# Synthesis and Surface Properties of Oxyethylenated 2-Alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes[1]

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**In acid-catalyzed reactions of long chain aliphatic aldehydes (I) (R = n - $C_7H_{15}$; n - $C_9H_{19}$; n - $C_{11}H_{23}$) with 1,1,1-tris(hydroxymethyl)propane (II), 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (III) were obtained. The latter were then reacted with ethylene oxide in the presence of sodium methoxide.**

**Three series of oxyethylenated cyclic acetal derivatives (IV) were obtained. They constitute a new group of chemodegradable surfactants which readily hydrolyze and oxidize in natural water reservoirs. Physical data of the new compounds and some surface properties such as cloud points (Cp), critical micelle concentrations (cmc), changes of free energy of micellization, ($\Delta G^\circ_{cmc}$), surface tensions of aqueous solutions near cmc, $\gamma_{min}$, and wetting and foaming properties, were determined. The surfactants (IV) have aqueous solution properties similar to those of oxyethylenated long-chain aliphatic alcohols. It is shown that the micellization of surfactants (IV), expressed in terms of $\Delta G^\circ_{cmc}$, depends both on the length of the aliphatic chain at the C-2 carbon atom and on the presence of ethyl group at C-5 of 1,3-dioxane ring which enhances the hydrophobic character of derivatives (III). Hence, the surfactants have a higher surface activity than oxyethylenated 2-alkyl-4-hydroxymethyl-1,3-dioxolanes or 2-alkyl-5,5-bis-(hydroxymethyl)-1,3-dioxanes. The use of 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (III) in surfactant synthesis is an example of applying hydrophobic intermediates obtained from aldehydes only. This, and the chemodegradability mentioned make the compounds a very interesting group of new surfactants.**

In our previous papers, we have reported on the synthesis and surface properties of oxyethylenated 2-alkyl-4-hydroxymethyl-1,3-dioxolanes (2) and 2-alkyl-5,5-bis-(hydroxymethyl)-1,3-dioxanes (3,4). The hydrophobic intermediates in the syntheses of these chemodegradable nonionic surfactants were derivatives of cyclic acetals which were obtained in a reaction of long chain aldehydes with the polyols glycerol and 2,2-bis(hydroxymethyl)-1,3-propanediol (pentaerithritol), respectively. Besides these polyols, 1,1,1,tris(hydroxymethyl)propane (trimethylolpropane) (II) is another widely available polyol. It is manufactured on a large scale by an aldol condensation of formaldehyde with n-butanal. This compound reacts with aldehydes (I) to yield 1,3-dioxane derivatives, e.g., 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxane (III), as shown in Figure 1.

In surfactant synthesis, derivatives (III) seem to be better hydrophobic intermediates than 2-alkyl-5,5-bis-(hydroxymethyl)-1,3-dioxanes because they contain only one primary hydroxy group and the $C_2H_5$ substituent at C-5 of the 1,3-dioxane ring (introduced with the polyol), plus the alkyl substituent at C-2 which comes from the starting aldehyde.

In this report, we describe the synthesis and some properties of a new group of chemodegradable surfactants containing an acetal grouping (5), starting with the aldehydes n-octanal, n-decanal and n-dodecanal, and with 1,1,1-tris(hydroxymethyl)propane. 2-n-Heptyl, 2-n-nonyl- and 2-n-undecyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (III) were synthesized. These hydrophobic intermediates subsequently were reacted with ethylene oxide (EO) to obtain three series of oxyethylenated derivatives (IV). The main purpose of this study was to determine the properties of these surfactants (IV).

## EXPERIMENTAL

$^1H$ NMR spectra were recorded on a Tesla BS 497 apparatus at 100 MHz. Tetramethylsilane (TMS) was

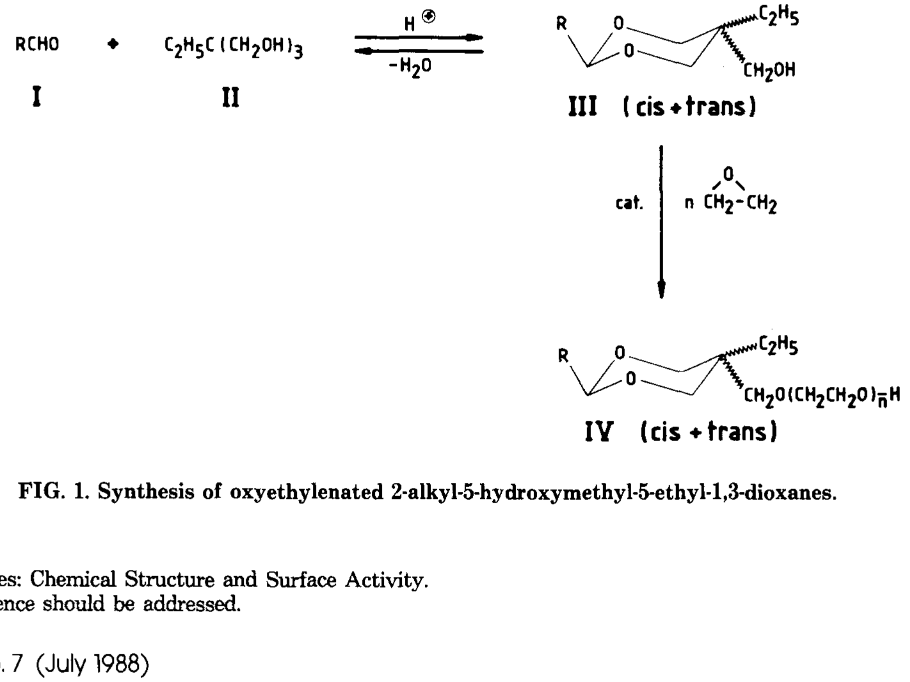

FIG. 1. Synthesis of oxyethylenated 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes.

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[1] Part XVII in the series: Chemical Structure and Surface Activity.
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used as internal standard and $CDCl_3$ as solvent. The signals of protons were differentiated using $Eu(dpm)_3$ as a shift reagent. GLC on a Giede G.CH.F.18.3 apparatus equipped with flame ionization detector (FID) was used to check the purity of substrates and the quantitative compositions of hydrophobic intermediates (III). A metallic column (3 mm i.d. and one m long) packed with 15% Silicone XE60 on Chromosorb G AW DMCS 60/80 mesh ($N_2$ as carrier gas) was used. Surface tensions of aqueous solutions were determined by using the Wilhelmy-plate method at 20±0.1 C. Wetting and foaming properties were determined according to the Polish Standards, PN-74/C-04800 and PN-74/C-04801, respectively.

*Materials.* Aldehydes: n-octanal (Merck-Schuchard, Federal Republic of Germany, FRG, pure) and n-decanal and n-dodecanal (Loba-Chemie, Austria, pure) were distilled before use. 1,1,1-Tris(hydroxymethyl)propane (Merck-Schuchard, Federal Republic of Germany, pure) was used without further purification. Ethylene oxide (EO) was of technical grade. It was distilled over KOH pellets before use.

*2-Alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes.* These compounds were synthesized according to the procedure described by Hannig and Wilhelm (6) as follows: 0.5 mol of aldehyde, 0.6 mol of 1,1,1-tris(hydroxymethyl)-propane, 0.2 g of p-toluene-sulfonic acid and 300 ml of toluene were placed in a round-bottomed flask equipped with a stirrer, thermometer and Dean-Stark adapter connected to a reflux condenser. The mixture was stirred and refluxed until all reaction water was collected in the adapter. The reaction mixture was then cooled to room temperature and washed once with 200 ml of 2 wt percent sodium carbonate solution and twice with 100-ml portions of water. The toluene layer was dried over $MgSO_4$, the solvent was distilled off and the residue was subjected to fractional distillation under reduced pressure. The physical constants, yields and diastereoisomer ratios of the products are listed in Table 1.

*Oxyethylenated derivatives of 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes.* 0.1 Mol of a 1,3-dioxane derivative (III) was placed in a round-bottomed flask equipped with a stirrer, thermometer, condenser and an inlet tube for EO. 0.02 Mol of sodium methoxide in methanol was then added with vigorous stirring. The reaction mixture was heated to 80 C under nitrogen gas flow until all the methanol was distilled off. The reaction mixture was then heated slowly to 120 C under nitrogen atmosphere and an appropriate amount (0.7, 1.0 and 1.5 mol) of gaseous EO was added while keeping the temperature in the range of 120-130 C. After completing the EO addition, the reaction mass was cooled to 60 C and the catalyst removed by using cation exchange resin Wofatit Y-37 (GDR) in the H-form. Light yellow, viscous liquids or solids were obtained.

## RESULTS AND DISCUSSION

*Physical properties and stereoisomer composition of hydrophobic intermediates.* 2-Alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes (III) are colorless liquids; their physical constants and the yields are presented in Table 1. The heptyl and undecyl derivatives were obtained by Hannig and Wilhelm (6), but the authors did not publish any data apart from boiling points and yields.

GLC and $^1H$ NMR spectra revealed that, as expected, the derivatives of 1,3-dioxane were mixtures of diastereoisomers. The chromatograms of products (III) indicate the presence of two substances with quite distinct retention times. In each of the three products differing in length of 2-alkyl chain, the one with a shorter retention time occurs in excess. The ratio of the two isomers exceeds 2:1.

Following the arguments of Eliel and Banks (7) concerning GLC parameters of isomeric 2-isopropyl-5-hydroxymethyl-5-methyl-1,3-dioxanes and the results of Löcsei et al. (8) obtained for 2-isopropyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes, to the compounds with the shorter retention time, we have ascribed the *cis* configuration with the axial hydroxy group at C-5.

Among 2-alkyl-5-hydroxy-1,3-dioxanes, too, *cis* isomers with axial hydroxy groups have shorter retention times in GLC than *trans* isomers (9,10). Detailed analysis of $^1H$ NMR spectra of n-heptyl derivative confirms the results of the chromatographic studies. Axial protons at C-4,6 carbon atoms of the 1,3-dioxane ring absorb at a higher field (3.41 ppm) in the *cis* isomer than in *trans* (3.60 ppm), in accord with literature data (8). The C-4,6 equatorial protons absorb at 3.91 and 3.83 ppm, respectively. The lower field of absorption of protons of axial $-CH_2OH$ group in the *cis* isomer (3.82 ppm) in relation to the equatorial group in the *trans* isomer (3.30 ppm) was also observed in isomeric 2-isopropyl-5-hydroxymethyl-5-methyl-(7) or 5-ethyl-1,3-dioxanes (8). The detailed analysis of $^1H$ NMR spectrum of the *cis* and *trans* isomer mixture was possible by using the lanthanide shift reagent $Eu(dpm)_3$, ($8.55 \times 10^{-5}$ mol for $4.69 \times 10^{-5}$ mol of acetal). *Cis* isomer: $\delta = 1.67$ (t, 3H, J = 7 Hz), 2.80 (q, 2H, J = 7 Hz), 4.51 (d, 2H, J = 11.5 Hz), 5.28 (t, 1H, J = 5 Hz), 5.76 (d, 2H,

TABLE 1

Characteristics of 2-n-Alkyl-5-Hydroxymethyl-5-Ethyl-1,3-Dioxanes

| | | | | | GLC analysis[a] | | |
|---|---|---|---|---|---|---|---|
| R | b.p. (°C/mmHg) | $d_4^{20}$ | $n_D^{20}$ | Yield (mol %) | Diastereomer ratio *cis: trans* | Retention time (min) *cis* | *trans* |
| $n-C_7H_{15}$ | 110/0.1 | 0.9707 | 1.4615 | 89 | 2.77 | 3.20 | 3.95 |
| $n-C_9H_{19}$ | 125/0.2 | 0.9544 | 1.4630 | 70 | 2.49 | 5.5 | 6.8 |
| $n-C_{11}H_{23}$ | 154/0.3 | 0.9407 | 1.4640 | 70 | 2.32 | 9.9 | 12.3 |

[a]220 C.

TABLE 2

**Physical and Surface Properties of Oxyethylenated 2-n-Alkyl-5-Hydroxymethyl-5-Ethyl-1,3-Dioxanes**

| Surfactant composition | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | EO content[a] | | | | | | | | |
| R | n | wt % | M | $d_4^{20}$ | $n_D^{20}$ | Cp[b] (°C) | cmc[d] (moldm$^{-3}$) | γmin. (mNm$^{-1}$) | $\Delta G°_{cmc}$ (kJmol$^{-1}$) |
| | 7.21 | 56.5 | 560 | 1.0473 | 1.4639 | 45.1 | $1.20 \times 10^{-3}$ | 29.6 | -26.2 |
| n-$C_7H_{15}$ | 9.85 | 64.0 | 680 | 1.0600 | 1.4650 | 70.4 | $1.23 \times 10^{-3}$ | 32.2 | -26.1 |
| | 15.0 | 73.0 | 905 | 1.0585 | 1.4659 | >100 (41.5)[c] | $1.26 \times 10^{-3}$ | 31.1 | -26.0 |
| | 7.08 | 53.4 | 580 | 1.0343 | 1.4641 | 35.7 | $1.35 \times 10^{-4}$ | 30.2 | -31.5 |
| n-$C_9H_{19}$ | 9.84 | 61.4 | 710 | 1.0497 | 1.4659 | 65.6 | $1.70 \times 10^{-4}$ | 32.0 | -30.9 |
| | 15.0 | 70.8 | 930 | solid | | 95.7 | $1.91 \times 10^{-4}$ | 34.2 | -30.7 |
| | 7.23 | 51.5 | 620 | 1.0239 | 1.4645 | 30.9 | $2.04 \times 10^{-5}$ | 30.4 | -36.1 |
| n-$C_{11}H_{23}$ | 9.97 | 58.4 | 740 | 1.0413 | 1.4663 | 66.7 | $2.69 \times 10^{-5}$ | 32.2 | -35.4 |
| | 14.88 | 68.6 | 955 | solid | | >100 (68.4)[c] | $3.93 \times 10^{-5}$ | 37.6 | -34.5 |

[a] From mass balance of the oxyethylenation reaction.
[b] 1 wt % solution.
[c] 1 wt % in 10 wt % NaCl solution.
[d] From surface tension measurements.

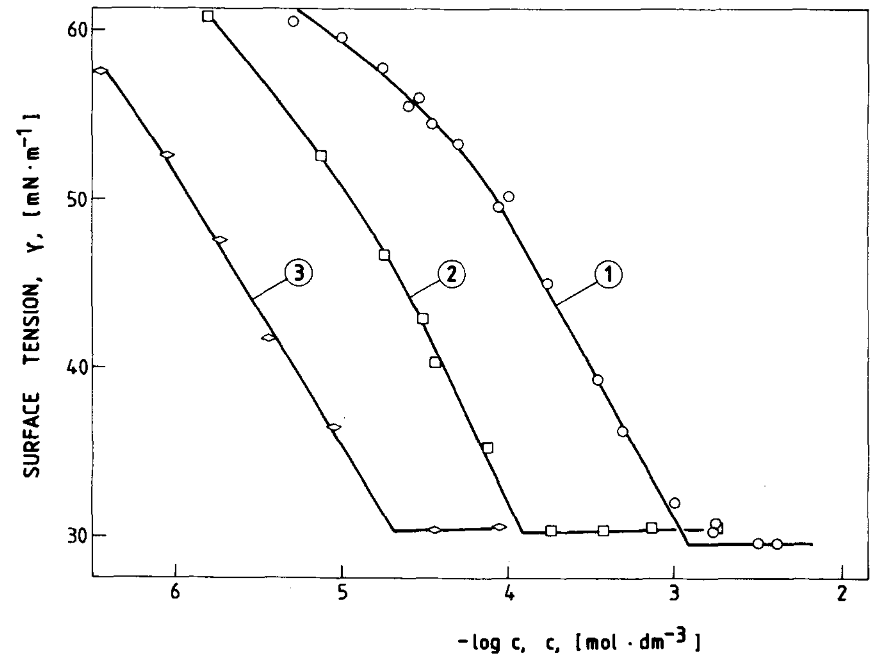


FIG. 2. The surface tension (γ) vs logarithm of molar concentration (log c) of solution of oxyethylenated compounds (IV) containing ca 7 EO units: 1, R = n-$C_7H_{15}$; 2, R = n-$C_9H_{19}$; 3, R = n-$C_{11}H_{23}$.

J = 11.5 Hz), 7.29 (s, 2H) and *trans* isomer: δ = 2.33 (t, 3H, J = 7 Hz), 3.95 (q, 2H, J = 7 Hz), 5.46 (t, 1H, J = 5 Hz), 6.10 (d, 2H, J = 11.5 Hz), 6.35 (d, 2H, J = 11.5 Hz) and 8.69 (s, 2H). The ratio of *cis* and *trans* isomers calculated from the spectra was close to that obtained from the GLC analysis.

*Physical and surface properties of oxyethylenated 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes.* The physical constants and surface properties of surfactants (IV) are listed in Table 2. The chemical composition of the products was confirmed by $^1$H NMR spectra. The content of oxyethylene groups determined from the spectra according to the method described in (11) agreed well with that calculated from the balance of mass in oxyethylenation reaction.

The surfactants are readily soluble in water at room temperature, as can be deduced from the values of cloud points (Cp) of their 1 wt% solutions. The Cp values, shown in Table 2, correspond to those reported for oxyethylenated aliphatic alcohols having a comparable number of carbon atoms in the aliphatic chain as well as the length of oxyethylene grouping [cf. (12)].

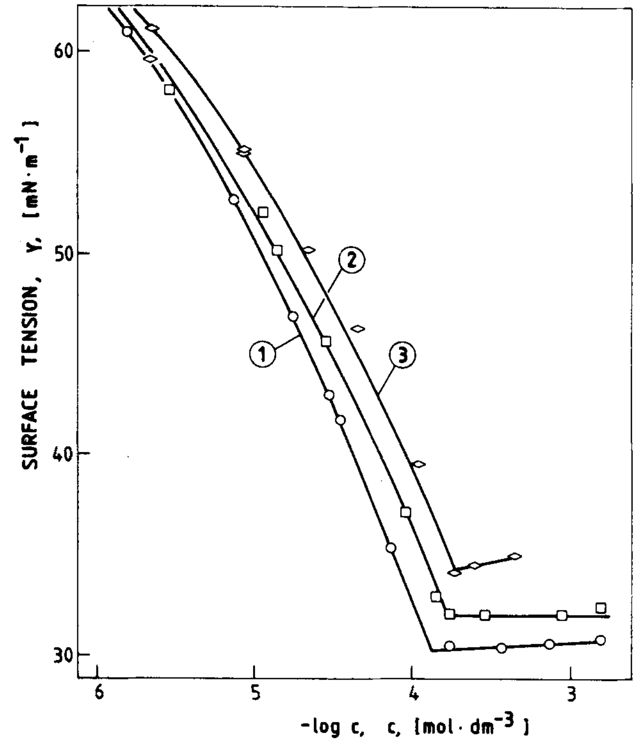


FIG. 3. The surface tension (γ) vs logarithm of molar concentration (log c) of solutions of oxyethylenated 2-n-nonyl-5-hydroxymethyl-5-ethyl-1,3-dioxane with: 1, 7.08; 2, 9.84; 3, 15.0 units of EO/molecule.

In order to assess the surface activity of the compounds, the surface tensions of their aqueous solutions were measured. Examples of surface tension isotherms are shown in Figures 2 and 3. It can be seen that the effects of the length of the alkyl chain (Fig. 2) and of the length of the polyoxyethylene chain (Fig. 3) upon the surface properties are competitive, similarly to the polyoxyethylenated aliphatic alcohols. All compounds substantially reduce the surface tension of water. In Table 2 are collected the $\gamma_{min}$ values, e.g., the surface tensions measured close to cmc. At the constant length of alkyl chain, $\gamma_{min}$ values increase with increasing length of polyoxyethylene grouping, similar to the oxyethylenated aliphatic alcohols. Some data are collected in Table 3, also for oxyethylenated cyclic acetal derivatives (2,4). As is seen, the surface tensions $\gamma_{min}$ are very similar to those of oxyethylenated 2-alkyl-4-hydroxymethyl-1,3-dioxolanes (2) and markedly smaller than the respective values for oxyethylenated 2-alkyl-5,5-bis(hydroxymethyl)-1,3-dioxanes (4).

The values of cmc determined from the surface tension isotherms are also presented in Table 2. As expected, the cmc values get smaller the longer are the alkyl chains and the shorter are the polyoxyethylene chains. The cmc's are smaller than those measured for oxyethylenated 2-alkyl-4-hydroxymethyl-1,3-dioxolanes (2) or for oxyethylenated 2-alkyl-5,5-bis(hydroxymethyl)-1,3-dioxanes (4) (Table 3). This increase in surface activity should account for the presence of the $C_2H_5$ group at C-5 of the 1,3-dioxane ring. The ethyl group is introduced into the molecules of cyclic acetals (III) with

TABLE 3

Cmc and $\gamma_{min}$ Values of Oxyethylenated Cyclic Acetal Derivatives

| Surfactant composition | | | | | |
|---|---|---|---|---|---|
| | | EO content | | cmc<br>(mol dm$^{-3}$) | γ min<br>(m N m$^{-1}$) |
| Hydrophobic intermediate | R | n | wt % | | |
| 2-Alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxane | n-$C_7H_{15}$ | 7.21 | 56.5 | $1.20 \times 10^{-3}$ | 29.6 |
| | | 9.85 | 64.0 | $1.23 \times 10^{-3}$ | 32.2 |
| | n-$C_9H_{19}$ | 7.08 | 53.4 | $1.35 \times 10^{-4}$ | 30.2 |
| | | 9.84 | 61.4 | $1.70 \times 10^{-4}$ | 32.0 |
| | n-$C_{11}H_{23}$ | 7.23 | 51.5 | $2.04 \times 10^{-5}$ | 30.4 |
| | | 9.97 | 58.4 | $2.69 \times 10^{-5}$ | 32.2 |
| 2-Alkyl-4-hydroxymethyl-1,3-dioxolane[a] | n-$C_7H_{15}$ | 6.82 | 59.8 | $2.2 \times 10^{-3}$ | 29.4 |
| | | 9.91 | 68.3 | – | 34.5 |
| | n-$C_9H_{19}$ | 6.90 | 57.3 | $5.2 \times 10^{-4}$ | 31.2 |
| | | 10.01 | 66.1 | $1.28 \times 10^{-3}$ | 35.2 |
| | n-$C_{11}H_{23}$ | 7.03 | 54.5 | $8.13 \times 10^{-5}$ | 32.6 |
| | | 9.95 | 62.9 | $9.55 \times 10^{-5}$ | 35.8 |
| 2-Alkyl-5,5-bis(hydroxymethyl)-1,3-dioxane[b] | n-$C_7H_{15}$ | 7.0 | 55.6 | $6.2 \times 10^{-3}$ | 34.6 |
| | | 9.9 | 63.9 | $1.0 \times 10^{-2}$ | 38.8 |
| | n-$C_9H_{19}$ | 7.0 | 52.9 | $9.5 \times 10^{-4}$ | 35.4 |
| | | 9.7 | 60.9 | $2.8 \times 10^{-3}$ | 42.0 |
| | n-$C_{11}H_{23}$ | 7.0 | 50.5 | $2.5 \times 10^{-4}$ | 38.6 |
| | | 9.5 | 58.0 | $7.7 \times 10^{-4}$ | 46.0 |

[a] From (2).
[b] From (4).

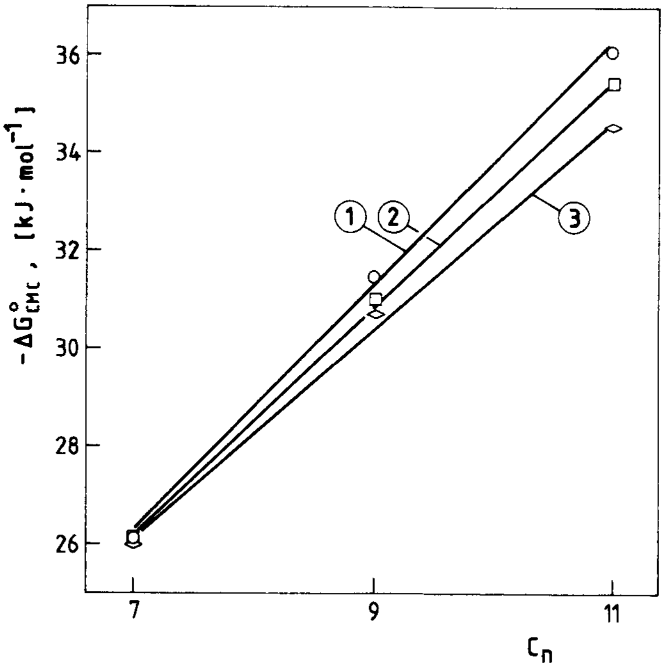


**FIG. 4. Standard free energy of micellization, ($\Delta G^{o}_{cmc}$) as a function of n-alkyl chain length at C-2 carbon atom of the 1,3-dioxane ring: 1, 7; 2, 10; 3, 15 units of EO/molecule.**

1,1,1-tris(hydroxymethyl)propane; the use of glycerol or pentaerythritol in the synthesis of cyclic acetals does not provide this possibility.

In order to characterize the micellization process, the standard free energies of micellization, $\Delta G^{o}_{cmc}$, were determined. Although the compounds were polydisperse and the values obtained had rather a qualitative character, they could be used for comparison with similar quantities determined by other authors for oxyethylenated alcohols or alkylphenols (13).

The values of $\Delta G^{o}_{cmc}$ were calculated from the equation (14):

$$\Delta G^{o}_{cmc} = 2.303\ RT\ (\log cmc - \log w)$$

where w is the molar concentration of water. They are presented in Table 2. Figure 4 shows the relationship between $\Delta G^{o}_{cmc}$ and the number of carbon atoms in alkyl chain for each degree of oxyethylenation. From the slopes of the straight lines thus obtained, the increments $\Delta G^{o}_{cmc}$ [$-CH_2-$] which illustrate the contribution of one methylene group in alkyl chains into the total standard free energy of micellization, $\Delta G^{o}_{cmc}$, were calculated.

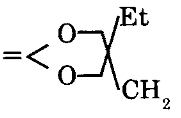
The values of $\Delta G^{o}_{cmc}$ [$-CH_2-$] are 2.50, 2.31 and 2.11 kJ mol$^{-1}$ for the oxyethylenation degree ca. 7, 10 and 15, respectively.

It seemed interesting to compare the values of $\Delta G^{o}_{cmc}$ obtained by us with similar quantities determined for oxyethylenated aliphatic alcohols. Such data were published recently by Ueno et al. (15) for a homologous series of n-alkyl ethers of octaoxyethylene glycol. Appropriate examples and numerical values are presented in Table 4. These data indicate that the surfactants with ca. seven EO units, obtained in this work, correspond (after taking into account differences in increments, $\Delta G^{o}_{cmc}$ [$-CH_2-$]), to oxyethylenated alcohols with eight EO units, but containing about two methylene groups more in the aliphatic chain.

This statement comes from the following assumptions:

$$\Delta G^{o}_{cmc}\ [C_m\ EO_8] \cong \Delta\ G^{o}_{cmc}\ [C_n\ X\ EO_7]$$

where m = n + 2 and X =



Now we assume that the increment of free energy change $\Delta G^{o}_{cmc}$ [$-X-$] is divisible into independent additive contributions from the component parts, i.e., $\Delta G^{o}_{cmc}$ [$-X-$] = $\Delta G^{o}_{cmc}$ [ $<^{o}_{o}\!\!\supset$ ] + $\Delta G^{o}_{cmc}$ [$-Et$] + $\Delta G^{o}_{cmc}$[$-CH_2-$]. If one takes into account that the hydrophilic character of the 1,3-dioxane ring, expressed in terms of standard free energy $\Delta G^{o}_{cmc}$ [ $<^{o}_{o}\!\!\supset$ ] $\cong$ $\Delta G^{o}_{t}$ [ $<^{o}_{o}\!\!\supset$ ] (where $\Delta G^{o}_{t}$ means standard free energy for transfer from aqueous solution to pure liquid phase), is 2.26 ± 0.36 kJ mol$^{-1}$ (16) and hence nearly balances the negative value of increment $\Delta G^{o}_{cmc}$ [$-CH_2-$] of the "excessive" (with respect to alcohols) methylene group at C-5, then the conclusion is that the whole difference of values of $\Delta G^{o}_{cmc}$ between oxyethylenated alcohols and the present compounds is because of the presence of the ethyl group in 1,3-dioxane derivatives (IV). In other words, the isolated $C_2H_5$ group in compounds (IV) seems to contribute to the micellization process similarly to the 2–2.5-$CH_2$- groups in straight aliphatic chains.

When characterizing the surface properties of surfactants (IV) one should also bear in mind that the hydrophobic intermediates are mixtures of di-

TABLE 4

**Standard Free Energy of Micellization**

| Oxyethylenated alcohols[a] | | Oxyethylenated derivatives (IV)[b] | |
|---|---|---|---|
| Composition | $\Delta G^{o}_{cmc}$ (kJmol$^{-1}$) | Composition | $\Delta G^{o}_{cmc}$ (kJmol$^{-1}$) |
| $C_9EO_8$ | -24.35 | $C_7EO_{7.21}$ | -26.2 |
| $C_{11}EO_8$ | -30.06 | $C_9EO_{7.08}$ | -31.5 |
| $C_{13}EO_8$ | -36.03 | $C_{11}EO_{7.23}$ | -36.1 |
| $\Delta G^{o}_{cmc}$ [$-CH_2-$] = -2.84 kJmol$^{-1}$ | | $\Delta G^{o}_{cmc}$ [$-CH_2-$] = -2.50 kJmol$^{-1}$ | |

[a] From (15) for individual compounds.
[b] Polydisperse products.

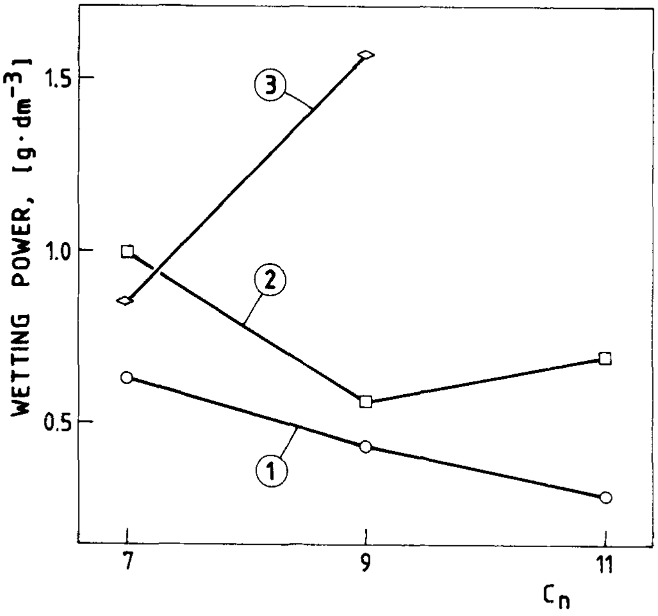


**FIG. 5. Wetting power (gdm$^{-3}$) vs n-alkyl chain length in oxyethylenated 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes: 1, 7; 2, 10; 3, 15 units of EO/molecule.**

astereoisomers. In our earlier paper (17), it was shown that the surface activity (expressed in terms of the standard free energy of adsorption) of *trans*-2-alkyl-5-hydroxy-1,3-dioxanes is by ca. 1.7-1.9 kJ/mol higher than that of respective *cis*- isomers. At present, however, we cannot guess whether or to what extent the oxyethylenated derivatives of *cis*- and *trans*-2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes differ in their surface activity.

*Performance properties.* Among the performance properties, we have studied the wetting and foaming properties of surfactants (IV). A good ability to wet textiles is an important quality of nonionic surfactants. The effects of length of both the aliphatic chain and polyoxyethylene grouping upon the wetting properties are shown in Figure 5. The wetting ability is expressed as the concentration of solution necessary to wet a standard cotton disc in 100 s.

Figure 5 shows that the wetting behavior of surfactants (IV) decreases along with increasing size of the polyoxyethylene chain. The alkyl chain optimum length of the 7-, 10- and 15-EO derivatives decreases from the n-undecyl to the n-heptyl derivative, respectively. The most effective wetting agent is the n-undecyl derivative containing ca. 7 EO units in the molecule.

The foaming ability was determined according to Polish Standard PN-74/C-04801, which uses the Ross-Miles method. Solutions of the surfactants containing 7 or 10 EO units/molecule were used. The concentration was 0.1 wt %. Distilled water and 3.57 mval CaO+MgO hard water were used.

As shown in Figure 6 the highest foam at the beginning of experiments (0 s) was formed by the products with n-nonyl chain, regardless of the experimental parameters.

The stability of foams, measured as their height after 300 s, was found, however, to depend on the parameters of measurements. In distilled water, the

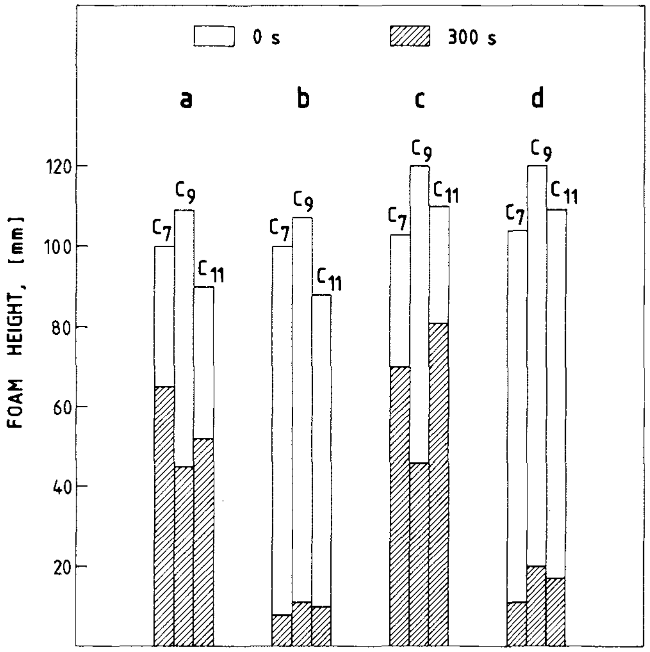


**FIG. 6. Foam height over 0.1 wt. % aqueous solution of oxyethylenated 2-alkyl-5-hydroxymethyl-5-ethyl-1,3-dioxanes: a, EO derivative (20 C, distilled water); b, EO$_7$ derivative (50 C, 3.5 mval CaO + MgO hard water); c, EO$_{10}$ derivative (20 C, distille water); d, EO$_{10}$ derivative (50 C, 3.57 mval CaO + MgO har water).**

stability of foams was quite high; the lowest value were recorded for n-nonyl derivatives (for both oxyethylenation degrees, Fig. 6). Water hardness and highe temperature significantly affected the foam stabilit but not the initial foam value, similar to the oxyethylenated alcohols (18). Under these conditions, th nonyl derivatives gave more stable foams, contrary t those at 20 C in distilled water.

It is interesting that among oxyethylenated straigh chain alcohols, the highest foam at the beginning of a experiment (0 s) was found for decyl derivatives (18 Hence, it appears that the foaming ability has bee shifted back by a methylene group on the scale of alky chain length for the present group of surfactants (IV)

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