Relationship of Structure to Properties of Surfactants. 16. Linear Decyldiphenylether Sulfonates

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The properties of some well-characterized sodium linear decyldiphenylether (C_{10}DPE)sulfonates have been studied. Among the properties investigated are dynamic and equilibrium surface tension, critical micelle concentration (CMC), area per molecule at the aqueous solution/air interface, wetting time by the Draves technique, foaming by the Ross-Miles method, solubilization, and hydrotropy. The decyldiphenylether moiety appears to be equivalent to a terminally substituted straight alkyl chain of 16 carbon atoms. The trialkyl- and dialkyl-mono-sulfonates have solubilities of < 0.01 g/dm^3 in water, but are readily soluble in hexane. The didecyldiphenyl ether disulfonate (DADS) has a very low CMC value (1.0×10^{-5} mol dm^{-3}) in aqueous 0.1 N Na^+ solution (NaCl), characteristic of surfactants with two hydrophilic and two hydrophobic groups. It also has a much larger area per molecule at the aqueous solution/air interface than the monodecyldiphenylether monosulfonate (MAMS) and a much higher surface tension at the CMC. MAMS has a much lower surface tension at a surface age of 1 second (γ_{1s}) than either DADS or the monodecyldiphenylether disulfonate (MADS). In agreement with γ_{1s} and γ_{eq} values, wetting times increase in the order: MAMS < DADS < MADS and initial foam heights decrease in the order: MAMS > DADS > MADS. Solubilization for three water-insoluble surfactants decreases in the order: DADS > MAMS > MADS, while hydrotropy is most pronounced with the disulfonates.

FIG. 1. Structures of the C_{10}DPE sulfonates studied.

Alkyldiphenylether (ADPE) sulfonates have recently received considerable attention in cleaning applications because of their stability in the presence of bleach (NaOCl). As a result of this increased interest, a systematic investigation was undertaken into the relationship between the chemical structures of the various types of sulfonates present in commercial ADPE sulfonate products and their interfacial and micellar properties.

Commercial ADPE sulfonates consist of mixtures of mono- and disulfonated mono-, di-, and trialkyldiphenylethers, usually present as the sodium salts. Because of the large differences in these structures, it is to be expected that the various components of these commercial mixtures will show different interfacial and micellar properties. This study investigates the properties of some linear decyldiphenylether sulfonates.

EXPERIMENTAL PROCEDURES

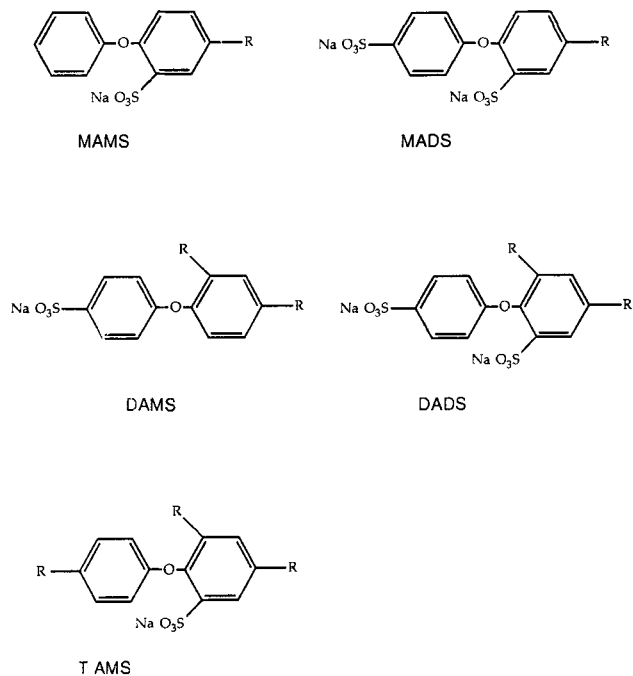The C_{10}DPE sulfonates studied were research samples, courtesy of Dr. Charles E. Coburn of the Dow Chemical

Co., Midland, Michigan. They were prepared by sulfonation (with $ClSO_3H$) of 3-decyldiphenylether (purity, 99.8%), 1,3-*bis*-decyldiphenyl ether (purity, 99.2%), or 1,3,3'-*tris*-decyldiphenylether (purity 99.8%), prepared by alkylation of diphenylether with 1-decene. As indicated by infrared (IR) analysis, the monoalkylmonosulfonate (MAMS) was sodium 3-decyl-1-sulfonato-diphenyl ether, the dialkylmonosulfonate (DAMS) was sodium 1,3-*bis*-decyl-3'-sulfonato-diphenyl ether, the trialkyl monosulfonate (TAMS) was sodium 1,3,3'-*tris*-decyl-5-sulfonato-diphenyl ether, the monoalkyl disulfonate (MADS) was disodium 3-decyl-3',5-disulfonato-diphenyl ether and the dialkyldisulfonate (DADS) was disodium 1,3-*bis*-decyl-3',5-disulfonato-diphenyl ether. High performance liquid chromatography (HPLC) indicated >99.9% monosulfonate content in monosulfonates, 99.7 disulfonate content in disulfonates. Structures are shown in Figure 1. Elemental analyses are given in Table 1. The disulfonates were further purified, to remove any corresponding monosulfonate impurities, by repeatedly passing aqueous solutions of the surfactant, at concentrations not above the critical micelle concentration (CMC), through mini-columns of octadecylsilonized silica (1,2).

Concentrations of the surfactant in aqueous solution were determined from their ultraviolet absorbance, using the molar absorptivities listed in Table 2.

All properties, except solubilization and hydrotropy, were measured in solutions of constant Na^+ concentra-

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RELATIONSHIP OF STRUCTURE TO PROPERTIES OF SURFACTANTS

TABLE 1

Elemental Analyses of C_{10} DPE Sulfonates

Compound	% C		% H		% S	
	Found	Theory	Found	Theory	Found	Theory
MAMS	63.50	64.00	6.96	7.04	7.42	7.77
MADS	50.10	51.36	5.25	5.45	11.74	12.45
DAMS	68.94	69.57	8.70	8.88	5.49	5.80
DADS	57.90	58.72	7.13	7.34	9.46	9.79

tion (NaCl). Sodium chloride used to increase the ionic strength of solutions was analytical-grade material, which was baked for several hours in a porcelain casserole at red heat to remove traces of organic compounds. A commercial sodium dodecylbenzenesulfonate (LAS)—C-550 LAS (Vista Chemical Co., Ponca City, OK)—was used for hydrotropy determinations.

Surface tension measurements. These were made at 25° ± 0.02°C by the Wilhelmy plate technique, with a sand-blasted platinum blade of *ca.* 5-cm perimeter. Instruments were calibrated against water that had been first deionized and then distilled twice, the last time from alkaline permanganate solution through a 3-ft Vigreaux column. Sets of measurements were taken until no significant change occurred. In some cases, this took several hours.

Dynamic surface tension measurements. These were taken at 25 ± 0.2°C with a maximum bubble pressure apparatus previously described (3).

Wetting measurements. Wetting times were measured at room temperature (≈25°C) by the Draves skein technique (4).

Foaming measurements. Initial foam heights and 5-min foam heights were measured by the Ross-Miles method (5) at 25°C and/or 60°C.

Solubilization measurements. Solubilization is defined here as producing a visually clear solution of the solubilizate (absorbance at 600 nm, 1 cm path length, < 0.008). Measurements were made in distilled water at a fixed concentration (1g/L) of the solubilizate, varying the amount of added C_{10}DPE sulfonate. The absorbance at 600 nm of the resulting well-mixed solution was measured after standing for three days at room temperature.

Hydrotropy measurements. A mixture of 5.0 g of 50% LAS, 5.9 g of distilled water, and 0.25 g of the C_{10}DPE sulfonate were warmed together until clear and then allowed to cool to 25°C or to 15°C.

RESULTS AND DISCUSSION

Solubilities. The monosulfonates all had low solubilities in aqueous 0.1M NaCl at 25°C. The monodecyl derivative (MAMS) is soluble clearly at 0.5 g/L concentration, but shows some cloudiness at 1.0 g/L. The *bis*-decyl derivative (DAMS) produces cloudy solutions with 0.1M NaCl at 25°C even at 0.01 g/L concentration, and the *tris*-decyl derivative (TAMS) is so insoluble, even in distilled water, that a few mg do not dissolve when heated with 800 mL of boiling water for several hours. Both DAMS and TAMS dissolved readily in hexane (solubility > 5 g/100 mL).

Critical micelle concentrations. The monosulfonates DAMS and TAMS are too insoluble in 0.1M NaCl at 25°C for accurate measurement of their surface tensions. The

TABLE 2

Molar Absorptivities of C_{10} DPE Sulfonates

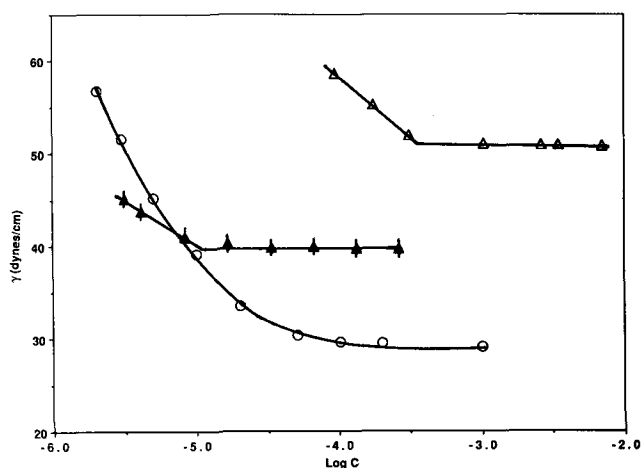| Compound	γ_{max} (nm)	$\varepsilon \times 10^{-4}$ (dm^3 mol^{-1} cm^{-1})
MAMS	232.0	1.32
MADS	233.0	1.85
DAMS	192.0	4.85
DADS	194.0	6.33
TAMS	192.0	6.25

FIG. 2. Surface tension *vs* log molar concentration of surfactant in aqueous solution at 25°C: O, C_{10}MAMS in 0.1N Na$^+$; ▲, C_{10}DADS in 0.1N Na$^+$; △, C_{10}MADS in 1N Na$^+$.

surface tension *vs* log molar concentration curves for MAMS and DADS in aqueous 0.1M Na$^+$ solution and MADS in 1M Na$^+$ solution are shown in Figure 2.

From the curves, the critical micelle concentration (CMC), the area per molecule at the aqueous solution/air interface, and the surface tension at the CMC (γ_{CMC}) can be determined. Values are listed in Table 3. Based upon the values for $C_{10}H_{21}SO_3Na$ (2.1 × 10^{-2} mol dm^{-3}) and $C_{12}H_{25}SO_3Na$ (2.5 × 10^{-3}) in 0.1M NaCl at 25°C (6), the CMC value of 3.2 × 10^{-5} mol dm^{-3} for MAMS (in 0.1M NaCl at 25°C) indicates that the decyldiphenyl ether moiety behaves equivalent to a terminally substituted 16-carbon straight alkyl chain. Since a phenyl group is generally equivalent to a straight alkyl chain of 3 1/2 carbon atoms in its effect on physical properties, the decyl group on the diphenyl ether nucleus appears to behave equivalent to a terminally substituted 9-carbon straight alkyl chain. This is reasonable, since the alkylation

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TABLE 3

Surface and Micellar Properties of Sodium Decyldiphenylether Sulfonates in aqu. 0.1N Na$^+$ soln. (NaCl)^a

Property	MAMS	DADS	MADS
	Surfactant		
CMC (mol/L)	3.2×10^{-5}	1.0×10^{-5}	3.7×10^{-4b}
$A_{min/mol}$ (Å^2)	48	101	75^b
γ_{cmc} (dyne/cm)	29.6	40.0	51.0^b
γ_{1s}, 1 g/L (dyne/cm)	35.2^c	54.3	64.7
Wetting, 1 g/L (sec)	16^c	126	>3600
Foaming (mm), 60°C			
2.5 g/L	195 → (183)^d	170 → (16)	77 → (18)
1.0 g/L	187 → (184)	162 → (21)	58 → (15)

^{a}At 25°C, unless indicated otherwise.

^{b}In IN Na$^+$ (NaCl) solution.

^{c}Cloudy solution.

^{d}Initial → (5 min).

reaction always occurs with attachment at a nonterminal position in the alkyl chain, making the equivalency of the decyl group less than 10 carbon atoms.

If we assume the same (9-carbon) equivalency for each of the two decyl groups in the dialkyldisulfonate (DADS), the entire hydrophobic portion of this molecule is equivalent to 25 carbon atoms, or about 12 carbon atoms per sulfonate group. Although the low CMC value (1.0 × 10^{-5} mol dm^{-3}) for DADS may at first appear unreasonable, this is consistent with recent work by Zhu and co-workers (7), who showed that surfactants with two hydrophilic and two lipophilic groups have CMC values one or two orders of magnitude smaller than the corresponding surfactants with one hydrophilic and one lipophilic group.

Area per molecule at the aqueous solution/air interface and γ_{CMC}. The area per molecule (48 Å^2) of MAMS in 0.1M NaCl at 25°C, obtained from the slope of the surface tension *vs* log molar surfactant concentration curve, is comparable to that of a commercial sodium linear dodecylbenzenesulfonate (46 Å^2) in the same medium at 25°C, indicating that the second phenyl ring, with no substituents on it, adds little to the cross-section of the molecule at the interface. On the other hand, in DADS and MADS, the second phenyl group with a second sulfonate group on it forces the two aromatic rings to lie prone in the interface, increasing the cross-sectional area considerably. This much looser packing of the disulfonate than the monosulfonate molecules at the interface results in a much smaller reduction in the surface tension of the solvent by the former molecule (γ_{CMC} of 51 and 40 dynes/cm for MADS and DADS, respectively; 29.6 dynes/cm for MAMS).

Dynamic surface tension (γ_{1s}) and wetting time. The monosulfonate, MAMS, produces a considerably lower surface tension at a surface age of one second, γ_{1s}, than either of the disulfonates, MADS and DADS. The γ_{1s} of surfactants with one hydrophilic group in the molecule has been shown to parallel the equilibrium γ_{CMC} value (8), and apparently that parallelism extends also to surfactants with two hydrophilic groups in the molecule as shown by the data for MAMS, MADS and DADS.

The γ_{1s} value has been shown to be related to wetting time in the Draves wetting test (8). In agreement with this,

TABLE 4

Absorbance at 600 nm of C$_{10}$ DPE Sulfonate Solutions of Water-insoluble Surfactants (conc. 1.0 g/L)

ADPE Sulfonate (Conc., g/L)	H$_2$O — Insoluble Surfactant^a		
	Sil	AE	APE
none	0.116	insol.	insol.
DADS (0.01)	0.020	0.008	0.014
MAMS (0.01)	0.011	0.023	0.079
DAMS (0.01)	0.007	0.044	0.145
MADS (0.01)	—	—	—
DADS (0.1)	0.008	0.008	0.006
MAMS (0.1)	0.008	0.007	0.008
MADS (0.1)	0.025	—	—
DADS (0.2)	0.005	0.006	0.006
MAMS (0.2)	0.007	0.007	0.007
MADS (0.2)	0.017	0.069	0.107

^{a}Sil = silicone-based surfactant; AE = alcohol ethoxylate; APE = alkylphenol ethoxylate.

TABLE 5

Hydrotropic Properties of C$_{10}$ DPE Sulfonates

ADPE sulfonate	Appearance^a
None	viscous, cloudy dispersion
MADS	clear, flowable at 15°C
DADS	clear, viscous at 25°C; cloudy at 15°C
MAMS	viscous, cloudy dispersion
DAMS	viscous, cloudy dispersion

^{a}Appearance of 23% LAS dispersion upon addition of 2.2% C$_{10}$ sulfonate.

the order of increasing wetting times is the same as that for increasing γ_{1s} (or γ_{CMC}) values: MAMS < DADS < MADS.

Foaming. Initial foam height by the Ross-Miles technique has been related to the γ_{CMC} value, the equilibrium surface tension at the CMC (9). The data for MAMS, DADS, and MADS are in agreement with that relationship, with initial foam heights decreasing in the order MAMS > DADS > MADS. It is noteworthy that the foam stability, as measured by the ratio of the foam height after 5 min to the initial foam height, is exceedingly poor for the disulfonates, presumably because of the loose packing of these molecules at the aqueous solution/air interface.

Solubilization. Aqueous solutions of ADPE sulfonates have the unusual property of solubilizing water-insoluble nonionic surfactants at low sulfonate/solubilizate ratios. Table 4 lists some absorbance data in the visible range (600 nm) for solutions or dispersions of the different C$_{10}$ ADPE sulfonates containing three water-insoluble nonionic surfactants in distilled water at 25°C. Solutions with an absorbance of 0.008 appear clear to the naked eye with only a trace of translucence; those of 0.020 have a slight translucence; those of 0.100 or more are cloudy.

From the data in Table 4 it is apparent that DADS, followed closely by MAMS, is the most effective and efficient compound for solubilizing these materials. The results probably reflect the much lower CMC values of these two materials, compared to MADS. The low water solubility of DAMS makes it unsuitable for use as a

solubilizing agent at concentrations above 0.01 g/L. Most noteworthy is the low $C_{10}DPE$/solubilizate ratio, down to 0.01 in some cases, at which solubilization is achieved.

Hydrotropy. Table 5 shows the effect of the addition of < 10% $C_{10}DPE$ sulfonate to a viscous, cloudy dispersion of a commercial sodium linear alkylbenzenesulfonate (LAS) in water. The phenomenon of hydrotropy is believed to be due to the inhibition by the hydrotrope of crystalline or liquid-crystalline (10,11) phase formation. Consequently, materials with chemical structures that prevent the parallel alignment of molecules show hydrotropic properties. In accordance with this, both DPE disulfonates, with their widely spread sulfonate groups, show better hydrotropic properties than the monosulfonates. MADS, with a larger hydrophilic/hydrophobic group volume ratio, is more effective than DADS.

ACKNOWLEDGMENT

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