, 2 $(CH_2)_7$, $(CH_3CH_2CH_2CH_2)_2CO_2$), 0.89 (m, 9 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 110.83 (CO_2), 81.25 (CHO), 63.05 (CH_2OH), 40.95, 32.93, 32.76, 31.87, 29.78, 29.71, 29.46, 29.35, 29.26, 26.19, 25.70, 22.66, 17.05, 14.41, 14.11. Anal. Calcd for $C_{27}H_{54}O_3$: C, 75.74; H, 12.76. Found: C, 75.74; H, 12.65.

Sodium *trans*-8-(2,2-Dimethyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (2a). Ketal alcohol **13a** was converted into surfactant **2a** using a modified literature procedure.[28] A mixture of 1.00 g (2.92 mmol) of **13a**, 0.558 g (4.01 mmol) of $SO_3·Me_3N$, and 0.354 g (3.50 mmol) of Et_3N was stirred under N_2 at 125 °C for 7 h. Then 3 M NaOH was added to pH 9, and the resultant mixture was lyophilized and the residue extracted with 120 mL of 1-BuOH (75 °C). Rotary evaporation left crude surfactant that by ^1H NMR analysis containined Me_3NH^+ as the counterion. This material was subjected to ion exchange using the procedure employed for **15** to give 0.80 g of surfactant that was flash chromatographed four times on 15- × 5-cm columns of silica gel with 1:4 MeOH–Et_2O as eluant to yield 0.62 g (48%) of **2a**, which was pure by TLC (R_f = 0.5). This material was recrystallized from 10:1 MeOH–Et_2O (5 °C) to give **2a**: mp 171–173 °C; ^1H NMR (400 MHz, CD_3OD) δ 4.00 (t, J = 6.8 Hz, 2 H, CH_2O), 3.57 (m, 2 H, CHO), 1.68 (m, 2 H, CH_2CH_2O), 1.23–1.61 (m with s at 1.33, 32 H, $(CH_2)_7$, $(CH_2)_6$, $(CH_3)_2CO_2$), 0.90 (t, 3 H, CH_3); ^{13}C NMR (100.6 MHz, CD_3OD) δ 108.94 (CO_2), 82.33 (CHO), 69.37 (CH_2O), 33.94, 33.02, 30.76, 30.72, 30.60, 30.58, 30.40, 30.37, 30.30, 27.59, 27.23, 27.21, 26.86, 23.71, 14.44; FAB HRMS calcd for $C_{21}H_{41}SO_6$ (anion) 421.2624, found 421.2633. Anal. Calcd for $C_{21}H_{41}SO_6Na·0.25H_2O$: C, 56.16; H, 9.31. Found: C, 56.21; H, 9.15. The cmc's of **2a** at 25 °C in 0.0010 M Na_2CO_3 and H_2O are given in Table I.

Triethanolammonium *trans*-8-(2,2-Dimethyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (3a). A mixture of 1.00 g (2.92 mmol) of **13a**, 0.511 g (3.21 mmol) of SO_3·pyridine (Aldrich), and 1.0 mL of pyridine was stirred under N_2 at 115 °C for 4 h. Then 0.46 g (3.1 mmol) of $(HOCH_2CH_2)_3N$ was added, and the mixture was stirred for 6 h at 25 °C, followed by the removal of pyridine at 25 °C (0.01 mmHg). The resultant crude surfactant was recrystallized four times from 5:1 heptane–$CHCl_3$ (−10 °C) with collection by filtration, in a drybox under N_2 using a jacketed filter funnel cooled with dry ice–Me_2CO, to give 0.84 g (50%) of **3a** as a wax: ^1H NMR (270 MHz, $CDCl_3$) δ 5.32 (br s, 4 H, NH, OH), 4.00 (t, J = 6.9 Hz, 2 H, $CH_2OSO_3^-$), 3.91 (m, 6 H, CH_2OH), 3.58 (m, 2 H, CHO), 3.32 (m, 6 H, CH_2CH_2OH), 1.20–1.79 (m with s at 1.38, 34 H, 2 $(CH_2)_7$, $(CH_3)_2CO_2$), 0.88 (t, 3 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 107.70 (CO_2), 81.05 (CHO), 68.66 ($CH_2OSO_3^-$), 55.74, 55.61, 33.06, 33.02, 31.85, 29.79, 29.49, 29.34, 29.30, 29.24, 27.34, 26.24, 26.18, 25.75, 22.65, 14.09; FAB HRMS calcd for $C_{21}H_{41}O_6S$ (anion) 421.2624, found 421.2604; $C_6H_{16}NO_3$ (cation) 150.1130, found 150.1136. Anal. Calcd for $C_{27}H_{57}NO_9S·0.75H_2O$: C, 55.40; H, 10.08. Found: C, 55.35; H, 9.85. The cmc of **3a** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

Sodium *trans*-8-(2,2-Diethyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (2b). With the procedure used for the preparation of **2a**, 1.00 g (2.70 mmol) of **13b** gave 0.80 g of surfactant that was flash chromatographed three times on 15- × 5-cm columns of silica gel with 1:4 MeOH–Et_2O as eluant to yield 0.70 g (55%) of **2b**, which was pure by TLC (R_f = 0.5). This material was recrystallized from 10:1 Et_2O–MeOH (5 °C) to give **2b**: mp 174–177 °C; ^1H NMR (270 MHz, CD_3OD), δ 4.01 (t, J = 6.6 Hz, 2 H, CH_2O), 3.55 (m, 2 H, CHO), 1.19–1.75 (m, 32 H, 2 $(CH_2)_7$, $(CH_3CH_2)_2CO_2$), 0.88 (m, 9 H, CH_3); ^{13}C NMR (270 MHz, CD_3OD) δ 112.67 (CO_2), 82.75 (CHO), 69.40 (CH_2O), 33.92, 33.89, 33.04, 31.75, 30.76, 30.60, 30.42, 30.38, 30.33, 27.33, 26.88, 23.74, 14.46, 8.43; FAB HRMS calcd for $C_{23}H_{45}SO_6$ (anion) 449.2937, found 449.2942. Anal. Calcd for $C_{23}H_{45}SO_6Na·0.5H_2O$: C, 57.35; H, 9.63. Found: C, 57.35; H, 9.45.

Triethanolammonium *trans*-8-(2,2-Diethyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (3b). With the same procedure as used for **3a**, 1.00 g (2.70 mmol) of **13b** was converted into crude **3b**. This material was recrystallized five times from 5:1 heptane–$CHCl_3$ (−10 °C) with the procedure used for **3a** to give 0.93 g (57%) of **3b** as a wax: ^1H NMR (270 MHz, $CDCl_3$) δ 5.20 (br s, 4 H, NH, OH), 3.97 (m, 8 H, $CH_2OSO_3^-$, CH_2OH), 3.55 (m, 2 H, CHO), 3.47 (m, 6 H, CH_2CH_2OH), 1.61 (q, J = 7.3 Hz, 4 H, $(CH_3CH_2)_2CO_2$), 1.19–1.55 (m, 28 H, 2 $(CH_2)_7$), 0.89 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 111.38 (CO_2), 81.38 (CHO), 68.64 ($CH_2OSO_3^-$), 55.62, 55.29, 33.01, 33.96, 31.85, 30.79, 29.82, 29.79, 29.52, 29.47, 29.35, 29.24, 26.26, 26.19, 25.76, 22.64, 14.09,

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8.08. Anal. Calcd for $C_{29}H_{61}NSO_9 \cdot H_2O$: C, 56.37; H, 10.28. Found: C, 56.52; H, 10.12. The cmc of **3b** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

Sodium *trans*-8-(2,2-Dipropyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (2c). With the procedure used for the preparation of **2a**, 1.00 g (2.51 mmol) of **13c** gave 0.95 g of surfactant that was flash chromatographed four times on 25- × 5-cm columns of silica gel with 1:4 MeOH–Et_2O as eluant to yield 0.78 g (62%) of **2c**, which was pure by TLC (R_f = 0.5): mp 175–177 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 4.00 (t, J = 6.4 Hz, 2 H, CH_2O), 3.54 (m, 2 H, CHO), 1.20–1.75 (m, 36 H, 2 $(CH_2)_7$, $(CH_3CH_2CH_2)_2CO_2$), 0.91 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, CD_3OD) δ 112.11 (CO_2), 82.58 (CHO), 69.27 (CH_2O), 41.96, 33.89, 33.83, 33.03, 30.73, 30.58, 30.44, 30.35, 27.33, 27.28, 26.88, 23.74, 18.18, 14.82, 14.46; FAB HRMS for $C_{25}H_{49}SO_6Na$ (anion) 477.3250, found 477.3264. Anal. Calcd for $C_{25}H_{49}SO_6Na \cdot H_2O$: C, 59.44; H, 9.88. Found: C, 59.33; H, 9.83.

Triethanolammonium *trans*-8-(2,2-Dipropyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (3c). With the same procedure as used for **3a**, 1.00 g (2.51 mmol) of **13c** was converted into crude **3c**. This material was recrystallized four times from 5:1 heptane–$CHCl_3$ (−10 °C) with the procedure used for **3a** to give 0.75 g (48%) of **3c** as a wax: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.19 (br s, 4 H, NH, OH), 4.00 (t, J = 6.6 Hz, 2 H, $CH_2OSO_3^-$), 3.86 (m, 6 H, CH_2OH), 3.53 (m, 2 H, CHO), 3.18 (m, 6 H, CH_2CH_2OH), 1.20–1.78 (m, 36 H, 2 $(CH_2)_7$, $(CH_3CH_2CH_2)_2CO_2$), 0.89 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 110.84 (CO_2), 81.28 (CHO), 68.64 ($CH_2OSO_3^-$), 56.80, 56.07, 40.97, 32.99, 32.94, 31.86, 29.80, 29.47, 29.33, 29.26, 29.00, 26.29, 26.22, 25.75, 25.68, 17.06, 14.41, 14.09. Anal. Calcd for $C_{31}H_{65}NSO_9 \cdot 1.5H_2O$: C, 56.85; H, 10.47. Found: C, 57.10; H, 10.38. The cmc of **3c** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

Sodium *trans*-8-(2,2-Dibutyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (2d). With the procedure used for the preparation of **2a**, 1.00 g (2.34 mmol) of **13d** gave 1.05 g of surfactant that was flash chromatographed five times on 25- × 5-cm columns of silica gel with 1:4 MeOH–Et_2O as eluant to yield 0.65 g (53%) of **2d**, which was pure by TLC (R_f = 0.5): mp 178–180 °C; ^{1}H NMR (270 MHz, CD_3OD) δ 4.00 (t, J = 6.6 Hz, 2 H, CH_2O), 3.54 (m, 2 H, CHO), 1.19–1.78 (m, 40 H, 2 $(CH_2)_7$, $(CH_3CH_2CH_2CH_2)_2CO_2$), 0.91 (m, 9 H, CH_3); ^{13}C NMR (67.9 MHz, CD_3OD) δ 112.25 (CO_2), 82.58 (CHO), 69.38 (CH_2O), 39.28, 33.92, 33.87, 33.04, 30.74, 30.60, 30.44, 30.37, 27.35, 27.28, 27.22, 26.90, 24.08, 23.75, 14.52. Anal. Calcd for $C_{27}H_{53}SO_6Na$: C, 61.33; H, 10.10. Found: C, 61.06; H, 10.00.

Triethanolammonium *trans*-8-(2,2-Dibutyl-5-octyl-1,3-dioxolan-4-yl)octane-1-sulfate (3d). With the same procedure as used for **3a**, 1.00 g (2.34 mmol) of **13d** was converted into crude **3d**. This material was recrystallized five times from 5:1 heptane–$CHCl_3$ (−10 °C) with the procedure used for **3a** to give 1.01 g (66%) of **3d** as a wax: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (br s, 4 H, NH, OH), 4.00 (t, J = 6.8 Hz, 2 H, $CH_2OSO_3^-$), 3.84 (m, 6 H, CH_2OH), 3.54 (m, 2 H, CHO), 3.15 (m, 6 H, CH_2CH_2OH), 1.20–1.71 (m, 40 H, 2 $(CH_2)_7$, $(CH_3CH_2CH_2CH_2)_2CO_2$), 0.90 (m, 9 H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 110.96 (CO_2), 81.20 (CHO), 68.63 ($CH_2OSO_3^-$), 56.93, 56.08, 38.28, 33.02, 32.94, 31.84, 29.83, 29.77, 29.50, 29.46, 29.33, 29.22, 26.26, 26.17, 25.95, 25.75, 22.99, 22.64, 14.10. Anal. Calcd for $C_{33}H_{69}NSO_9 \cdot 1.5H_2O$: C, 58.03; H, 10.63. Found: C, 57.97; H, 10.32. The cmc of **3d** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

Sodium *threo*-9,10-Dihydroxyoctadecane-1-sulfate (6). A solution of 1.00 g (2.25 mmol) of **2a** in 100 mL of 1.0 M HCl was stirred at 25 °C for 4 h, adjusted to pH 9 with 3 M NaOH, lyophilized, and extracted with 100 mL of 1-BuOH (75 °C). The residue after rotary evaporation was recrystallized from 4:1 Et_2O–MeOH (5 °C) to give surfactant that was further purified by flash chromatography four times on 25- × 3-cm columns of silica gel with 1:4 MeOH–Et_2O as eluant to yield 0.60 g (66%) of **6**: mp 205–207 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 3.98 (t, J = 6.3 Hz, 2 H, CH_2O), 3.37 (m, 2 H, CHOH), 1.19–1.62 (m, 28 H, 2 $(CH_2)_7$), 0.89 (t, 3 H, CH_3); ^{13}C NMR (67.9 MHz, CD_3OD) δ 75.22 (CHOH), 69.13 (CH_2O), 33.98, 33.06, 30.85, 30.74, 30.65, 30.44, 30.31, 27.06, 26.86, 23.74, 14.45. Anal. Calcd for $C_{18}H_{37}SO_6Na$: C, 53.44; H, 9.22. Found: C, 53.38; H, 9.10. The cmc of **6** at 75 °C in 0.0010 M Na_2CO_3 is given in Table I.

Triethanolammonium *threo*-9,10-Dihydroxyoctadecane-1-sulfate (7). A solution of 0.500 g (0.874 mmol) of **3a** in 15 mL of 1.0 M HCl was stirred at 25 °C for 6 h and adjusted to pH 8.5 with $(HOCH_2CH_2)_3N$. Then the mixture was lyophilized and the residue extracted with 50 mL of MeOH. The extract was concentrated to 4 mL, and Et_2O was added to precipitate $(HOCH_2CH_2)_3NH^+Cl^-$. This extraction and precipitation procedure was repeated five times to give a MeOH–Et_2O solution that was concentrated to 10 mL. From this solution (25 °C) was obtained 0.20 g (43%) of **7**: mp 78–79 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 3.98 (t, J = 6.6 Hz, 2 H, $CH_2OSO_3^-$), 3.90 (t, J = 5.1 Hz, 6 H, CH_2OH), 3.43 (t, J = 5.1 Hz, 6 H, CH_2CH_2OH), 3.36 (m, 2 H, CHO), 1.65 (p, J = 7.0 Hz, 2 H, $CH_2CH_2OSO_3^-$), 1.22–1.56 (m, 26 H, $(CH_2)_7$, $(CH_2)_6$), 0.89 (t, 3 H, CH_3); ^{13}C NMR (100.6 MHz, CD_3OD) δ 75.30 (CHOH), 69.13 ($CH_2OSO_3^-$), 56.86, 56.51, 33.94, 33.06, 30.86, 30.75, 30.66, 30.45, 30.33, 27.09, 27.06, 26.88, 23.73, 14.44. Anal. Calcd for $C_{24}H_{53}NSO_9 \cdot H_2O$: C, 52.43; H, 10.08. Found: C, 52.56; H, 9.79. The cmc of **7** at 25 °C in the pH 8.5 triethanolamine buffer is given in Table I.

DLLS. Measurements were made at 23 °C on a Nicomp 370 submicron particle sizer (90° scattering angle) equipped with a Uniphase Model 2013 variable-power (75 mW max) Ar ion laser. A solution of the surfactant in $CHCl_3$ (stored over K_2CO_3) was rotary evaporated at 30 °C to give a thin film that was dried for 12 h (25 °C, 0.05 mmHg). Then 1.00 mL of the appropriate solvent was added, and the resultant solution at 25 °C was shaken for 10 min, aged for 30 min, and filtered through a Millipore Millex HV_1 filter unit (contains a 0.45-μm Durapore membrane) into a 6- × 50-mm culture tube (Kimble 73500-650). Immediately thereafter, the tube was placed into a 1- × 1-cm cuvette fitted with upper and lower inserts to effect centered, vertical alignment of the tube, and the cuvette was filled with C_6H_5Me or dodecane. Then the cuvette was inserted into the particle sizer, the laser power adjusted to give a photopulse rate of 300–400 KHz, and the run begun. Data were analyzed by the Nicomp distribution analysis procedure to give histograms of relative volume vs hydrodynamic diameter. The results are summarized in Table II.

DSC. To a thin film of ca. 1.5 mg of **1** prepared as above was added 1.0 mL of the appropriate solvent, and the resultant system was sonicated at 55 °C for 30 min and then held at 55 °C for 30 min and at 25 °C for 30 min. Calorimetry of 0.50-g portions of the these samples was performed on a Hart Scientific Model 7708 differential scanning calorimeter. Scans at 1 °C/min were made from 5 to 70 °C and from 70 to 5 °C for samples in H_2O containing 0.010 M $NaHCO_3$ and 0.010 M NaBr, and from −25 to 50 °C and from 50 to −25 °C for those in 1:1 (w/w) $HOCH_2CH_2OH$–H_2O.

Hydrolyses of 1a–d. The procedure for a typical run is as follows. To 20.0 mL of 5.5 M HCl at 25 °C was added 10.6 mg (0.0221 mmol) of **1a**. The resultant solution was stirred at 25 °C, and at various times a 3-mL sample was withdrawn and its pH adjusted to 8.0 with 1.0 M NaOH while maintaining its temperature at 25 °C. The sample was then lyophilized, and the entire residue was transferred to a 5-mm NMR tube with 0.5 mL of $CDCl_3$ (stored over Na_2CO_3). The extent of hydrolysis was determined by ^{1}H NMR analysis by comparing the areas for the $(CH_3)_3N$ singlets for **1a** and **4**. The accuracy of the analytical method was verified by analysis of synthetic mixtures of **1a** and **4**. Triplicate hydrolysis runs for **1a–d** are summarized in Table III.

The acid-catalyzed hydrolysis of micellar **1d** was monitored by surface tensiometry as follows. A 4.0×10^{-5} M solution of **1d** in 5.5 M HCl was stirred at 25 °C. The surface tension of the solution was measured at various times: within 1 min after it was prepared, γ = 32 dyn/cm; after 200 min, γ = 49 dyn/cm. For **4** in 5.5 M HCl at 25 °C, the cmc is 4.2×10^{-4} M, and γ = 53 dyn/cm for a 4.0×10^{-5} M solution. A solution of 4.0 mg (0.0091 mmol) of **4** in 3.0 mL of 5.5 M HCl was stirred at 25 °C for 300 min and lyophilized. The residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. Since only **4** was detected, it was stable during the 300-min period.

Hydrolyses of 3a–d. The procedure for a typical kinetic run is as follows. To 1.00 mL of 0.010 M HCl at 25 °C was added 7.2 mg (13 mmol) of **3a**. The resultant solution was stirred at 25 °C, and at various times a 20-μL sample was withdrawn and

analyzed by reversed-phase HPLC with 4:1 MeOH–aqueous 0.0030 M Na_2SO_4 as eluant and flow rate = 1.2 mL/min. The extent of hydrolysis at each time was determined by comparison of the peak area for **7** in the analysis with that for **7** corresponding to 100% hydrolysis.[32] The latter values for **3a–d** were obtained by analysis of 20-μL samples of reaction mixtures after 100% hydrolysis. The retention times for **3** and **7** were ca. 13.5 min and 4.6 min, and those for Me_2CO (from **3a**), Et_2CO (**3b**), Pr_2CO (**3c**), and Bu_2CO (**3d**) were 3, 3, 3.5, and 5.3 min, respectively. Least-squares plots of ln (% unreacted ester) vs reaction time yielded the pseudo-first-order rate constants, k_ψ. The results are summarized in Table IV.

The acid-catalyzed hydrolysis of micellar **3a** was monitored by surface tensiometry as follows. A 4.1×10^{-4} M solution of **3a** in 0.010 M HCl was stirred at 25 °C. The surface tension of the solution was measured at various times: within 2 min after it was prepared, γ = 29 dyn/cm; after 120 min, γ = 44 dyn/cm. For **7** in 0.010 M HCl at 25 °C, the cmc is 1.55×10^{-3} M, and γ = 45 dyn/cm for a 4.1×10^{-4} M solution. A solution of 4.0 mg (0.0075 mmol) of **7** in 3.0 mL of 0.010 M HCl was stirred at 25 °C for 200 h and lyophilized. The residue was dissolved in D_2O and analyzed by ^1H NMR. Since only **7** was detected, it was stable during the 200-h period.

(32) Bentley, T. W.; Gream, G. E. *J. Org. Chem.* **1985**, *50*, 1776.

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Supplementary Material Available: ^1H NMR spectrum of **9** and ^1H and ^{13}C NMR spectra of **15** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.