Synthesis and Surface Properties of Chemodegradable Anionic Surfactants: Sodium Salts of Sulfated 2-*n*-Alkyl-5-Hydroxymethyl-5-Methyl-1,3-Dioxanes[1]

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In acid-catalyzed reactions of long-chain aliphatic aldehydes (Ia–d) (a,R = n-C_5H_{11}; b,R = n-C_7H_{15}; c,R = n-C_9H_{19}; d,R = n-$C_{11}H_{23}$) with 1,1,1-*tris*(hydroxymethyl)ethane (II), 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (IIIa–d) were obtained. Then they were reacted with SO_3·pyridine complex in dry carbon tetrachloride solution, to obtain trisubstituted derivatives of 1,3-dioxane (IVa–d). They constitute a new group of chemodegradable, acetal-type anionic surfactants, which may readily hydrolyze and oxidize to nonsurfactant compounds. Physical data of the new compounds and some surface properties, such as Krafft point, critical micelle concentration (CMC), surface tension of aqueous solution near CMC (γ_{CMC}) and wetting and foaming properties, were determined. Sodium salts of sulfated 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (IVa–d) exhibit aqueous solution properties similar to those of the well-known sodium alkyloligooxyethylene sulfates. Presence of the 5-methyl-1,3-dioxane moiety in molecules of compounds IVa–d introduces hydrophobic character comparable to the effect of three oxyethylene groups (-CH_2CH_2O-) or of two methylene groups (-CH_2-) of the alkyl chain in sodium alkyl ether sulfates [$R(OCH_2CH_2)_mOSO_3Na$] with equal R value.

KEY WORDS: Acetal-type surfactants, chemodegradable surfactants, CMC of aqueous solutions, 2,5-dialkyl-5-hydroxymethyl-1,3-dioxane sodium sulfates, foaming ability, surface tension isotherms, surfactant synthesis, wetting properties.

Previous papers report the synthesis and surface properties of new nonionic surfactants containing the acetal grouping, which make them liable to chemical degradation. The surface-active chemodegradable compounds were obtained by addition of oxirane (ethylene oxide) to 2-alkyl-4-hydroxymethyl-1,3-dioxolanes (1,2), 2-alkyl-5,5-*bis*(hydroxymethyl)-1,3-dioxanes (3,4) and 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (5); the cyclic hydrophobic intermediates were synthesized from aliphatic aldehydes and glycerine, 2,2-*bis*(hydroxymethyl)-1,3-propanediol and 1,1,1-*tris*-(hydroxymethyl)propane, respectively.

Other acetal group-containing surfactants of the nonionic (6,7), cationic (8,9) and anionic (10) type have also been described. They were characterized as "hydrolyzable" (6,7), and/or "destructible" (8,9) surfactants. The term "cleavable" for surface-active acetals (8–10) and disulfides (11) has also been used.

We proposed to use the term "chemodegradable surfactants" to describe all the surface-active compounds that contain in their molecules at least one functional group susceptible to chemical reactions in aqueous environment (12). In such reactions, surface-active substances lose their chemical identity and, in many cases, surface properties as well. In this respect, "chemodegradability" is similar to "primary biodegradability" (13) because the surface-active substance is degraded in these processes to an extent that is environmentally acceptable. Moreover, the chemodegradation products, contrary to the surfactants themselves, may undergo easier biodegradation. Hydrolysis splits acetals to aldehydes, which are, among others, intermediates in the biochemical β-oxidation reaction of hydrocarbon chains. On the other hand, the oxidation process of acetals leads to monoesters (14), which readily hydrolyze both in acidic and alkaline media. The above-mentioned degradation processes of acetal-type hydrophobic intermediates and surfactants derived from them have been well documented in the literature (6–11,14–17).

Sulfated polyoxyethylenated surfactants have great technical and economic importance (18). Their broad applicability is mainly due to the specific properties arising from the oligooxyethylene group, thus combining some of the peculiar characteristics of anionic and nonionic surfactants (19). The unusual surface and thermodynamic properties of the polyoxyethylenated anionics may be the result of complex formation between ether oxygen atoms of the oligooxyethylene group and the Na^+ counterion (20). If this hypothesis is true, the alkali-metal cations must be capable of complexing with two acetal oxygen atoms in sodium salts of sulfated derivatives of 5-hydroxymethyl-1,3-dioxanes (IVa–d) and may impart a partial zwitterionic character to the cyclic acetal-type anionic surfactants.

In this work we report our findings concerning the synthesis and some properties of new chemodegradable anionic surfactants containing an acetal grouping (21). By using the aldehydes *n*-hexanal, *n*-octanal, *n*-decanal and *n*-dodecanal, as well as the polyol 1,1,1-*tris*(hydroxymethyl)ethane, we obtained 2-*n*-pentyl-, 2-*n*-heptyl-, 2-*n*-nonyl- and 2-*n*-undecyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (IIIa–d, Fig. 1). These hydrophobic intermediates were reacted with SO_3·pyridine complex to obtain, after neutralization, sodium salts of sulfated 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (IVa–d), as shown in Figure 1. The main purpose of this study was to determine the properties of these anionic surfactants with a 1,3-dioxane ring. Thus we determined physical data of the new compounds, such as surface tension, wetting and foaming properties.

EXPERIMENTAL PROCEDURES

Materials. Aldehydes *n*-hexanal, *n*-octanal (Merck-Schuchard, Darmstadt, Germany, pure), *n*-decanal and

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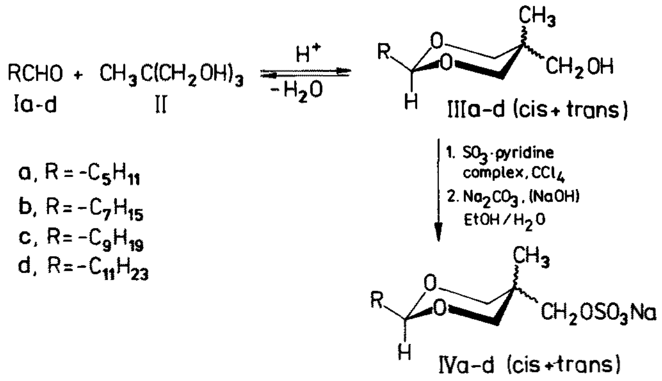


FIG. 1. Synthesis of sodium salts of sulfated 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes.

n-dodecanal (Loba-Chemie, Vienna, Austria, pure) were used after fractional distillation. 1,1,1-*Tris*(hydroxymethyl)ethane (Merck-Schuchard, pure) was used without further purification.

Synthesis of 2-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes. These compounds were synthesized by the procedure presented earlier (4,5). First, 0.5 mol of aldehyde, 0.6 mol of 1,1,1-*tris*-(hydroxymethyl)ethane, 0.2 g of *p*-toluenesulfonic acid and 300 mL of benzene were placed in a round-bottom flask equipped with a stirrer, thermometer and Dean-Stark adapter connected to a reflux condenser. The mixture was then stirred and refluxed until all reaction water was collected in the adapter. The reaction mixture was then cooled to room temperature and washed with 200 mL of 2 wt% sodium carbonate solution and twice with 100 mL portions of water. The benzene layer was dried over $MgSO_4$, the solvent was distilled off and the mixture of *cis*- and *trans*-1,3-dioxane derivatives (IIIa–d) was isolated and purified by repeated fractional distillation under reduced pressure (average yield 80–85 mol%). Purity and chemical structure of the isomer mixtures were confirmed by gas-liquid chromatography (GLC) analysis and ^{1}H NMR spectroscopy. The physical constants, yields and diastereoisomer ratios of the 1,3-dioxane derivatives (IIIa–d) are listed in Table 1.

Synthesis of sodium sulfates of 2-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes. To a well-stirred solution, maintained at 0–5°C, of 0.1 mol of a 1,3-dioxane derivative (IIIa–d) in 400 mL of dry carbon tetrachloride was added 17.5 g (0.1 mol) of SO_3·pyridine complex (21) in several portions during 1–1.5 h. After an additional 4 h of stirring at room temperature, solvent was evaporated under reduced pressure and the residue was slowly introduced into a cold solution of 0.115 mol NaOH or Na_2CO_3 in 400 mL of EtOH/H_2O (3:1). Solvent was evaporated and a crude sodium sulfate of the 1,3-dioxane derivative (IVa–d) was extracted four times with 150 mL portions of boiling ethanol. The solvent was evaporated and the residue was recrystallized twice from ethanol/isopropanol (1:3). Pure sodium sulfates of 2-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxane (IVa–d) crystallize as long white needles.

TABLE 1

Characteristics of 2-*n*-Alkyl-5-Hydroxymethyl-5-Methyl-1,3-Dioxanes (IIIa–d)

Compound	b.p. (°C/mm Hg)	n_D^{20}	Yield (mol%)	Diastereoisomer ratio *cis:trans*^{a}
IIIa	96.5/0.15	1.4570	85	2.6:1
IIIb	110/0.06	1.4586	83	2.5:1
IIIc	135/0.2	1.4600	84	2.5:1
IIId	155/0.2	26–33^b	79	2.4:1

^{a}From GLC. ^{b}Melting point, °C.

Krafft point determination. Krafft points of the synthesized compounds were measured by the electroconductivity method according to T. Hikota *et al.* (22).

Measurements of solution properties. Surface tensions of aqueous solutions of sulfates (IVa–d) were measured at 25.0 and 40.0 ± 0.1°C by the Wilhelmy-plate method with a micro-roughened platinum plate of 3.4 cm width. The equilibrium was checked by repeated measurements at 10-min intervals until no changes occurred. Water was triply distilled from alkaline permanganate solution. The method was accurate to ±0.1 mNm^{-1}.

Wetting properties were determined as the concentration (gdm^{-3}) of surfactant solution necessary for immersion of a cotton-fabric ring (3.5 cm in diameter) in 100 s (23). The solutions were stored for 24 h before determinations. The results were averaged from 10 determinations.

Foaming properties were measured by the beating method with a perforated disk of 5.2 cm diameter with 24 symmetrical holes of 0.2 cm inside diameter oscillated vertically in a glass cylinder. The frequency of beating was 1 sec^{-1} and the foam generation time was 60 s. The foaming ability was defined as the volume of foam formed over 100 mL of surfactant solution at 0 and 60 s after the end of beating. The measurements were carried out for 0.2 wt% solutions in distilled water at 25 and 40°C.

RESULTS AND DISCUSSION

Physical properties and stereoisomer composition of hydrophobic intermediates. 2-Alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes (IIIa–d) are colorless liquids; their physical constants and the diastereoisomer ratios are presented in Table 1. GLC and ^{1}H nuclear magnetic resonance (NMR) spectra revealed that, as expected, the trisubstituted derivatives of 1,3-dioxane are mixtures of diastereoisomers. The chromatograms of IIIa–d indicate the presence of two compounds with quite distinct retention times. The one with a shorter retention time is present in excess. The ratio of the two isomers exceeds 2:1. Following the arguments of Eliel and Banks (24) concerning analysis of stereoisomer composition of 2-isopropyl-5-hydroxymethyl-5-methyl-1,3-dioxanes and our previous detailed analysis of ^{1}H NMR spectra by using the lanthanide shift reagent Eu(dpm)$_3$ obtained for 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (5), we have ascribed the *cis* configuration with the axial hydroxymethyl group at C-5 to the compounds with the shorter retention time.

Physical and surface properties of sodium salts of sulfated 2-n-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes. The physical constants of surfactants (IVa–d) are listed in Table 2. The yield of the products was high (21), and the starting materials were all commercially available. The Krafft point is one of the most fundamental properties of the anionic surfactants. The Krafft point values

TABLE 2

Characteristics of Sodium Salts of Sulfated 2-*n*-Alkyl-5-Hydroxymethyl-5-Methyl-1,3-Dioxanes (IVa–d)

Compound	R	Molecular formula	Melting point[a] (°C)	Yield[b] (mol%)	Elemental analysis found (calcd) (%) C	H	S
IVa	n-C_5H_{11}	$C_{11}H_{21}SO_6Na$	179.5–181	91.8	43.3 (43.4)	7.2 (7.0)	10.5 (10.5)
IVb	n-C_7H_{15}	$C_{13}H_{25}SO_6Na$	163.5–165.5	96.0	46.8 (47.0)	7.8 (7.6)	9.7 (9.6)
IVc	n-C_9H_{19}	$C_{15}H_{29}SO_6Na$	179.5–180	93.8	50.1 (50.0)	8.2 (8.1)	8.9 (8.9)
IVd	n-$C_{11}H_{23}$	$C_{17}H_{33}SO_6Na$	160–165	99.1	52.8 (52.6)	8.9 (8.6)	8.2 (8.2)

[a] With decomposition. [b] After crystallization.

determined by the electroconductivity method for studied sulfates (IVa–d) are listed in Table 3.

The surface tension, γ, of aqueous surfactant solutions at 25 and 40°C, is plotted *versus* the logarithm of the concentration (Fig. 2). The surface activity of these anionic surfactants increased inversely with alkyl chainlength. It can be seen that the undecyl derivative (IVd) substantially reduces the surface tension of water, similar to the sodium sulfates of oligooxyethylenated 1-dodecanol. Surface properties of cyclic acetal-type anionic surfactants (IVa–d) are presented in Table 3. Based on the Gibbs adsorption equation for a 1:1 electrolyte, the surface excess concentration was determined from the surface tension-log concentration plot (Equation 1):

$$\Gamma = \frac{d\gamma}{nRT \cdot d\ln c} \qquad [1]$$

where Γ, γ, and c denote the surface excess in mol per square meter, the surface tension in Newton per meter, and the bulk concentration in molarity, respectively. In the absence of NaCl, the factor n = 2 is used in the denominator of this equation (25). The surface area (A_{CMC}) in square meter per molecule near the CMC is given as (Equation 2):

$$A_{CMC} = \frac{1}{\Gamma_{CMC}\, N} \qquad [2]$$

where N is Avogadro's number.

The molecular area (A_{CMC}) decreases with the alkyl chain increase. With the temperature increase from 20 to 45°C, there is almost a steady decrease in the minimum area per molecule and a corresponding increase in the maximum surface excess concentration. Incorporation of the 1,3-dioxane ring between the hydrophobic alkyl chain and the hydrophilic head group caused the molecules to orient horizontally to the air/solution interface with a resulting value of Γ_{CMC} about one-half of that observed for *n*-alkyl sulfates (22,26–30) at the same temperature. The effectiveness of surface tension reduction, given by π_{CMC}, decreases with temperature increase. Surfactants (IVa–d) show almost the same π_{CMC} value as sodium sulfates of oligooxyethylenated alcohols (19,20,28,31).

For the nonionic hexaethyleneglycol alkyl ethers and the zwitterionic surfactants $C_nH_{2n+1}N^+(CH_3)_2CH_2COO^-$ (32), linear relationships of log CMC *vs.* carbon number of the hydrocarbon chain are observed with slopes equal to approximately −0.5. Ionic surfactants without added electrolyte show lower slopes (33). For example, the anionic sodium alkyl carboxylates (28), sodium alkyl sulfates (28) and sodium alkyl tetrahydropyranyl sulfates (34) give slope values equal to −0.28, −0.30, and −0.32, respectively. For surfactants (IVa–d), this slope was determined as −0.33 at 25°C. Taking sodium alkyl sulfates as standard surfactants, one can observe that the insertion of a 1,3-dioxane ring, tetrahydropyranyl ring (34), and oxyethylene groups (19,20) between the alkyl chain and sulfate group leads to a CMC decrease of the new surfactants, *i.e.*, to a surface activity increase (Table 4). In

TABLE 3

Surface Properties of Sodium Salts of Sulfated 2-*n*-Alkyl-5-Hydroxymethyl-5-Methyl-1,3-Dioxanes (IVa–d)

Compound	Krafft point (°C)	T (°C)	$CMC \cdot 10^3$[a] (mol/dm^3)	$\Gamma_{CMC} \cdot 10^6$ (mol/m^2)	$A_{CMC} \cdot 10^{20}$ (m^2)	pC_{20}[b] (mN/m)	Π_{CMC} (mN/m)	CMC/c_{20} (mN/m)
IVa	—	25	180	1.73	96	1.16	28.2	2.6
IVb	—	25	39.8	1.99	83	1.84	30.0	2.8
IVc	13.0	25	8.93	1.91	87	2.53	30.5	3.0
		40	8.11	1.94	85	2.49	29.3	2.5
IVd	26.5	25	1.86[c]	1.99	83	3.13	29.2	2.5
		40	1.59	2.06	81	3.13	28.2	2.1

[a] From surface tension measurements. [b] Efficiency of surface tension reduction, ref. (28). [c] Solubility point.

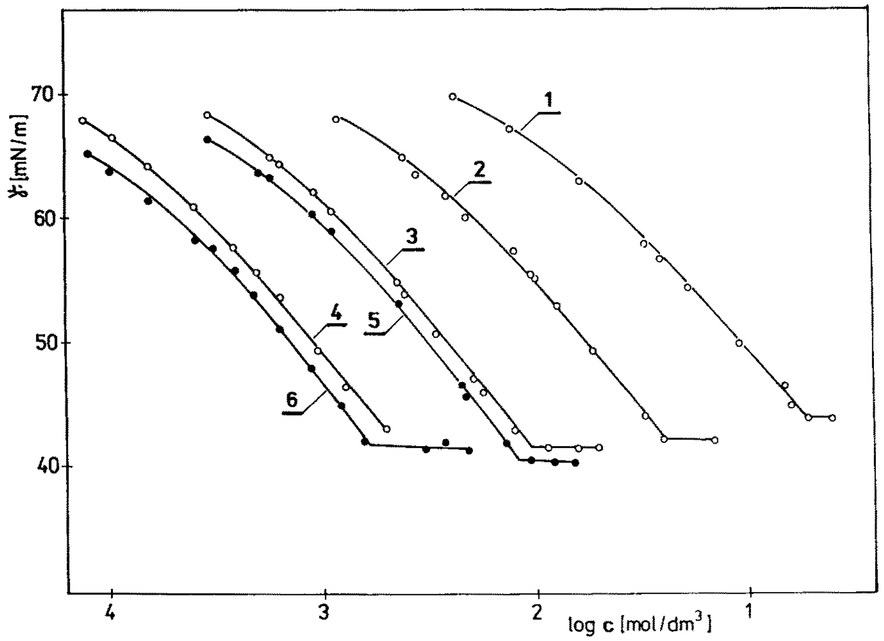
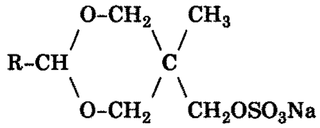
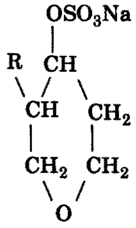


FIG. 2. The surface tension (γ) *vs.* logarithm of molar concentration (log c) of sodium salts of sulfated 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes: 1, IVa at 25°C; 2, IVb at 25°C; 3, IVc at 25°C; 4, IVd at 25°C; 5, IVc at 40°C; 6, IVd at 40°C.

TABLE 4

CMC Values and Krafft Points of Some Surface Active Sodium Sulfates

Surfactant	R	CMC·10^3 (mol/dm^3)	Krafft point (°C)
	C_9H_{19}	8.93 (25°C) 8.11 (40°C)	13.0
	$C_{11}H_{23}$	1.86 (25°C) 1.59 (40°C)	26.5
$ROSO_3Na$	$C_{12}H_{25}$	8.2 (25°C) [ref. (26–29)] 8.6 (40°C) [ref. (28,30)]	15.0 [ref. (22)]
	$C_{14}H_{29}$	2.05 (25°C) 2.2 (40°C)	33.2
$R(OCH_2CH_2)_3OSO_3Na$	$C_{12}H_{25}$	2.0 (50°C) [ref. (28,31)]	—
	$C_{13}H_{27}$	1.51 (25°C) [ref. (34)]	<25 [ref. (34)]

particular, the incorporation of the 5-methyl-1,3-dioxanoyl group of sulfates (IVa–d) into $ROSO_3Na$ molecules causes an increase of their surface activity, which can be expressed in terms of either two ($-CH_2-$) units or three oxyethylene groups.

Performance properties. The foaming properties of aqueous solutions of the examined compounds were determined as previously described. The foam volumes obtained just after the end of beating and still maintained after 60 s are presented in Table 5. Foaminess of surfactants (IVa–d) and sodium alkyl sulfates is small when R is C_7H_{15} and $C_{10}H_{21}$, respectively, or shorter. The most foam is observed for undecyl derivative (IVd) and dodecyl sulfate at 20°C. This statement is similar to that obtained by Goette (35) or Bikerman (36) when the foam was generated over solutions with constant concentration (w/w) by a vibrating perforated plate; the foam volume was greater for dodecyl than for tetradecyl and hexadecyl sulfate as long as the concentration was small.

We studied surfactant wetting ability by measuring the time cotton-fabric rings floated on surfactant solutions. The relationships between wetting time and concentration are shown in Figure 3. From this plot the wetting ability was expressed as the concentration of a given substance necessary for immersion of a cotton ring in 100 s. Wetting ability is small when the alkyl chain is C_9H_{19} or shorter (sinking times of over 600 s, even at a 0.5 wt% concentration). Compound (IVd) is a more effective wetting agent than sodium dodecyl sulfate (Table 5).

The presented results can be summarized as follows: (i) chemodegradable cyclic acetal-type anionic surfactants (IVa–d) show surface properties comparable with those of the well-known sodium alkyloligooxyethylene sulfate; (ii) presence of the 5-methyl-1,3-dioxane moiety in molecules of compounds (IVa–d) introduces hydrophobic character comparable to the effect of either three oxyethylene groups ($-CH_2CH_20-$) or two methylene groups ($-CH_2-$) in the alkyl chain in sodium alkyl ether sulfates $R(OCH_2CH_2)_mOSO_3Na$ with equal R value.

TABLE 5

Foaming and Wetting Properties of Sodium Salts of Sulfated 2-*n*-Alkyl-5-Hydroxymethyl-5-Methyl-1,3-Dioxanes and Alkyl Sulfates

Surfactant series	R	Foam volume, V (cm^3) 20°C	Foam volume, V (cm^3) 40°C	Wetting ability (g/dm^3)
IV	C_5H_{11}	0 (26[a])	0	>5
	C_7H_{15}	0 (66[a])	0	>5
	C_9H_{19}	620	330	1.5
	$C_{11}H_{23}$	940	—	0.38
$ROSO_3Na$	C_6H_{13}	16	—	—
	C_8H_{17}	28	—	—
	$C_{10}H_{21}$	32	—	—
	$C_{12}H_{25}$	960	940	0.6
	$C_{14}H_{29}$	—[b]	355	—

[a] Immediately after shaking. [b] Insoluble at 20°C.

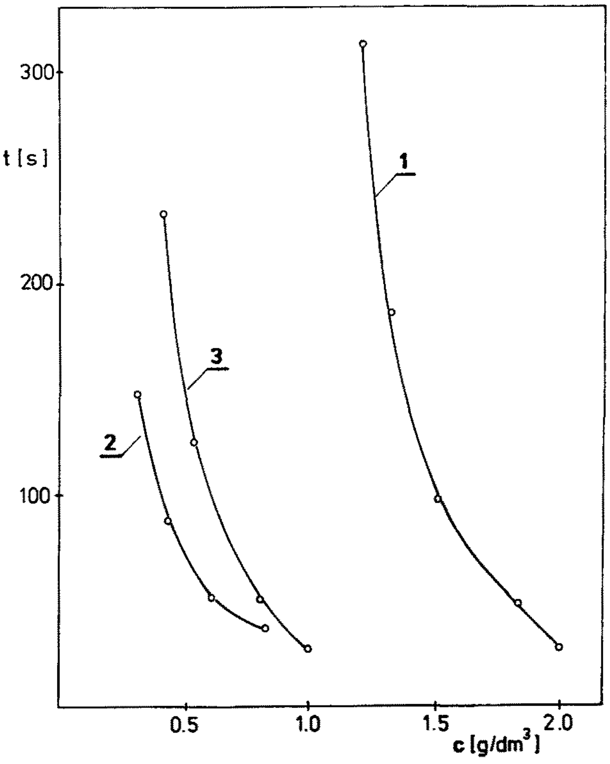


FIG. 3. The wetting time (t) *vs.* concentration (c) for aqueous solutions of sodium salts of sulfated 2-*n*-alkyl-5-hydroxymethyl-5-methyl-1,3-dioxanes: 1, IVc; 2, IVd; 3, sodium dodecyl sulfate.

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