Ecologically safe alkyl glucoside-based gemini surfactants

Mariano J. L. Castro[a], José Kovensky,[b*] and Alicia Fernández Cirelli[a*]

[a] *Centro de Estudios Transdisciplinarios del Agua (CETA) and Area de Química Orgánica, Facultad de Ciencias Veterinarias, Universidad de Buenos Aires, Av. Chorroarín 280, C1427CWO Buenos Aires, Argentina*

[b] *Laboratoire des Glucides CNRS FRE 2779, Faculté des Sciences, Université de Picardie Jules Verne, 33 rue St. Leu, 80039 Amiens, France*

E-mail: afcirelli@fvet.uba.ar

Dedicated to Professor R. Lederkremer on her 70th Anniversary

Abstract

Gemini surfactants have appeared in the early 1990s as a new type of surfactants with two polar heads and two alkyl tails linked by an spacer. These structural feature give to these type of surfactants unprecedented and better interfacial properties in comparison with their monomeric counterparts. Alkyl glycosides are monomeric non-ionic surfactants prepared in industrial scale from fatty alcohols and carbohydrates. They are gradually replacing the non-ionic surfactants derived from petrochemical materials. The interesting properties of gemini surfactants prompted us ten years ago to design and synthesize gemini surfactants from alkyl glucoside. Butyl, octyl, dodecyl and tetradecyl glucosides were prepared and linked through O-6 or O-2 via succinyl, glutaryl and terephthaloyl spacers. The effect of the position of the linkage, the anomeric configuration of the glucoside, the spacer functionality and the spacer type (rigid or flexible) on the interfacial properties were analized. The physico-chemical parameters of these gemini surfactants were compared with those of their monomeric conterparts. Synergist effects were studied. Molecular modelling and inverse micelle formation are summarized.

Keywords: Gemini surfactants, alkyl glucosides, interfacial properties

Contents

Introduction

Surfactants are one of the most ubiquious and important families of organic compounds. In fact we are living because special kinds of surfactants are present in all our cell membranes. We can find surfactants in different formulations used in a lot of industries like cosmetic, personal care, household, painting, coating, textile, dyes, polymer, food, agrochemical, oils and other applications such waste water treatment. The world production is 10 millions tons per year and most of the products used in every day life are formulations that contain surfactants. Surfactants are included there for their two essential properties, their ability to lower the surface or interfacial tension, and their capacity to solubilize water insoluble compounds.

Soap, the oldest synthetic washing and cleaning agent known, was developed around 2500 BC by Sumerians who also described its use as a washing and cleaning agent. Over the four and a half thousand years which have passed since them, the soap and other synthetic surfactants (anionic, cationic and non-ionic) have undergone constant improvement, but their key structural feature consisting of one polar head and one non polar tail, remained intact until 15 years ago.[1] In the early 1990s a new class of twinned (gemini) surfactants characterized by the presence of two polar heads, charged or uncharged, and two hydrophobic chains linked by a spacer were introduced (Fig. 1).

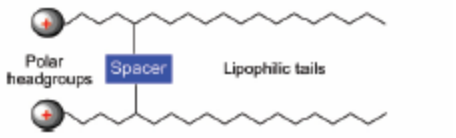


Figure 1. General structural representation of cationic gemini surfactants.

This important structural difference gives to these types of surfactants unprecedented and better interfacial properties in comparison with the usual ones.[1] The critical micellar concentration (CMC) is generally at least one order of magnitude lower than that of the corresponding conventional (monomeric) surfactant. They are 10-100 times more efficient at reducing the surface tension of water and the interfacial tension in oil/water systems.[2]

Nowadays at least two of the most important surfactant manufacturing companies have included into their formulation gemini surfactants to get better interfacial and/or surface tension in their products. One of the latest applications of gemini surfactants is in molecular biology as

potential agent in gene therapy, and their properties as vehicle for gene delivery into cells (transfection) have been reported.[2] All the most important pharmaceutical companies are developing different kind of gemini surfactants suitable for this particular application.

On the other hand, alkyl glycosides are monomeric non-ionic surfactants. Natural alkyl glycosides are biosynthesized as glycolipids by microorganisms from rhamnose, or sophorose. In industrial scale, they are prepared from fatty alcohols and carbohydrates and they are gradually replacing the other known non-ionic surfactants derived from petrochemical industry. Due to 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.[3]

The interesting properties of gemini surfactants prompted us ten years ago to design and synthesize a new type of amphiphilic molecules, composed of two alkyl glucosides linked through a spacer.[6] Our choice 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. Finally, interesting publications of gemini surfactants using carbohydrate as starting material have been reported in the litarature,[3] but they are out of the scope of this review.

1. Synthetic approach

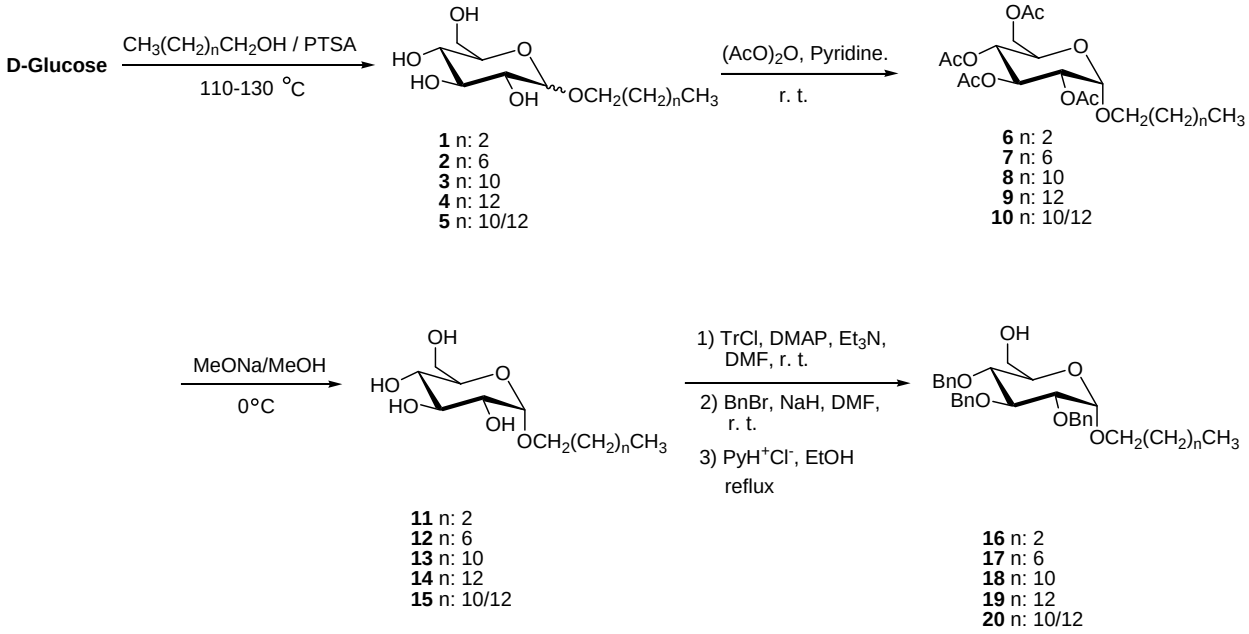
The different industrial applications of surfactants require increasingly the use of natural and renewable starting materials, a reduced number of high yield synthetic steps, a minimization of purification protocols, and final products devoid of toxicity and easily biodegradable in reasonable time.

We therefore started our work preparing alkyl glucosides through Fischer glycosylation.[5] As the thermodynamic ratio of α/β anomers obtained was about 2:1, we rapidly realized that the following condensation reactions would give complex mixtures difficult to analyze. Moreover, the interpretation of physicochemical properties of those mixtures would not be straightforward, and the risk of changes in their composition in different reactions could make difficult to evaluate the contribution of each compound.

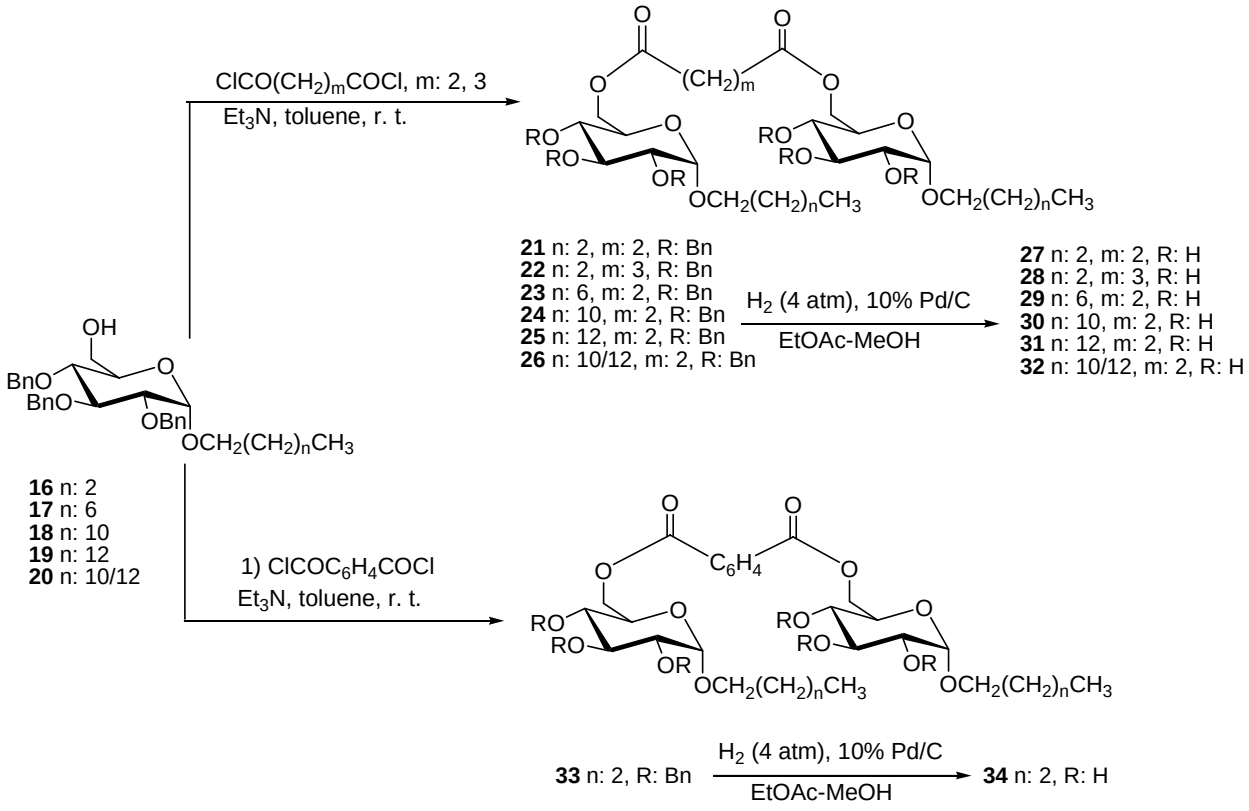
We decided to modify our synthetic strategy including some chromatographic steps in order to obtain pure compounds, allowing a complete characterization of the products and detailed studies of their properties.[4,5] In a second time of our work, we used commercially available alcohols mixtures to adapt our procedures to industrial preparations, and we found synergistic effects for some of them.[4]

The synthesis of our first generation of gemini surfactants is shown in Schemes **1** and **2**. Butyl-, octyl-, dodecyl-, tetradecyl- and dodecyl/tetradecyl-α-D-glucopyranosides **11-15** were obtained from glucose by Fischer glycosidation followed by acetylation, chromatographic purification and deacetylation. Selective tritylation of the 6-OH, benzylation and detritylation

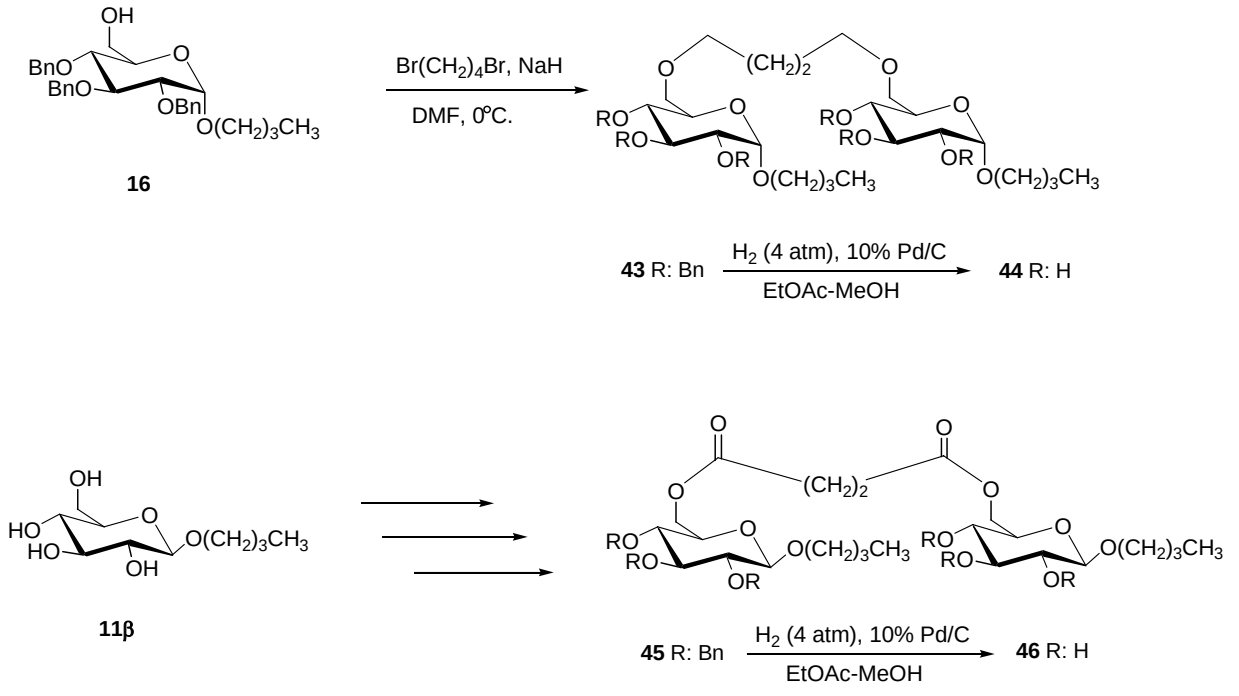
gave the key precursors **16-20** for the condensation step. The monomers were linked through *O*-6 using aliphatic (succinyl, glutaryl) and aromatic (terephthaloyl) dicarboxylic acid chlorides in a parallel combinatorial approach, to give compounds **21-26** and **33**, respectively. A final smooth catalytic hydrogenation lead to gemini surfactants **27-32** and **34**. In both schemes, n = 10/12 denotes the use of a 3:1 commercial mixture of dodecyl:tetradecyl alcohols. This ratio has been verified for each reaction step by mass spectrometry and NMR.



Scheme 1

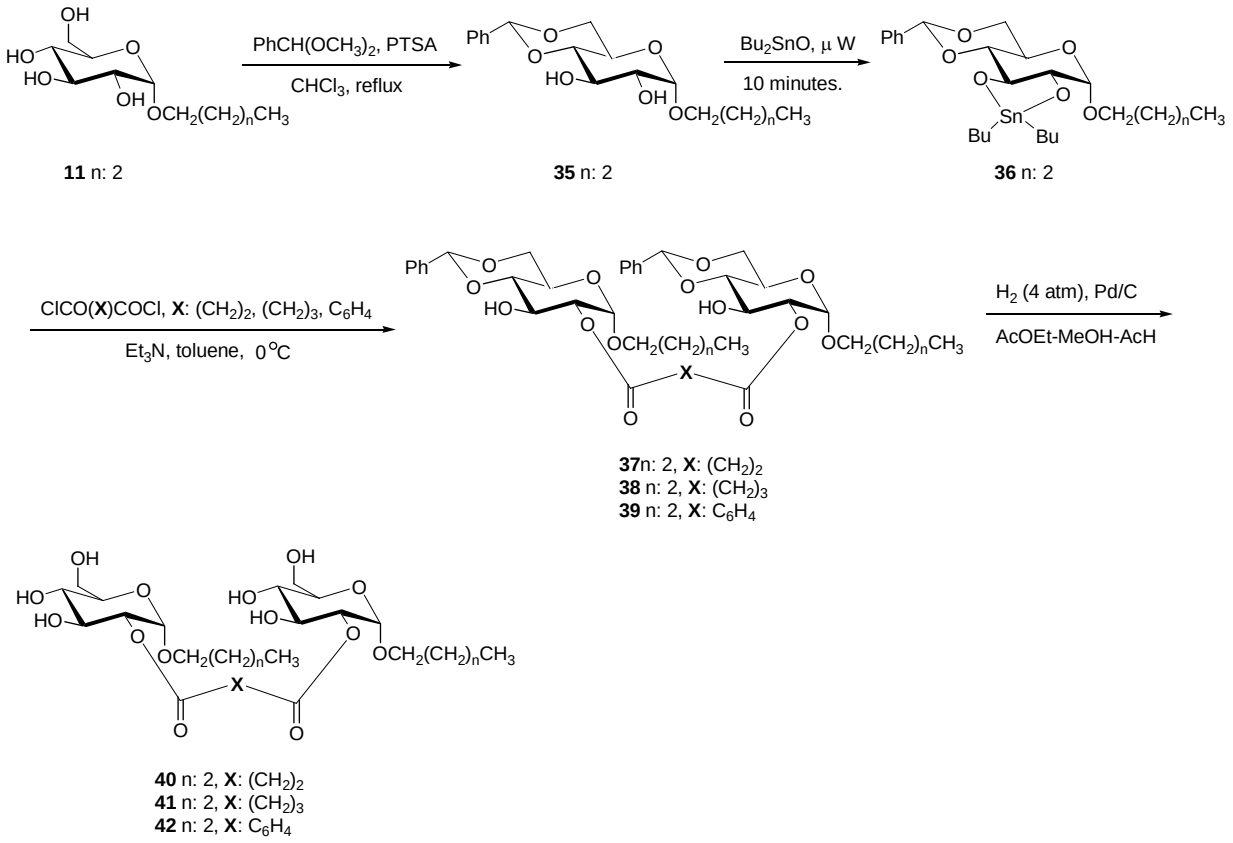


Scheme 2



Scheme 3

A second generation of dimeric surfactants linked through *O*-2 was prepared as shown in Scheme **3**. Hydroxyls 4- and 6- were protected as a benzylidene acetal **35**, and selective activation of *O*-2 was achieved *via* a stannylidene derivative **36**, readily obtained in 10 minutes in a microwave reactor.[7] After coupling with the diacyl chlorides and deprotection, compounds **40-42** were isolated. No traces of tin species were detected on these final products.



Scheme 4

Finally, compounds **44** and **46** were prepared (Scheme **4**) in order to analyze the influence of the spacer functionality (ether instead of ester) and the anomeric configuration, respectively, on surfactant properties.[1]

2. Interfacial properties

2.1 General

The physicochemical parameters of the dimeric surfactants are summarized in Table **1**.[1] As expected similar HLB values are observed for alkyl glucosides and their gemini counterparts, in

spite of the spacer used. However, dimeric compounds show different interfacial properties in comparison with monomeric ones. The usual explanation to this kind of behaviour involves the hydrophobic effect concept and the higher number of alkyl chain carbon atoms per molecule present in the gemini surfactants. It is well known, that an increase in the number of carbon atoms in the alkyl chain of a conventional surfactant increases its surface activity, i.e., decreases its CMC and C_{20} values. This is due to the increased distorsion of the water structure by the increased length of the alkyl chain.

Table 1. Interfacial properties of sugar-based gemini surfactants

Compound	Alkyl Chain	Spacer (linkage)	CMC (mM)	γ_{CMC} (mN/m)	a_m^s (Å^2)	ΔG^o_{mic} (kJ/mol)	ΔG^o_{ads} (kJ/mol)	pC_{20}	CMC/C_{20}	HLB
11	4	---	77.0	47.8	52	-16.3	-23.3	1.22	1.3	16.2
11β	4	-------	110.0	42.2	48	-15.4	-22.8	1.2	1.7	16.2
12	8	---	10.0	36.4	53	-21.4	-32.7	2.7	4.5	13.1
13	12	---	2.3	36.9	43	-25.0	-32.0	3.9	1.8	11.0
14	14	---	0.76	48.8	43	-27.7	-33.1	3.2	1.1	10.2
15	12/14	---	0.42	30.6	38	-29.2	-38.1	3.9	3.5	10.7
27	4	Succinyl (O-6)	8.7	46.7	82	-22.2	-34.7	2.5	2.2	16.8
28	4	Glutaryl (O-6)	9.6	40.5	62	-20.7	-32.3	2.3	2.9	16.2
29	8	Succinyl (O-6)	1.8	39.1	72	-25.7	-36.8	3.0	1.9	13.5
30	12	Succinyl (O-6)	3.4	46.7	79	-24.0	-34.9	2.6	1.3	11.6
31	14	Succinyl (O-6)	2.6	54.4	92	-24.7	-33.3	2.5	0.8	10.8
32	12/14	Succinyl (O-6)	1.30	41.7	76	-26.4	-40.0	3.3	2.5	11.4
34	4	Terephthal. (O-6)	---	---	---	---	---	---	---	15.28
40	4	Succinyl (O-2)	2.0	44.4	72	-25.3	-35.5	2.9	1.6	16.8
41	4	Glutaryl (O-2)	3.1	51.7	92	-24.3	-34.2	2.4	1.5	16.2
42	4	Terephthal. (O-2)	9.7	47.1	87	-21.4	-33.2	2.2	1.5	15.3
44	4	Ether (O-6)	5.6	37.7	92	-22.8	-40.0	2.7	2.7	15.0
46	4	Succinyl (O-6)	13.0	46.8	92	-20.7	-33.2	2.1	1.7	16.8

However, the increase in the length of the chain also decreases the solubility of the surfactant in water. With two hydrophilic groups, the solubility of gemini in water is increased greatly and this permits the gemini molecule to contain many more alkyl chain carbon atoms and still remain water soluble, with the resulting great increase in the surface activity. Comparison of compounds

11 and **40** shows that although, they have almost the same HLB, the interfacial properties are so much better in the gemini compound than in the conventional one, i.e. the CMC is 40-fold lower for the gemini surfactant **40**.

The CMC values of dimeric compounds **27**, **28**, and **40**-**42** are 5-39 times lower than those of their monomeric counterpart (compound **11**), and they are therefore more efficient surfactants. The linkage position on the carbohydrate moiety produces relatively small changes in the CMC values. However, from Table **1**, it emerges that compounds **40** and **41**, which are linked through O-2, present lower CMC values than their isomers linked through O-6 (compounds **27** and **28**, respectively). A different behavior is also observed for the dimers linked through the rigid terephthalic spacer: the O-6-linked dimer **34** is insoluble in water, whereas its O-2 isomer **42** is soluble enough to allow for the determination of its interfacial properties.

The a_m^s values of the dimers **27**, **28**, and **40**-**42** (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. The free energy of micellization and the free energy of adsorption ($\Delta G°_{mic}$ and $\Delta G°_{ads}$, 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 pC_{20}, showing that the surfactant concentration at which the surface tension is decreased by 20 mN/m is strongly reduced for the dimeric compounds prepared from **11**.

We have extended our studies to β-anomers. The dimeric compound **46** was obtained from two molecules of *n*-butyl β-D-glucopyranoside (**11β**) linked through O-6 by a succinyl spacer (Scheme **4**).[9] The monomer **11β** displayed a higher CMC value than the corresponding α-anomer **11**. The dimers **27** and **46** showed the same relative behaviors. The values obtained for the different parameters suggest that the β-dimer presents an ordered structure that allows for better packing of the alkyl chains inside the micelles formed.

An analogue of compound **27** was prepared in which the ester groups were replaced by ether groups with the same number of carbon atoms (compound **44**, Scheme **4**), with little change in CMC.[9] The CMC/C_{20} ratio for compound **44** is, however, 2 times higher than that for compound **27** (Table **1**), 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 results obtained for the derivative **14** 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 log CMC values of the monomers **11** and **12**-**14** decrease linearly with the alkyl chain length. On the other hand, this behavior is not observed for the dimeric compounds, and it is difficult to correlate the CMC or log CMC values of the gemini compounds **27** and **29**-**31** with the alkyl chain length. A preliminary explanation is related to known traditional (monomeric) surfactants: their CMC values decrease 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 result of hydrophobic bonding between parts of the chain itself (self-coiling).[11]

An alternative explanation might be the formation of submicellar aggregates such as dimers or tetramers. When two gemini molecules are fitted together into a dimer, the extent of intramolecular contact is expected to be somewhat larger than that for single-chain amphiphiles. Premicellar aggregation would be a consequence of the reduction in the area of a dimer compared to two gemini molecules. 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. Therefore, premicellar aggregation would have the effect of reducing the disturbance of the arrangement of water molecules.[1]

2.2 Molecular modelling

We have performed preliminary molecular modelling to determinate the preferred conformation of our compounds linked through O-2 and O-6 with different kind of spacers (rigid or flexible). 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 **27** and **40** (Fig. 2), and the glutarate derivative **41** has a CMC value 4 times smaller than that of **28**. Because compound **34** is insoluble in water, a comparison between terephthalates **34** and **42** is not possible. To explain the observed behavior, conformational features were analyzed through preliminary molecular modelling. Succinate **40** and terephthalate **42**, 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. However, compound **34** has shown a disordered conformation of its alkyl tails that could explain its insolubility in water. Compounds **34** and **42** have the same HLB and their interfacial properties are drastically different. Molecular modelling has shown high differences in the spatial conformation of the alkyl chains that would promote a different arrangement of the water network to produce the micellar aggregates.

In general, for all type of surfactants, adsorption on the surface of an aqueous solution is preferred over the formation of micelles. The larger CMC/C_{20} 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. The relatively favored micellization process for O-2-linked dimeric surfactants **40** and **41** 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 modelling.[12]

a b

Figure 2. Optimized conformation of compounds **27** (a) y **40** (b).

2.3 Inverse micelles

As we have shown above, the compounds linked through O-2 have a molecular structure more ordered in comparison with their O-6 isomers, then they can adopt a properly shape into the water system to afford CMC values lower than the compounds linked through O-6. ^{13}C NMR Spectroscopy provided additional experimental data in accordance with this hypothesis. Whereas O-6-linked compounds **27**, **28** and **34** showed similar spectra either in CD_3OD or in $CDCl_3$, the gemini compounds **40**-**42** linked through O-2 with rigid and flexible spacers gave the expected ^{13}C NMR spectra only in deuterated methanol (Fig. 3a). When the spectra were recorded in $CDCl_3$ (Fig 3b), only the resonances corresponding to the alkylchain carbon atoms could be seen, suggesting the formation of inverse micelles.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 (CH_2O), 62.5 (C6 of glucopyranose), 32.5, 20.3, and 14.0 (alkyl chain), Fig.3a. In contrast, in the spectrum recorded in $CDCl_3$, only the resonances corresponding to the hydrophobic chains are observed (Fig. 3b).

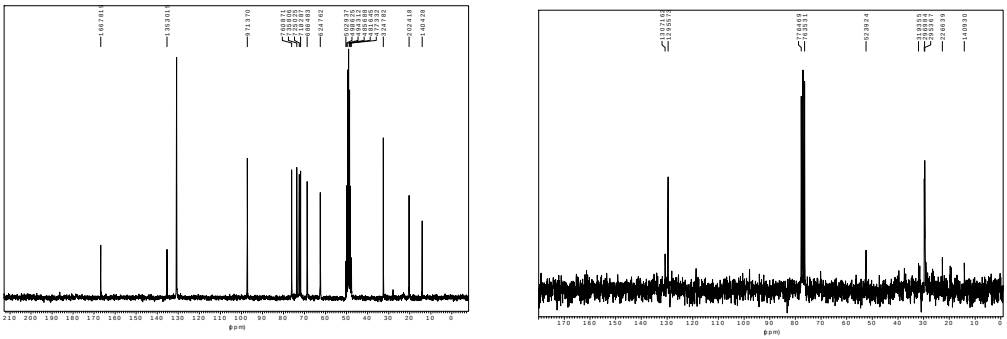


Figure 3. NMR spectra of compound **42** in CD_3OD (a) and in $CDCl_3$ (b).

2.4 Synergistic effects

In view of the outstanding properties exhibited by our family of gemini surfactants, synergistic effects were studied with the aim of simplifying the synthetic procedures. Synergistic effects were analized for the dodecyl/tetradecyl-α-D-glucopyranoside **15** obtained from the commercial

mixture of dodecyl and tetradecyl alcohols and glucose by the described procedure. This commercial mixture is one of the most widely distributed in the market since it is readily available from coconut and palm kernel oils.[8] Compound **15**, which was characterized as a 3:1 mixture of the pure glucosides **13** and **14** by ^{13}C-NMR spectroscopy presents improved properties, considering almost any of the different parameters displayed, when compared with the pure compounds **13** and **14** separately.

The CMC value of **15** is not intermediate, but lower than that of both pure C-12 and C-14 glucosides. The solubilization, that is the dissolving of normally water insoluble organic compounds into aqueous solutions of surfactants, occurs only above their CMC, where micelles are present. In consecuence, the synergistic effect will operate for solubilization, because the lower CMC value of the mixture indicates that it is a more efficient solubilizer than any of its pure components. Although both dodecyl and tetradecyl glucosides **13** and **14** have identical a_m^s values, the 3:1 mixture (compound **15**) showed a different value. Both micellisation and adsorption processes are favoured by the synergistic effect, as it can be seen from the $\Delta G°_{mic}$ and $\Delta G°_{ads}$ (Table **1**). The larger difference is found in the CMC/C_{20} ratio. The higher value for this parameter suggests that for compound **15** the micellization process is less favoured than the adsorption process.

Synergistic effects were also observed for gemini compounds linked through O-6 of the sugar moieties by succinic acid as spacer. Compound **32** was prepared from the mixed dodecyl/tetradecyl-α-D-glucopyranoside **15**. The product, characterized by ^{13}C-NMR spectroscopy, is a 7 : 3 mixture of two molecules of dodecyl-α-D-glucopyranoside linked through the succinyl spacer, and a dodecyl-α-D-glucopyranoside linked to a tetradecyl-α-D-glucopyranoside molecule. Compound **32** is thus not exactly a mixture of compounds **30** and **31**, but a mixture of **30** and a mixed dodecyl/tetradecyl-α-D-glucopyranoside dimer. Nevertheless, the considerations of synergistic effects still operate, because compound **32** is in fact constituted by two different gemini compounds.

The interfacial properties of compound **32** displayed in Table **1** showed that its CMC is lower than those of both pure C-12 and C-14 dimeric surfactants (compounds **30** and **31**), indicating an improvement of micelle formation. The behaviour of compound **32** suggests that the mixed product would be less affected by the self-coiling effect than compounds **30** and **31**. Both micellisation and adsorption processes are favoured by the synergistic effect, as it can be seen from the $\Delta G°_{mic}$ and $\Delta G°_{ads}$ (Table 1), but a larger effect is observed for the adsorption process. The CMC/C_{20} ratio shows the most striking synergistic effect, suggesting some influence of the presence of two different alkyl chains on the micelle formation process.

On the other hand, the pC_{20} values are distinctly affected in the monomeric surfactants and the dimers. While for dodecyl/tetradecyl-α-D-glucopyranoside **15**, this parameter is identical to dodecyl-α-D-glucopyranoside **13**, the pC_{20} value for compound **32** is higher than those calculated for the gemini compounds **30** and **31**. The mixed compound **32** has a greater efficiency to adsorb at the surface than **30** or **31** separately.

3. Conclusions

The new family of ecologically safe sugar-based gemini surfactants designed and synthesized in our laboratory from easily renewable natural resources represent an interesting alternative to replace known non-ionic surfactants derived from petrochemical industry. Since they are easily prepared, show excellent biodegradability, are non toxic, and exhibit improved properties in comparison with their monomeric counterparts, they have a broad spectrum of application.[13] The study of their interfacial properties is useful for the design of new members of the family and 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.

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).

We have estimated the critical length of the alkyl chains needed to prevent self-coiling between C-8 and C-12, 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 to design dimeric surfactants with improved interfacial properties compared to those of their monomeric counterparts.

Synergistic effects were observed between nonionic, sugar-based gemini surfactants. The results indicate that the use of the commercial mixture of long-chain alcohols (C-12/C-14) rather than pure alcohols as starting material is more convenient for the preparation of sugar-based surfactants not only in terms of cost but also in the surfactant efficiency of the products.

The interesting properties of this new type of amphiphilic compounds open the field of their use in personal care and household formulations, as they are nontoxic, biodegradable, and easily obtained from natural renewable resources.[14]

4. New trends

The introduction of new products in the market should take into consideration not only their cost of production and their suitability for the desired application, but also their environmental properties. Surfactants are one of the more widely distributed anthropogenic compounds in the ecosystems because of most of the product used in the every day life contain different kind of this amphiphilic molecules. It is therefore imperative to replace the nonionic surfactants that are at present petroleum derivatives by new surfactants prepared from renewable materials.

Petrochemical derived surfactants should be gradually replaced by sugar-based gemini surfactants. Moreover, the improved interfacial properties of latter allow to reduce the amount of active compound needed to obtain similar effects.

Further studies regarding synergistic effect in sugar-based gemini surfactants would be necessary to evaluate and rationalize the influence of the alkyl chain length, and to find the best C-12:C-14 ratio in the total surfactant mixture. Shorter synthetic routes and the evaluation of a variety of formulations would be helpful to promote the use of this kind of mixed gemini surfactants in commercial formulations. The results obtained suggest that α/β and alcohol mixtures can be used without any further purification simplifying the synthetic scheme.

Acknowledgements

The whole work reviewed here was carried out with the financial support of UBA (Universidad de Buenos Aires) and CONICET (Consejo Nacional de Investigaciones Cientificas y Técnicas). J.K. and A.F.C. are Research Members of CONICET.

References and Notes

1. (a) F. M. Menger and C. A. Littau, *J. Am. Chem. Soc.* **1991**, *113*, 1451. (b) F. M. Menger and C. A. Littau, *J. Am. Chem. Soc.* **1993**, *115*, 10083.
2. K. Holmberg, In *Novel Surfactants Preparation, Applications, and Biodegradability*; Marcel Dekker: New York, 1998; Vol. 74, p 241.
3. 3.(a) F. M. Menger and J. S. Keiper, *Angew. Chem., Int. Ed.* **2000**, *112*, 1980. (b) R. Zana and J. Xia, *Gemini Surfactants*, Marcel Dekker: New York, 2004, Vol. 117.
4. A. J. Kirby, P. Camilleri, J. B. F. N. Engberts, M. C. Feiters, R. J. M., Nolte, O. Söderman, M. Bergsma, P. C. Bell, M. L. Fielden, C. L., García Rodríguez, P. Guédat, A. Kremer, C. McGregor, C. Perrin, G. Ronsin and M. C. P. van Eijk, *Angew. Chem., Int. Ed.* **2003**, *42*, 1448.
5. K. Hill, W. von Rybinski, G. Stoll, *Alkyl Polyglucosides Technology, Properties and Applications*, VCH, 1996.
6. (a) J. Eastoe, P. Rogueda, B. J. Harrison, A. M. Howe, A. R. Pitt, *Langmuir* **1994**, 10, 4429. (b) C. B. A. Briggs, I. M. Newington, A. R. Pitt, *J. Chem. Soc. Chem. Comun.* **1995**, 379.(c) J. Eastoe, P. Rogueda, A. M. Howe, A. R. Pitt, R. K. Heenan *Langmuir* **1996**, 12, 2701. (d) J. M. Pestman, R. Terpstra, M. C. A. Stuart, H. A. van Doren, A. Brisson, R. M. Kellogg, J. B. F. N. Engberts *Langmuir* **1997**, 13, 6857. (e) H. A. van Doren, E. Smits, J. M. Pestman, J. B. F. N. Engberts, R. M. Kellogg *Chem. Soc. Rev.* **2000**, 29, 183. (f) M. Bergsma, M. L. Fielden, J. B. F. N. Engberts *J. Colloid Interface Sci.* **2001**, 243, 491. (g) M. L. Fielden, C. Perrin, A. Kremer, M. Bergsma, M. C. Stuart, P. Camilleri, J. B. F. N. Engberts *Eur. J.*

Biochem. **2001**, *268*, 1269. (h) M. Wathier, A. Polidori, K. Ruiz, A. S. Fabiano, B. Pucci New J. Chem. **2001**, *25*, 1588. (i) F. M. Menger, B. N. A. Nbadugha *J. Am. Chem. Soc.* **2001**, *123*, 875. (j) A. R. van Buuren, H. J. C. Beredsen *Langmuir* **1994**, *10*, 1703. (k) C. Gao, A. Millqvist-Fureby, M. J. Whitxombe, E. N. Vulfson *J. Surfact. Detergents* **1999**, *2*, 293.

7. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, *Tetrahedron Lett.* **1997**, *38*, 3995.
8. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, *Tetrahedron* **1999**, *55*, 12711.
9. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, *Tenside Surf. Det.* **2002**, *39*, 28.
10. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, *J. Carbohydr. Chem*. **2000**, *19*, 1174.
11. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, *Langmuir* **2002**, *18*, 2477.
12. P. Mukerjee *Adv. Colloid Interface Sci.* **1967**, 241.
13. *CS CHem 3D Pro and MOPAC Pro*, CambridgeSoft, Cambridge, MA, 1998
14. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, National Patent (Arg.) AR990196476 in progress
15. M. J. L. Castro, J. Kovensky, A. Fernández Cirelli, National Patent (Arg.) AR010101084 in progress

Authors' biographical data

Professor *Alicia Fernández Cirelli* Ph.D. in chemistry (1972), on structural characterization of fungal polysaccharides at the University of Buenos Aires, she worked as visiting researcher at the Institüt für Organische Chemie, Universität Düsseldorf, Germany, in 1973. She is Professor at the University of Buenos Aires since 1975, as well as Research Member of the Argentine Research Council CONICET, at the Organic Chemistry Department (FCEyN), since 1983. She founded in 2002 the Centro de Estudios Transdisciplinarios del Agua (CETA).

Fields of work: carbohydrates analysis and synthesis, synthesis and interfacial properties of gemini surfactants, characterization and distribution of humic substances, analysis of organic contaminants in water.

Professor *José Kovensky* obtained his Ph.D. in Chemistry in 1992 at the Organic Chemistry Department (FCEyN) of the University of Buenos Aires, working on glycosaminoglycan chemistry. After a post-doctoral training of 2 years at the Ecole Normale Supérieure, Paris, France with Prof. Pierre Sinaÿ, he returned to the University of Buenos Aires, as Professor and Research Member of the Argentine Research Council CONICET. He was also Invited Professor at the Ecole Normale Supérieure (2000-2002). Since september 2002 he is Professor at the UPJV, Amiens, France. His field of work is carbohydrate chemistry, oligosaccharides.

Dr. *Mariano J. L. Castro* studied chemistry at the University of Buenos Aires, where he obtained his PhD on gemini surfactants in 2000 in Department of Organic Chemistry (FCEyN), where he was teacher assistant. He then joined to the University Chemical Laboratory at Cambridge University, in 2001 working during the three years on synthesis of cationic gemini

surfactants. He joined the CETA in 2005. His field of work includes carbohydrate chemistry, peptide chemistry, gemini surfactants and analysis of organic contaminants in water.