

New Family of Nonionic Gemini Surfactants. Determination and Analysis of Interfacial Properties

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The interfacial properties of a new family of nonionic surfactants derived from alkyl glucosides were studied. The physicochemical parameters of these dimeric compounds were compared with those of their monomeric counterparts. The effect of the position of the linkage, the anomeric configuration, the spacer functionality, and the spacer type (rigid or flexible) on the behavior of these surfactants was analyzed for a short-chain (butyl) series of compounds. Slight structural variations have a significant influence on their properties. The maximum length of the hydrophobic chains for obtaining gemini surfactants with improved efficiencies compared to those of the starting monomeric alkyl glucosides was estimated.

Introduction

Alkyl glycosides are biosynthesized as glycolipids by microorganisms from rhamnose, sophorose, and trehalose. They are currently prepared in industry from long-chain alcohols and carbohydrates. As these compounds display surfactant properties, they are gradually replacing other known nonionic surfactants in industry, on account of their excellent biodegradability and the absence of toxic effects. Food elaboration, polymer manufacture, and solubilization of biological membranes are some of the wide spectrum of applications of alkyl glycosides.

The carbohydrate polar head has multiple hydroxyl groups with defined orientations, allowing for the formation of strong cooperative hydrogen bonds between the surfactant molecules. This fact, together with the hydrophobic interactions between the long hydrocarbon chains, leads to spontaneous association in water.¹

In the past few years, a new class of surfactants called gemini, carrying two hydrophobic chains and two hydrophilic groups connected by a spacer, has been prepared. These dimeric compounds show improved surfactant properties when compared to monomer surfactants.²

The interesting properties of gemini surfactants prompted us to design and synthesize a new type of amphiphilic molecules, composed of two alkyl glucosides linked through a spacer. Our use of the ecologically safe alkyl glycoside surfactants as monomers is mainly due to their biodegradability and the fact that they can be easily prepared starting from renewable raw materials such as carbohydrates and long-hydrocarbon-chain alcohols.

Two molecules of butyl α -D-glucopyranoside (**1**) were connected through ester linkages.^{3,4} Selective protection/deprotection sequences led to the synthesis of gemini surfactants linked through O-2 or O-6 of the sugar moieties by different types of spacers. We have also prepared a gemini surfactant containing β -anomers and changed the spacer functionality from ester to ether.⁵

The dimers reported here constitute a new family of gemini surfactants. The influence of structural features on their behavior was analyzed through changes in interfacial properties, including the critical micellar concentration (cmc); the surface excess concentration at surface saturation (Γ_m), a useful measure of the effectiveness of adsorption; the area per molecule at the interface at surface saturation (a_m^s); the standard free energy of micellization (ΔG_{mic}°); the standard free energy of adsorption (ΔG_{ads}°); the negative logarithm of the bulk liquid-phase concentration of surfactant required to depress the surface tension of the solvent by 20 mN/m (pC_{20}), a good measure of the efficiency of the adsorption of the surfactant; and the cmc/ C_{20} ratio, a convenient way of measuring the relative effects of structural factors on the micellization and adsorption processes.

The main purpose of this type of analysis is to compare the dimers with the corresponding monomers and to study the influence of different structural features to evaluate the surfactant efficiency of the new gemini compounds prepared.

The use of two carbohydrates as polar heads of nonionic gemini surfactants connected through a spacer allows for great structural variability. In this paper, we report on the interfacial properties of this new type of surfactants and discuss the influence of the linkage position between the spacer and the carbohydrate moieties, the rigid or flexible nature of the spacer, the anomeric configuration of the alkyl glucoside, the functional group linking the spacer to the carbohydrate, and the length of the alkyl chain.

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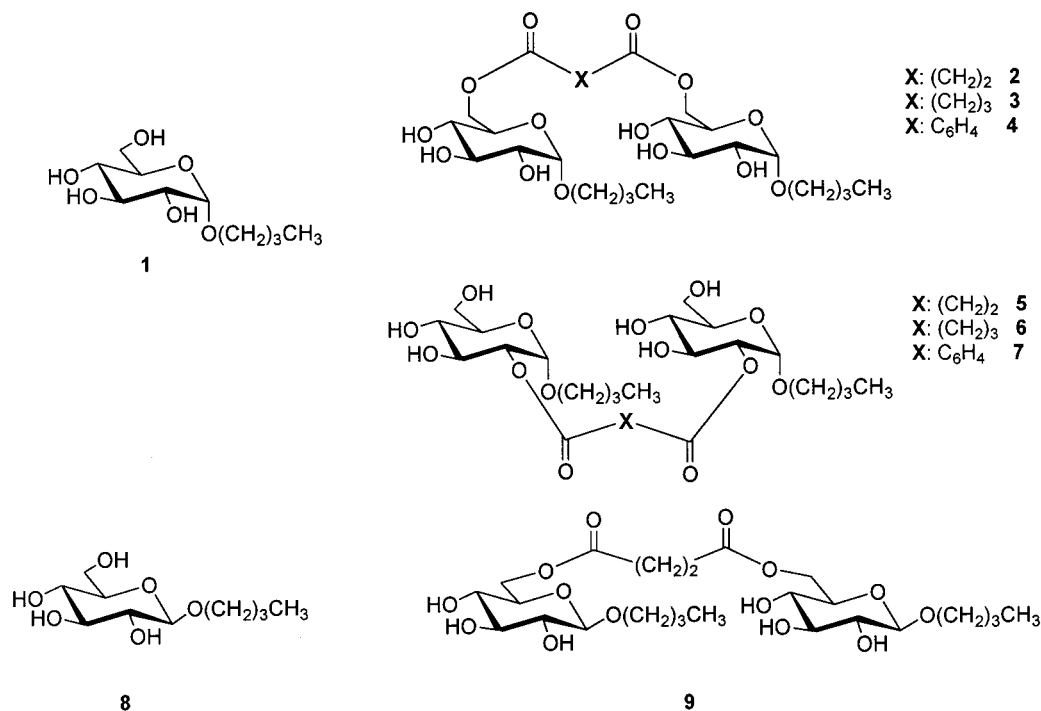
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**Figure 1.** Structures of ester-linked gemini surfactants from butyl glucopyranosides.**Table 1.** *n*-Butyl D-Glucopyranoside Derivatives

compound	spacer	linked through	cmc (mM)	γ_{cmc} (mN/m)	Γ_m (mol/cm ² x 10 ¹⁰)	a_m^s (Å ²)	ΔG_{mic}° (kJ/mol)	ΔG_{ads}° (kJ/mol)	pC ₂₀	cmc/C ₂₀	HLB
1	—	—	75 ± 2	47.4	3.2	52 ± 3	-16.4	-23.3	1.2	1.3	16.2
2	succinyl	O-6	7.2 ± 0.4	46.7	2.0	82 ± 7	-22.2	-34.7	2.5	2.2	16.8
3	glutaryl	O-6	13.1 ± 0.6	40.5	2.7	62 ± 9	-20.7	-32.3	2.3	2.9	16.2
4	terephth	O-6	—	—	—	—	—	—	—	—	15.3
5	succinyl	O-2	2.0 ± 0.2	44.4	2.3	72 ± 6	-25.3	-35.5	2.9	1.7	16.8
6	glutaryl	O-2	3.1 ± 0.3	51.7	1.8	92 ± 10	-24.3	-34.2	2.4	0.8	16.2
7	terephth	O-2	15.8 ± 0.4	46.7	1.9	87 ± 7	-20.2	-33.2	2.2	2.4	15.3
8 (β)	—	—	110 ± 3	42.2	3.4	48 ± 6	-15.4	-22.8	1.2	1.7	16.2
9 (β)	succinyl	O-6	13.0 ± 0.5	46.8	1.8	92 ± 9	-20.7	-33.2	2.1	1.7	16.8
10	ether	O-6	8.9 ± 0.3	38.6	1.8	92 ± 11	-21.6	-40.0	2.7	4.2	15.0

^a Nonsoluble.**Table 2.** Alkyl Chain Analysis of *n*-Alkyl α -D-Glucopyranosides

compound	alkyl chain	cmc (mM)	γ_{cmc} (mN/m)	Γ_m (mol/cm ² x 10 ¹⁰)	a_m^s (Å ²)	ΔG_{mic}° (kJ/mol)	ΔG_{ads}° (kJ/mol)	pC ₂₀	cmc/C ₂₀	HLB
1	4	75 ± 2	47.4	3.2	52 ± 3	-16.4	-23.3	1.2	1.3	16.2
11	8	10 ± 1	36.4	3.2	53 ± 6	-21.4	-32.7	2.6	4.5	13.1
12	12	2.3 ± 0.3	36.9	3.9	43 ± 4	-25.0	-32.0	3.9	1.8	11.0
13	14	0.8 ± 0.2	48.8	3.9	43 ± 4	-27.7	-33.1	3.2	1.1	10.2

Results and Discussion

Short-Chain Dimers. Butyl α -D-glucopyranoside (**1**) was employed as the starting material for the first series of this new family of nonionic gemini surfactants. The monomers were linked through O-2 or O-6 of the glucose moieties. Succinic and glutaric acids were used as flexible spacers, and terephthalic acid was used as a rigid spacer.^{3,4} The dimeric surfactants prepared are shown in Figure 1, and their interfacial properties are reported in Table 1.

The cmc values of dimeric compounds **2**, **3**, and **5–7** are much smaller than those of their monomeric counterparts, and they are therefore more efficient surfactants.

This behavior has previously been observed for cationic gemini surfactants prepared from arginine, which display cmc values about 2 orders of magnitude lower than those of the corresponding single-chain homologues.⁶ The cmc values of the new nonionic gemini compounds **2**, **3**, and **5–7** are 5–39 times lower than that of compound **1**. It is

important to note here that butyl glucosides are poor surfactants and they are currently used as hydrotropes, whereas these synthetic dimeric compounds display cmc values of the same order of magnitude as that of *n*-octyl α -D-glucopyranoside (**11**, Table 2). Recently, it has been shown that the incorporation of short-chain surfactants into household and personal-care formulations presents multiple benefits, taking into account their lower toxicity when compared to long-chain surfactants.⁷

The linkage position on the carbohydrate moiety produces relatively small changes in the cmc values. However, from Table 1, it emerges that compounds **5** and **6**, which are linked through O-2, present lower cmc values

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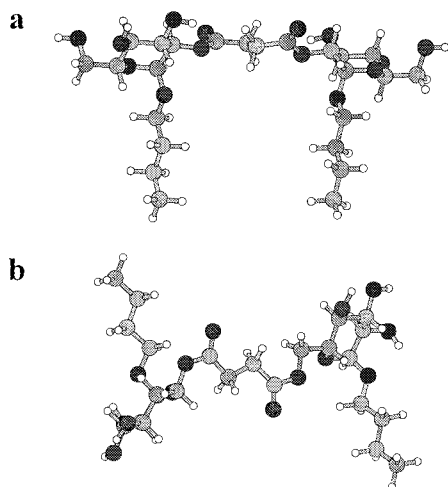


Figure 2. Optimized structures for (a) 1,4-bis[2-*O*-(*n*-butyl α -D-glucopyranosid)] succinate (**5**) and (b) 1,4-bis[6-*O*-(*n*-butyl α -D-glucopyranosid)] succinate (**2**).

than their isomers linked through O-6 (compounds **2** and **3**, respectively). A different behavior is also observed for the dimers linked through the rigid terephthalic spacer: the O-6-linked dimer **4** is insoluble in water, whereas its O-2 isomer **7** is soluble enough to allow for the determination of its interfacial properties.

The nature of the spacer also influences the cmc values. A change in the position of attachment from O-6 to O-2 leads to a product with a 3-fold-lower cmc for the succinyl derivatives **2** and **5**, and the glutarate derivative **6** has a cmc value 4 times smaller than that of **3**. Because compound **4** is insoluble in water, a comparison between terephthalates **4** and **7** is not possible. To explain the observed behavior, conformational features were analyzed through preliminary molecular modeling.⁸ Succinate **5** (Figure 2a) and terephthalate **7**, exhibited very ordered conformations, with the two alkyl chains parallel to each other and orthogonal to the plane formed by the carbohydrate moieties and the linker. This arrangement could improve intermolecular interactions and therefore the formation of micelles, as the sugar moieties would be more exposed to the solvent.

Regarding the dimeric compounds containing flexible spacers, few data can be obtained from the literature. For cationic dimeric surfactants, it has been reported that the cmc values reach a maximum when the spacer contains 5 or 6 methylene groups.² This statement is related to the distribution of distances between polar heads in the interface and to the shape of the aggregates formed from the different lengths of alkyl chains.

This effect appears evident if we compare cmc values between compounds **2** and **3** and, on the other hand, between compounds **5** and **6**. In both cases, the cmc values are lower for the succinyl derivatives **2** and **5** than for the glutaryl derivatives **3** and **6**.

On the other hand, compound **7** shows the cmc highest value of the three dimers linked through O-2, suggesting that rigid spacers produce changes in the molecular structure of the gemini surfactant and modify its behavior in solution. This result is interesting as stable bilayer membranes have been generated from monomeric amphiphiles by restricting their conformational mobility through the incorporation of rigid aromatic segments.⁹

This conformational restriction is reinforced for compounds **4** and **7** because the terephthalic moiety is linking two monomers to build the dimeric structure.

In general, for both ionic and nonionic surfactants, the value of the surface area per molecule, a_m^s , appears to be determined by the area occupied by the hydrated hydrophilic group, rather than by the hydrophilic group, because the chains in typical ionic or nonionic surfactants with hydrophilic groups at one end do not lie flat on an interface but rather are somewhat tilted with respect to it. If a second hydrophilic head is present in the molecule, the a_m^s value increases.¹⁰ The a_m^s values of the dimers **2**, **3**, and **5–7** (Table 1) were found to be up to 60% higher than that of the monomer, in accord with previous studies of ionic gemini surfactants where a_m^s was found to be larger for gemini surfactants. Errors in a_m^s determinations do not allow for further comparisons.

The excess of surface concentration (Γ_m) decreases as a_m^s increases. The free energy of micellization and the free energy of adsorption (ΔG_{mic}° and ΔG_{ads}° , respectively) of the dimers are considerably lower than those of the monomer, indicating that both processes are thermodynamically favored. A similar improvement is observed for pC₂₀, showing that the surfactant concentration at which the surface tension is decreased by 20 mN/m is strongly reduced for the dimeric compounds **2**, **3**, and **5–7**.

From Table 1, it is also interesting to compare the cmc/C₂₀ ratio. The monomer presents a value lower than those of the dimers linked through O-6 but similar to those of the O-2-linked dimers. In the latter, adsorption would therefore be inhibited with respect to micellization, whereas for the dimers linked through O-6, the favored process is adsorption. This result illustrates the effect of subtle structural differences (such as the position of attachment of the spacer) on the interfacial properties of dimeric surfactants.

A higher cmc/C₂₀ ratio indicates that the hydrophobic groups are less suitably oriented for accommodating themselves in the interior of the micelles. In general, for all type of surfactants, adsorption on the surface of an aqueous solution is preferred over the formation of micelles.¹¹ The larger cmc/C₂₀ values for the gemini surfactants compared to conventional surfactants indicate that the gemini surfactants have a greater preference to be adsorbed at the water–air interface relative to their preference to form micelles than do the conventional surfactants. This might be due to the steric inhibition of convex micelle formation by the two hydrophobic groups of the gemini surfactant.¹² The relatively favored micellization process for O-2-linked dimeric surfactants **5** and **6** provides evidence of a higher order in their molecular structures. On the other hand, the structures of the dimeric surfactants linked through O-6 are less ordered, and for them, adsorption is the preferred process. These findings are in complete agreement with the preferred conformations obtained by molecular modeling⁷ (Figure 2b).

Additional experimental data in accordance with this hypothesis was provided by ¹³C NMR spectroscopy. Whereas O-6-linked compounds **2–4** showed similar spectra either in CD₃OD or in CDCl₃, the gemini compounds **5–7** linked through O-2 with rigid and flexible spacers gave the expected ¹³C NMR spectra only in deuterated methanol. When the spectra were recorded in CDCl₃, only the resonances corresponding to the alkyl-chain carbon atoms could be seen, suggesting the formation

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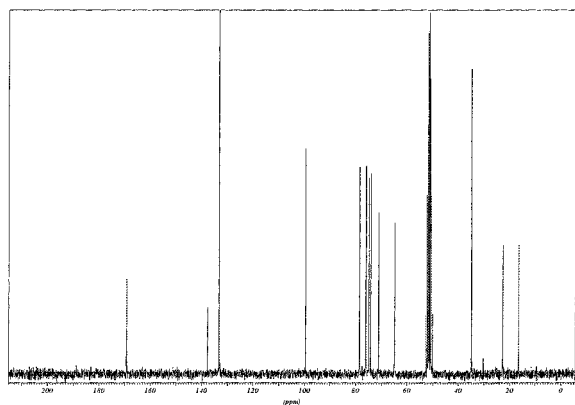


Figure 3. Compound 7 dissolved in CD₃OD.

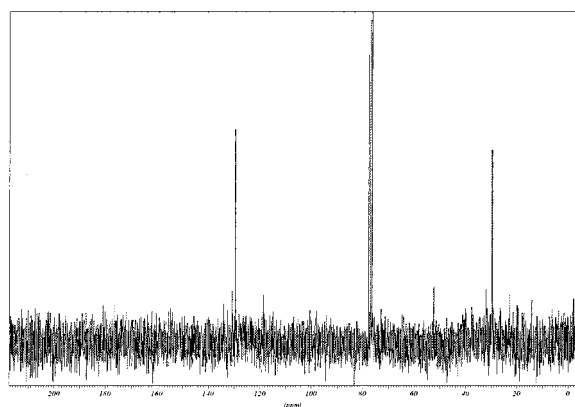


Figure 4. Compound 7 dissolved in CDCl₃ (inverse micelles).

of inverse micelles.¹³ As an example, the ¹³C NMR spectra in CD₃OD and CDCl₃ of compound 7 are shown in Figures 3 and 4, respectively.

In Figure 3, the main resonances appear at 166.8 ppm (COO⁻ of the spacer), 135.3 and 130.8 (Ph), 97.1, 76.1, 73.6, 72.5, 71.8 (C1–C5 of the carbohydrate moieties), 68.7 (CH₂O), 62.5 (C6 of glucopyranose), 32.5, 20.3, and 14.0 (alkyl chain). In contrast, in the spectrum recorded in CDCl₃, only the resonances corresponding to the hydrophobic chains are observed.

We have extended this study to β-anomers, taking into account literature reports on the effect of anomeric configuration on interfacial properties.¹⁴ The dimeric compound of *n*-butyl β-D-glucopyranoside (**8**) linked through O-6 (succinyl spacer) was chosen for comparison (compound **9**, Figure 1, Table 1).⁵

n-Butyl β-D-glucopyranoside (**8**) displayed a higher cmc value than the corresponding α-anomer **1**. The dimers **2** and **9** showed the same relative behaviors, illustrating the influence of the change of the butyl chain from the α to the β position on the cmc. The different values of Γ_m , a_m^s , ΔG_{mic}° , ΔG_{ads}° , and pC₂₀ again indicate an important change from the monomer to the dimer (Table 1). For the cmc/C₂₀ ratios, no difference was observed between the β-monomer **8** and the dimer **9** (cmc/C₂₀ = 1.7 for both compounds). This finding changes from that observed for the α-anomer (compound **2**), where the cmc/C₂₀ ratio is 2.2 and, therefore, micellization is inhibited relative to adsorption. This difference suggests that the β-dimer

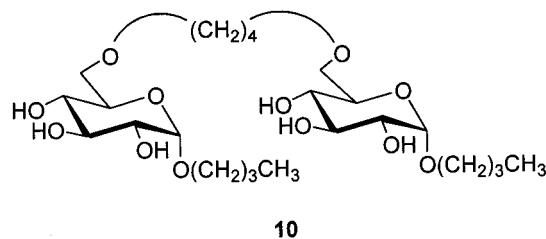


Figure 5. Structure of ether-linked gemini surfactant from α-butyl glucopyranoside.

presents an ordered structure that allows for better packing of the alkyl chains inside the micelles formed.

The two carbohydrate molecules forming the polar heads can be assembled through different functional groups. An analogue of compound **2** was prepared in which the ester groups were replaced by ether groups with the same number of carbon atoms (compound **10**, Figure 5).⁵ This change led to a dimeric surfactant displaying a cmc value similar to that of the ester **2** (Table 1). The cmc/C₂₀ ratio for compound **10** is, however, 2 times higher than that for compound **2**, suggesting that, for the ether-linked compound, the adsorption process is favored. This behavior would be a consequence of the increased rotational freedom about the σ carbon–carbon bonds of the spacer.

The environmental fate of surfactants is inextricably linked to their biodegradation behavior. Rapid and complete biodegradability, the most important requirement for environmentally compatible surfactants, can be expected for the gemini compounds prepared here on the basis of the nature of the starting materials.¹ The biodegradation of **7**, a representative compound of this new family of gemini surfactants, was tested by internationally used and accepted standard methods.¹⁵ The result showed that the dimeric compound is readily biodegradable.

Medium- and Long-Chain Dimers. The outstanding results obtained for the dimeric butyl glucosides led us to prepare similar compounds from longer-chain alkyl glucosides, to determine whether a similar improvement in surfactant properties (monomer to dimer) could be observed. Therefore, we prepared three dimeric surfactants linked through O-6 using succinic acid as the spacer from the alkyl glucopyranosides of C-8, C-12, and C-14 (compounds **14–16**, respectively, Figure 6).¹⁶

The interfacial properties of the monomers are given in Table 2, and those of the new dimers are reported in Table 3. The results for the C-14 derivative **16** were quite disappointing, because the dimer displayed higher cmc values than the starting monomer. The adsorption and micellization free energies were higher than those of the monomer, clearly indicating a deviation from the behavior observed in the butyl series.

The a_m^s values of the dimers **14–16** (Table 3) were up to 2 times higher than those of the corresponding monomers **11–13** (Table 2), as was observed for the butyl series.

The log cmc values of the monomers **1** and **11–13** decrease linearly¹⁷ with the alkyl chain length (Table 2). On the other hand, this behavior is not observed for the dimeric compounds. It is difficult to correlate the cmc or log cmc values of the gemini compounds **2** and **14–16**

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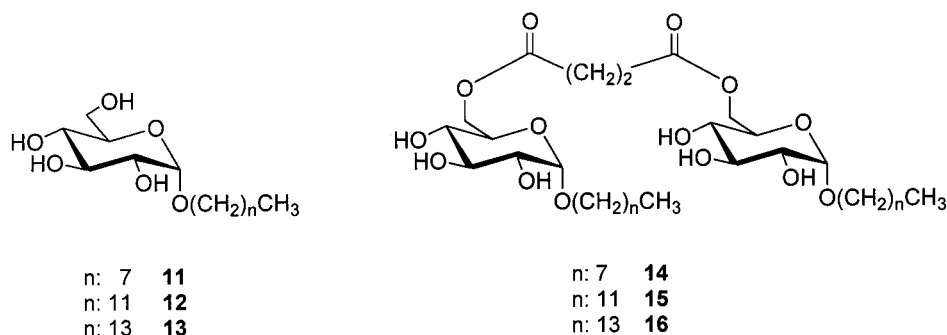


Figure 6. Structures of gemini surfactants from medium- and long-chain alkyl glucopyranosides.

Table 3. Gemini Surfactants of *n*-Alkyl α -D-Glucopyranosides

compound	spacer	linked through	cmc (mM)	γ_{cmc} (mN/m)	Γ_{m} (mol/cm ² × 10 ¹⁰)	a_{m}^{s} (Å ²)	ΔG^{mic} (kJ/mol)	ΔG^{ads} (kJ/mol)	pC ₂₀	cmc/C ₂₀	HLB
2 (<i>n</i> = 4)	succinyl	O-6	7.2 ± 0.4	46.7	2.0	82 ± 7	-22.2	-34.7	2.5	2.2	16.8
14 (<i>n</i> = 8)	succinyl	O-6	1.8 ± 0.2	39.1	2.3	72 ± 13	-25.7	-36.8	3.0	1.9	13.5
15 (<i>n</i> = 12)	succinyl	O-6	3.4 ± 0.3	46.7	2.1	79 ± 15	-24.0	-34.9	2.6	1.3	11.6
16 (<i>n</i> = 14)	succinyl	O-6	2.6 ± 0.3	54.4	1.8	92 ± 14	-24.7	-33.3	2.5	0.8	10.8

with the alkyl chain length. However, it is useful to plot the $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio vs the number of carbon atoms in the alkyl chain (Figure 7). This relationship gives an idea of the improvement in surfactant efficiency of the gemini compounds in comparison with their monomeric counterparts.

The best $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio is 10.4 for the C-4 (compounds **1** and **2**). For C-8 (compounds **11** and **14**), an improvement is still observed, but the ratio is lower (5.5). On the other hand, the $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio for the C-12 (compounds **12** and **15**) is 0.68, indicating that the dimer is a poorer surfactant than the starting monomer. The addition of two methylene groups does not produce a significant change (compounds **13** and **16**).

A preliminary explanation is related to the cmc values of known traditional (monomeric) surfactants containing a long alkyl chain as their hydrophobic group. The cmc value decreases continuously with the addition of a methylene group to the alkyl chain, but when the number of carbon atoms approaches to 16, this effect is no longer observed.

For very long chains (C₁₆–C₁₈), there is a transition to a coiled state over certain chain lengths, as a result of hydrophobic bonding between parts of the chain itself. Such intramolecular hydrophobic bonding will reduce the effect of intermolecular hydrophobic bonding on transfer to an organic medium or dimerization. This effect is called self-coiling.¹⁸

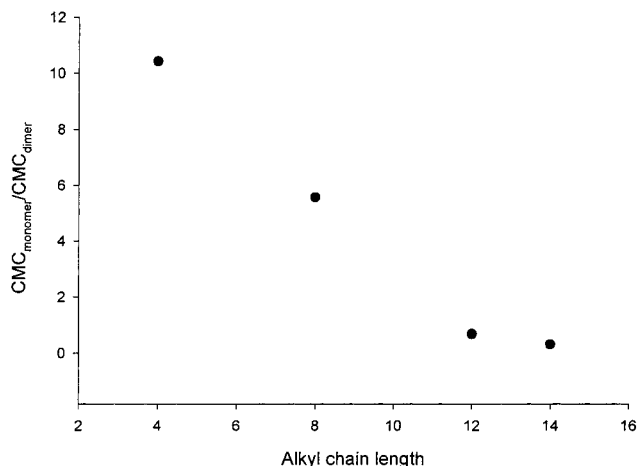


Figure 7. $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio vs alkyl chain length.

On the other hand, a similar anomalous behavior was reported¹⁹ for ionic dimeric surfactants. The cmc values of cationic and anionic dimeric surfactants with alkyl chains of more than 16 and 12 carbon atoms, respectively, showed deviations similar to those observed with our nonionic dimeric surfactants **14**–**16**.

The $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio could be useful for dimeric surfactants of different types (anionic, nonionic, cationic, amphoteric) in estimating the length of alkyl chain beyond which the self-coiling must be taken into account. When considering the carbohydrate-based gemini surfactants **2** and **14**–**16**, it is clear that self-coiling of alkyl chains occurs beginning with a dodecyl chain.

An alternative explanation for the results obtained might be the formation of submicellar aggregates such as dimers or tetramers.¹⁹ When two gemini monomers are fitted together into a gemini dimer, the extent of intramolecular contact is expected to be somewhat larger than that for single-chain amphiphiles. It has been estimated that 25% of the CH₂ groups would be involved in intramolecular contacts in single-chain amphiphiles and about 60% in gemini compounds.²⁰ Premicellar aggregation would be a consequence of the reduction in area of a gemini dimer compared to two gemini monomers. These areas are a measure of the change in the arrangement of the water molecules due to the presence of the nonpolar *n*-alkyl chain. Despite its coiled configuration, a gemini surfactant in an aqueous medium maintains extensive contact with the solvent. The water molecules closest to the hydrocarbon part of the amphiphile arrange themselves in a more regular fashion.

In premicellar aggregates, the molecules of gemini surfactants are arranged with their hydrophilic groups at opposite ends and their hydrophobic groups oriented toward each other in a manner somewhat similar to a very fine bilayer or lamellar micelle.¹⁰ Therefore, premicellar aggregation would have the effect of reducing the disturbance of the arrangement of water molecules.

From an analysis of the $\text{cmc}_{\text{monomer}}/\text{cmc}_{\text{dimer}}$ ratio plot, it is possible to estimate the critical length of the alkyl chain where these distortions start to operate. The inflection point in the improvement of interfacial proper-

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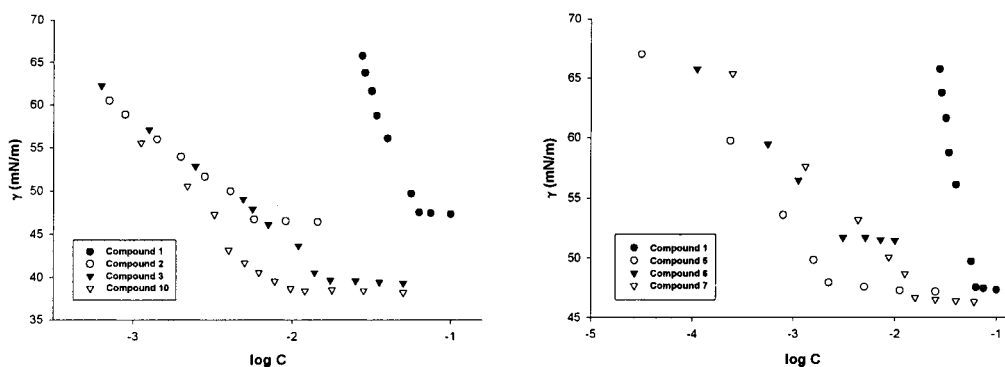


Figure 8. Surface tension (γ) vs log concentration plots for compounds **1–3**, **5–7**, and **10**.

ties for the monomer-to-dimer conversion can be placed between C-8 and C-12, although it appears from Figure 7 that it would be closer to C-12.

Conclusions

It is clear from the above results that more ordered tridimensional structures lead to products with improved surfactant properties. The dimers linked through O-2 in the butyl series displayed better cmc values than did their O-6 isomers, with the difference between the succinyl and glutaryl derivatives probably arising as a consequence of the change in orientation of the alkyl chains produced by the addition of a methylene group in the spacer. As for other gemini surfactants, the use of rigid spacers such as aromatic compounds leads to products with poorer surfactant properties. A change in the anomeric configuration of the glucoside (from α to β) is also reflected in the behavior. The β -dimer compound **9** allows for better packing of hydrophobic chains inside the micelles formed, favoring micellization over adsorption, although the cmc values are higher than those of α -anomers. When the polar heads are assembled through an ether instead of an ester group, a higher cmc/C₂₀ ratio is obtained.

Therefore, we have shown that, for the butyl series, interfacial properties are significantly influenced by slight structural variations in the position of linkage, the anomeric configuration, the linker functionality, and the spacer type (rigid or flexible).

It is widely known that the cmc values of alkyl glucosides decrease with increasing alkyl chain length up to a certain value. The critical length of the alkyl chains needed to prevent self-coiling has been estimated on the basis of the surfactant behavior of gemini surfactants derived from *n*-octyl, *n*-dodecyl, and *n*-tetradecyl glucopyranosides. Knowledge of this parameter is of exceptional significance in obtaining dimeric surfactants with improved interfacial properties compared to those of their monomeric counterparts.

The interesting properties of this new type of amphiphilic compound open the field of their use in personal-care and household formulations, as they are nontoxic, biodegradable, and easily obtained from natural renewable resources. They can be used as minor additives to conventional surfactants, enhancing their properties and thus justifying the added cost. Moreover, carbohydrate moieties allow for the design and synthesis of related families of nonionic gemini surfactants.

Experimental Section

Materials and Methods. Compounds **1–10** were prepared and characterized as previously reported.^{3–5} Octyl α -D-glucopyranoside²¹ (**11**), dodecyl α -D-glucopyranoside²² (**12**), and

tetradecyl α -D-glucopyranoside^{22b} (**13**) were synthesized from glucose. 1,4-bis[6-*O*-(*n*-octyl α -D-glucopyranosid)]succinate (**14**), 1,4-bis[6-*O*-(*n*-dodecyl α -D-glucopyranosid)]succinate (**15**), 1,4-bis[6-*O*-(*n*-tetradecyl α -D-glucopyranosid)]succinate (**16**) were prepared as described previously.¹⁶ Spectra (¹³C NMR) were recorded at 50.13 MHz in CDCl₃ and CD₃OD.

Determination of Interfacial Properties. Air–water surface tensions were measured at 25 °C in a specially adapted tensiometer based on the bubble pressure method.²³ Calibration was performed against a range of standard liquids; excellent agreement with literature values was found.²⁴ Critical micellar concentrations (cmc's) were determined by extrapolation of surface tension vs log concentration curves. All compounds exhibited the typical plots, with an abrupt change in slope at the zone corresponding to the cmc. Plots of γ vs log *C* for several compounds (**1–3**, **5–7**, and **10**) are shown in Figure 8. Other interfacial properties were calculated according to known methods.²⁵ For example, $\Delta G_{\text{ads}}^{\circ}$ and $\Delta G_{\text{mic}}^{\circ}$ were calculated using the equations

$$\Delta G_{\text{ads}}^{\circ} = -\frac{RT \ln C_{\pi}}{55.5} - \pi a_{\text{m}}^{\text{s}} \quad \Delta G_{\text{mic}}^{\circ} = RT \ln \left(\frac{\text{cmc}}{55.5} \right)$$

Modeling. Optimized structures of compounds **2** and **5** (Figure 2) were obtained by the AM1 method.⁷

Biodegradability. The test was carried out as described in ref 15 for a concentration of 30 mg/L of compound **7**. Sodium dodecylbenzene sulfonate and benzoic acid were used as reference standards. After 20 days of adaptation to microbial inoculation, the biodegradation test was performed with control of the abiotic lost, the basal medium used, and the inhibitory effect of the substance tested. After the adaptation period, the product reach a 90.2% degree of biodegradability within 8 days.

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