Synthesis and electrochemical behaviour of new electroreducible amphiphilic saccharide derivatives†

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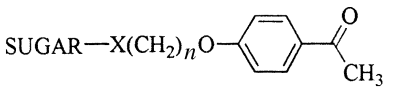
The synthesis of electroreducible amphiphilic molecules derived from sugars is performed by condensation of activated glucose or maltose with hydroxy- or bromoalkoxyacetophenones of various chain lengths. The electrochemical reduction of the conjugated π-system could be a convenient route for obtaining, by radical–radical coupling, surfactants possessing two sugar moieties and two new stereogenic centres. The polarographic and voltammetric behaviours of these new surfactants are defined in aqueous and non-aqueous media. In an aprotic solvent (DMF), the maltoside and thiomaltoside exhibit a reversible one-electron reduction step while that of the corresponding glucoside is irreversible. This particular property is analysed by taking into account the possibility for maltose to form strong intramolecular hydrogen bonds, even in an aprotic medium. The polarographic curves recorded in aqueous solutions (pH = 3.4 and 10.5) are disturbed by adsorption phenomena. The adsorption mode of these surfactants has therefore been studied by means of differential capacitive measurements (tensammetric method). Their adsorption behaviours, compared to those previously published with non-electroducible glycosidic surfactants, are related to their possible micellar properties. In particular, the critical micellar concentrations (CMC) of the maltoside surfactants have been estimated.

Synthèse et étude électrochimique de nouveaux tensioactifs électroréductibles dérivés de sucres. La synthèse de molécules amphiphiles électroréductibles dérivées de sucres est réalisée par condensation du glucose ou du maltose activés avec des hydroxy- et bromoalkoxyacétophénones. La réduction électrochimique de cétones aromatiques peut être une méthode intéressante permettant d'obtenir, par couplage radicalaire, des tensioactifs possédant deux mono- ou disaccharides dans leur molécule. Le comportement électrochimique de ces nouveaux tensioactifs a été étudié par polarographie et voltammétrie cyclique en milieu aqueux et non aqueux respectivement. Dans un solvant aprotique (DMF), le maltoside et le thiomaltoside présentent une étape de réduction monoélectronique réversible tandis que les dérivés du glucose sont caractérisés par une vague irréversible. Cette propriété particulière des dérivés du maltose pourrait être expliquée par l'existence de liaisons hydrogène intramoléculaires fortes même en milieu aprotique. Les courbes polarographiques enregistrées en milieu aqueux (pH = 3,4 et 10,5) sont perturbées par des phénomènes d'adsorption. Le mode d'adsorption de ces tensioactifs à l'interface électrode de mercure-solution d'électrolyte a été étudié par tensammétrie. Leurs comportements en adsorption, comparés à ceux précédemment publiés de tensioactifs glycosidiques non réductibles, sont reliés à leurs propriétés micellaires éventuelles. En particulier, les concentrations micellaires critiques des maltosides ont été estimées.

Alkylglucosides and alkylpolyglucosides have received much attention during the past two decades.[1–6] Alkylpolyglucosides are classified as non-ionic surfactants since the hydrophilic part bears no charge. In addition to the classical characteristics of non-ionic surfactants, they exhibit advantages relative to their foaming power and their wetting time of added substances.[1] Besides their capability to solubilize organic molecules, they are extremely efficient in a wide range of detergent and industrial applications because of their ability to enhance the effectiveness of anionic, non-ionic or cationic surfactants by forming mixed aggregates.[7] Glycoside derivatives possessing very low toxicity are often used in biochemistry for purification or reconstitution of membrane proteins.[8,9]

From another point of view, chiral micelles have been used as biomimetic analogues of enzymes. Regioselective and enantiogenic reduction of ketones in chiral micelles of glycosidic surfactants have been reported.[10,11] During the past decade we have studied the electrochemical behaviour of synthesized electroreducible surfactants, showing the role played by adsorption and micellization phenomena in the partitioning and the stereochemistry of the electrochemically generated reaction products.[12–19] In this context, we have studied the adsorption mode of glycosidic surfactants at the mercury electrode[20] and synthesized new alkylglycosides bearing a carbonyl group as an electrochemical probe:



n = 3, 8

X = O, S

Our final goal is electrochemically to convert the prochiral carbonyl group into the corresponding two-chain pinacols

† Non-SI unit employed: 1 kcal ≈ 4.18 kJ.

(radical–radical coupling) or single-chain alcohols (two-electron reduction process) in order to generate new stereogenic centres that may cause an interesting change of the surfactant properties.

In this article, we present the first part of this work, which consists in the study of the electrochemical behaviour (investigated by polarography and cyclic voltammetry) of these different molecules bearing a mono- or a disaccharidic head group (glucopyranosides or maltopyranosides) and two different chain lengths ($n = 3$ and 8). In particular we will compare their adsorption properties at a mercury electrode, determined by AC polarography (tensammetry), to those previously observed with non-electroactive glycosidic surfactants.[20]

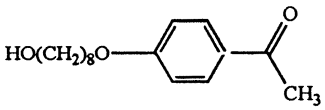
Experimental

NMR spectra were recorded on a Bruker AC 400 spectrometer. Infrared spectra were obtained with a Nicolet Impact 400 FT spectrometer. Elemental analyses and mass spectroscopy were performed by the Centre National de la Recherche Scientifique (CNRS) at Vernaison (France). Preparative column chromatography was performed on silica gel (Merck, 70–230 mesh). The air- and water-sensitive reactions were carried out under an argon atmosphere in purified solvents. Reactions were followed by thin layer chromatography (TLC) (silica gel on aluminium foil, Merck 1.05554). The critical micellar concentration (CMC) was determined in aqueous medium at 48 °C by measuring the stripping strength of a lamella using a Prolabo-Tensimat TD 2000 tensiometer.

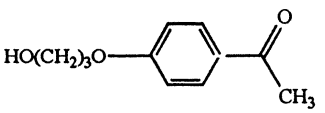
All the ^1H and ^{13}C chemical shifts and IR frequencies of compounds **5**, **7**, **11a**, **12a** and **12b** have been deposited. See http://www.rsc.org/suppdata/njc/1998/1469.

Syntheses

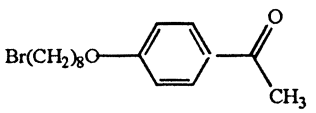
The alcohols **1a** and **1b** and the bromide **2** were synthesized as described in a previous work.[15] All solvents were distilled before use. Anhydrous dichloromethane (Carlo Erba) was obtained by distillation over calcium hydride.



1a



1b



2

1i - *O* - (4 - Acetyl - 1 - phenoxyoctyl) β - D- maltopyranoside (MALTACO8), 5. The crude unstable bromide **3** obtained from maltose peracetate (2 g, 2.95 mmol) as previously described[20] was dissolved in 60 ml of dry dichloromethane. Molecular sieves (4 Å, 2 g), alcohol **1a** (2.16 g, 8.2 mmol), Ag_2CO_3 (3 g) and I_2 (0.1 g) were added to the solution under vigorous stirring. The mixture was stirred for 24 h at room temperature. The solution was filtered and the filtrate concentrated under reduced pressure. The crude product was dissolved in 50 ml of a 2 : 1 : 1 (v/v/v) methanol–triethylamine–water mixture and allowed to stand for 4 h at room temperature. The solvents were then evaporated under reduced pressure and the residual solid dissolved in ethyl acetate–methanol (80 : 20 v/v). The insoluble maltose was filtered and the filtrate chromatographed on a silica gel column [eluent: ethyl acetate–methanol (80 : 20 v/v)]. Thin layer chromatography (same eluent): R_f (**5**) = 0.18. Compound **5** was obtained as a white powder in 14% yield (0.240 g). $[\alpha]_D^{25} = +32.3$ ($c = 1.00$, DMSO). HRMS (FAB+) calcd for $[C_{28}H_{44}O_{13} + Na]^+$: 611.2679; found 611.2699.

1-*S*-(4-Acetyl-1-phenoxyoctyl) β-D-thiomaltopyranoside (MALTACS8), 7. K_2CO_3 (1 g, 7.23 mmol) and $NaHSO_3$ in H_2O (37%, 1.5 ml) were successively added to 50 ml of a acetone–water (1 : 1 v/v) solution of the bromide **2** (2.4 g, 7.4 mmol) and the crude adduct **6** [6.09 g, obtained from maltose peracetate (5 g, 7.4 mmol) as previously described[20]]. The reaction was followed by thin layer chromatography [eluent: cyclohexane–ethyl acetate (1 : 1 v/v), R_f (**2**) = 0.91, R_f of the coupling product = 0.55]. After 12 h at room temperature the reaction mixture was filtered. The filtrate was extracted with dichloromethane (2 × 40 ml), then the organic phase was washed with water (25 ml), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product (6.93 g) was dissolved in 50 ml of a 5 mM solution of NaOH in methanol and allowed to stand for 12 h at room temperature. After neutralization by addition of acetic acid, the solution was concentrated under reduced pressure and the residual solid dissolved in ethyl acetate–methanol (70 : 30 v/v). The insoluble maltose was filtered and the filtrate chromatographed on a silica gel column [eluent: ethyl acetate–methanol (70 : 30 v/v)]. Thin layer chromatography (same eluent): R_f (**2**) = 0.90, R_f (**7**) = 0.45. Product **7** was obtained as a white powder in 17% yield (0.750 g). $[\alpha]_D^{25} = +40.0$ ($c = 1.57$, DMSO). HRMS (FAB+) calcd for $[C_{28}H_{44}O_{12}S + Na]$: 627.2451; found 627.2460.

1-*O*-(4-Acetyl-1-phenoxyoctyl) β-D-glucopyranoside tetraacetate, 11a. In a dry previously deaerated 500 ml round bottom flask, equipped with a reservoir allowing a controlled argon flow, was placed 150 ml of anhydrous dichloromethane. The trichloroacetimidate[21,22] **10** (5 g, 10.2 mmol) and alcohol **1a** (1.8 g, 6.8 mmol), dissolved in small amounts of anhydrous dichloromethane, were added with syringes. The reaction mixture was cooled to 0 °C. Then 10 ml of a 0.1 M solution of BF_3–Et_2O in anhydrous dichloromethane was introduced in the reservoir and added quite quickly at 0 °C. The temperature was kept at 5 °C until the complete consumption of trichloroacetimidate was noticed by TLC [eluent: dichloromethane–ethyl acetate (80 : 20 v/v), R_f (**10**) = 0.66]. After return to room temperature, $NaHCO_3$ (10 g) was added and the reaction mixture vigorously stirred then filtered. The filtrate was washed with water and then the organic layer dried over $MgSO_4$. After filtration and evaporation of the solvent under reduced pressure, product **11a** was purified by chromatography on a silica gel column [eluent: dichloromethane–ethyl acetate (90 : 10 then 85 : 15 v/v), TLC: R_f (**11a**) = 0.46 in same eluent 90 : 10 v/v)]. The colourless compound **11a** was obtained in 45% yield (1.8 g). $[\alpha]_D^{25} = -12.7$ ($c = 1.07$, $CHCl_3$). Anal. calcd for $C_{30}H_{42}O_{12}$ (594.65 g mol^{-1}): C, 60.60; H, 7.12. Found: C, 59.94; H, 7.36.

1 - *O* - (4 - Acetyl - 1 - phenoxyoctyl) β - D- glucopyranoside (GLUACO8), 12a. First compound **11a** (1.75 g, 2.95 mmol), then 15 ml of a 2 : 1 : 1 (v/v/v) methanol–triethylamine–water mixture were placed in a 50 ml round bottom flask. After 24 h at room temperature, the reaction mixture was concentrated under reduced pressure. Ethyl acetate addition led to quanti-

tative precipitation of a white powder. After filtration, the product **12a** was collected as a white solid in more than 90% yield. $[\alpha]_D^{25} = -21.0$ ($c = 1.49$, DMSO). Anal. calcd for $C_{22}H_{34}O_8$ (426.50 g mol^{-1}): C, 61.96; H, 8.03; O, 30.01. Found: C, 61.20; H, 8.00; O, 29.85.

1 - *O* - (4 - Acetyl - 1 - phenoxypropyl) β - D- glucopyranoside (GLUACO3), 12b. A dry 500 ml round bottom flask equipped with a reservoir with an inlet was first purged with argon. Then, trichloroacetimidate **10** (2.7 g, 5.5 mmol) and alcohol **1b** (0.97 g, 5 mmol) were dissolved in 150 ml of anhydrous dichloromethane and 4 Å molecular sieves (15 g) added to the mixture. After 2 h stirring at room temperature, the reaction mixture was cooled to −50 °C and 5 ml of a 0.1 M solution of BF_3–Et_2O in anhydrous dichloromethane was added. Then, the temperature was progressively raised. The reaction was stopped when complete consumption of trichloroacetimidate was noticed by TLC [eluent: cyclohexane–ethyl acetate (50 : 50 v/v), R_f (**10**) = 0.66]. The reaction mixture was then treated as described for compound **11a**. Chromatographic purification [eluent: cyclohexane–ethyl acetate (40 : 60 v/v), silica gel] led to the crude product **11b** still containing trichloroacetimidate degradation products. Intermediate **11b**, $C_{25}H_{32}O_{12}$ (524.52 g mol^{-1}): MS (EI): *m/z* 524 (M^+, 12%), 509 ($[M - CH_3]^+$, 1%), 481 ($[M - C_2H_3O]^+$, <1%), 43 ($[C_2H_3O]^+$, 100%).

Without further purification, product **11b** was dissolved in 30 ml of a mixture of methanol–triethylamine–water (2 : 1 : 1 v/v/v). After 12 h at room temperature, the reaction mixture was concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column [eluent: ethyl acetate–methanol (80 : 20 v/v)]. TLC (same eluent): R_f (**12b**) = 0.33. Ether addition led to quantitative precipitation of a white powder. After decanting, the ether was evaporated and product **12b** obtained as a white powder in 30% yield (0.530 g). $[\alpha]_D^{25} = -12.6$ ($c = 1.20$, DMSO). HRMS (FAB+) calcd for $[C_{17}H_{24}O_8 + Na]^+$: 357.1549; found 357.1563.

Electrochemical characterisation

The cyclic voltammetry study of compounds **5**, **7**, **12a** and **12b** was performed in aprotic medium (DMF). A solution of 0.1 M Bu_4NPF_6 (Fluka) in DMF was used as electrolyte. The cathode was a hanging mercury electrode and the aqueous saturated calomel electrode (SCE) with an extension (DMF saturated with Bu_4NPF_6) was used as reference electrode. Experiments were carried out at room temperature and the electrolyte was deaerated with argon prior to the measurement. Experiments were performed on a PAR 273 potentiostat equipped with a computer system.

The polarographic study was performed in acidic and alkaline aqueous solutions on a Tacussel Model PRG5 polarograph equipped with a SEFRAM-TGM X-Y recorder. A mercury electrode was used as cathode and an aqueous saturated calomel electrode (SCE) as reference electrode. Recording conditions were as follows: drop time of 0.5 s, scan rate of 4 mV s^{-1}, mercury column height of 50 cm. Aqueous solutions used (pH = 3.4 and 10.5) were Britton–Robinson buffer solutions with an ionic strength adjusted to 0.5 M by adding KCl or NaCl. Experiments were carried out at 48 °C and the electrolyte was deaerated with argon prior to the measurement.

The tensammetry experiments with GLUACO3 and GLUACO8 were performed at a PAR-303A mercury electrode (dropping mercury electrode, DME) connected to a PAR 273 potentiostat coupled with a lock-in amplifier PAR-5208 and equipped with a computer system controller and a SEFRAM-TGV X-Y recorder. Recording conditions were as follows: drop time of 5 s (DME), scan rate of 2 mV s^{-1}, ac frequency 120 Hz, ac amplitude ±5 mV, phase angle 90°. The experiments with MALTACO8 and MALTACS8 were performed on a Tacussel Model PRG 30-01 polarograph equipped with a SEFRAM-PE recorder. Recording conditions were as follows: drop time of 3 s, scan rate of 1 mV s^{-1}, ac frequency 120 Hz, ac amplitude ±5 mV, phase angle 90°. All electrode potentials were referenced to an SCE. Due to the fact that the use of alkaline solutions allows the investigation of a large potential range without any perturbation of either the proton reduction or the ketone reduction, Britton–Robinson buffer solutions (pH = 9.1 and 10.5) were used. The ionic strength was in all cases 0.5 M in KCl or NaCl. The three-electrode cell was thermostated at 30 or 48 °C depending on the Krafft point of the studied surfactant. It was maintained under an inert atmosphere by argon previously saturated by the studied solution.

Computer modelling

First, exploration of the conformational space of MALTACO8, **5**, in the vapour phase by a Monte-Carlo sampling method was performed using the Batchmin program within the MM2 force field of the Macromodel package.[23] In the vapour phase, the conformation of lowest potential energy found has two intramolecular hydrogen bonds: $C_2—O—H_{12}\cdots O_{24}—C_3$, and $C_4—O—H\cdots O—C_6$. Then we simulated, with the Silverware program of the Sybyl package,[24] a solution of MALTACO8 in DMF using the conformation found previously in the vapour phase. We built a periodic cubic box of 44.47 Å sides with one molecule of solute and 633 molecules of solvent. The calculated density of the solution is 0.8818 g cm^{-3}. After minimizing, we performed a molecular dynamics calculation for 28 ps in the NVT ensemble ($T = 300$ K) using the Sybyl package software to follow the temporal evolution of the intramolecular $H_{12}\cdots O_{24}$ hydrogen bond during the process.

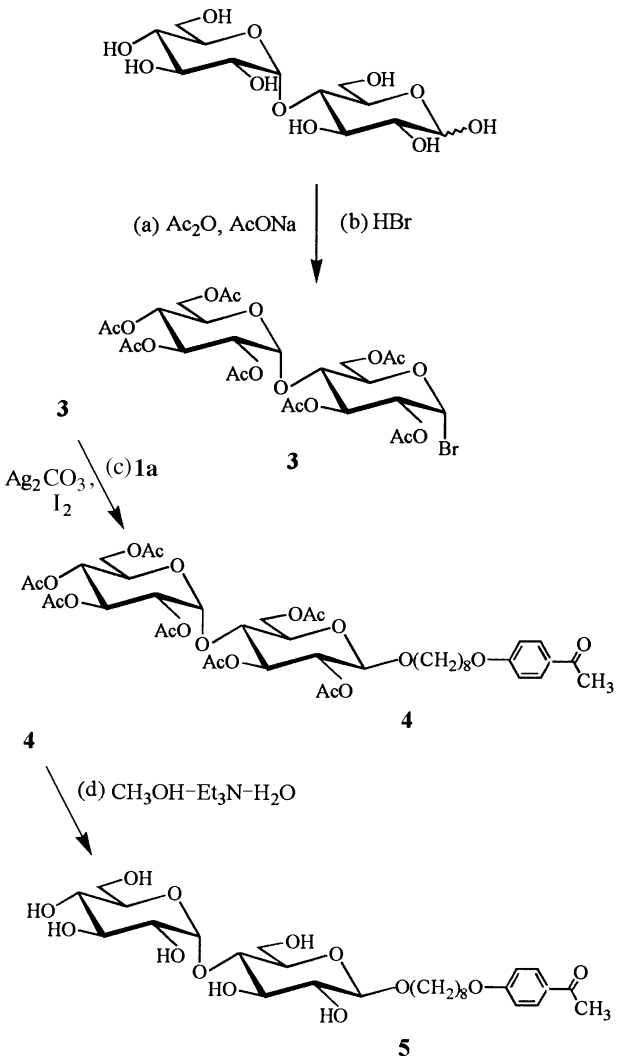
Results

In this work we present an analytical study of four surfactants (**5**, **7**, **12a** and **12b**) derived from saccharides by tensammetry, polarography and cyclic voltammetry in aqueous and DMF solutions, respectively.

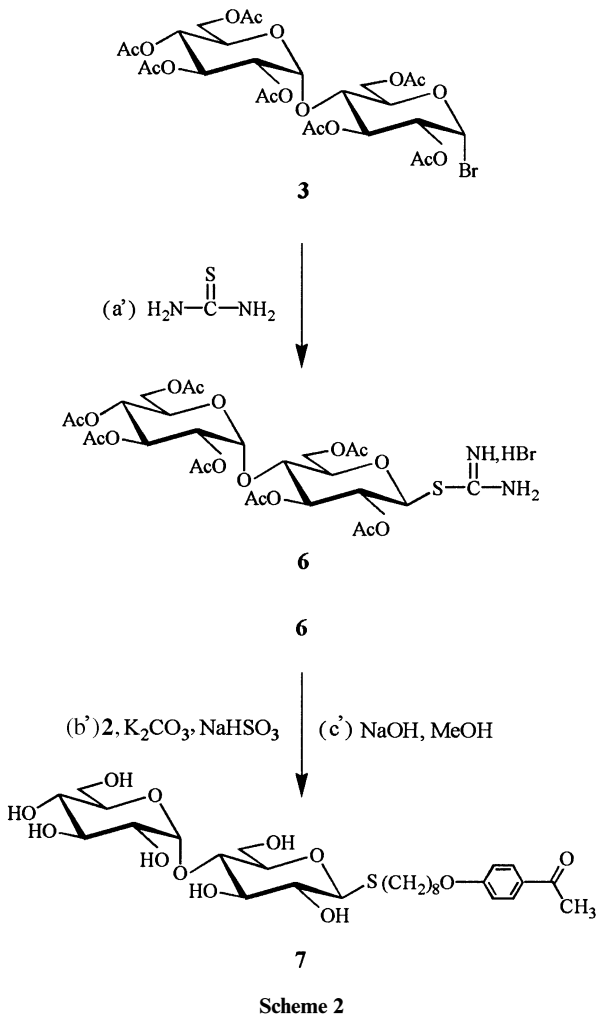
The synthesis of these new oxo- and thioalkylglycosides has been achieved by the condensation of the activated saccharides glucose and maltose with three derivatives of acetophenone: **1a**, **1b** and **2**. The synthesis of maltopyranoside (MALTACO8), **5**, is performed by starting from maltose, which is converted into 1-bromoheptaacetate, **3**, according to the procedure of Rosevear *et al.*[25] Applying the Koenigs–Knorr method,[26] the bromide **3** was reacted with the alcohol **1a** in the presence of silver carbonate and iodide at room temperature. The resulting (crude) product was deprotected by hydrolysis of the acetate groups giving the maltopyranoside **5** (Scheme 1).

The analogue thiomaltopyranoside (MALTACS8), **7**, was synthesized according to a process published by Saito and Tsuchiya[27] for other thioglycoside surfactants. The bromide **3** was substituted by thiourea[20] and the crude adduct **6** was then reacted with the bromide **2** under basic conditions in the presence of $NaHSO_3$. The intermediate thioglycoside was converted into the final product **7** by deprotection of the hydroxyl groups (Scheme 2).

The synthesis of the glucopyranosides (GLUACO8), **12a**, and (GLUACO3), **12b**, was based on the Schmidt glycosylation.[22] In a first step, glucose pentaacetate was converted into the free hemiacetal **9**, which then gave, in a nucleophilic addition to CCl_3CN, the corresponding trichloroacetimidate **10**. Its BF_3 catalysed glycosylation with the alcohols **1a** and **1b**



Scheme 1



Scheme 2

led to compounds **11a** and **11b**, bearing an eight- or a three-membered alkyl chain, respectively. The surfactants **12a** and **12b** were obtained after basic deprotection of the hydroxyl groups (Scheme 3).

Polarography in aqueous medium

The polarograms of the four electroreducible glycosides present in each case a cathodic wave very close to the electrolyte discharge (Figs. 1 and 2). The half-wave potentials are listed in Table 1. The proximity of the electrolyte reduction makes the measurement of electricity consumption hazardous. We observe in basic medium the presence of a more or less pronounced prewave, depending on the structure of the substrate, located in the potential range where desorption of the compounds occurs at the mercury electrode (see the tensammetric study).

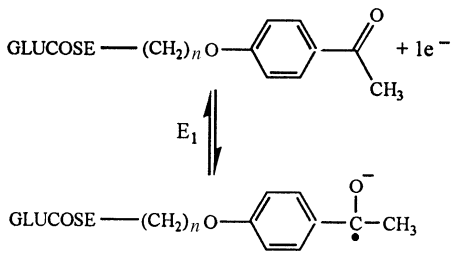
Table 1 Half-wave reduction potentials (V *vs.* SCE) in acidic and basic media at $T = 48\,°C$ and $c = 5 \times 10^{-4}$ M

Compound	pH = 3.4	pH = 10.5
MALTACO8	−1.275	−1.67[a]
MALTACS8	−1.275	−1.67[a]
GLUACO8	−1.280	−1.685
GLUACO3	−1.285	−1.670

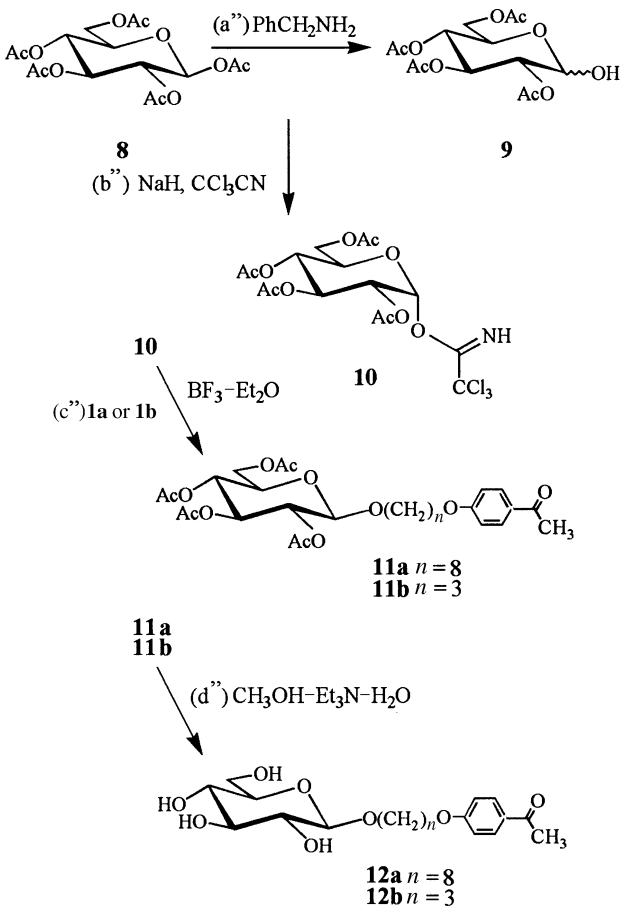
[a] The half-wave reduction potentials could not be calculated with accuracy because of a high desorption prewave.

Cyclic voltammetry in non-aqueous medium

In media of very low acidity, aromatic ketones are reduced in two monoelectronic exchanges, the second generally not being observed for the less conjugated aryl-alkyl derivatives because its potential is as negative as that of the supporting electrolyte.[28] In dry DMF, the two ketones derived from glucose (GLUACO8 and GLUACO3) give an irreversible one-electron wave (Fig. 3) corresponding to formation of the anion radical:

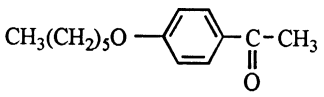


In the case of maltose derivatives bearing an eight-membered alkyl chain (MALTACO8 and MALTACS8), an anodic peak is observed on the reversed scan for a scan rate of 0.1 V s^{-1} (Fig. 4). It can be attributed to oxidation of the anion radical. The current intensities I_{Pc} and I_{Pa} vary as a function of $v^{1/2}$ and the anodic peak disappears on addition of a strong proton donor (Bu_4NHSO_4). For comparison, the same experiment realized with the non-glycosidic molecule **13** exhibits an irreversible wave at 0.1 V s^{-1}, which becomes



Scheme 3

more and more reversible by increasing the scan rate up to 5 V s^{-1} (Fig. 5).



13

The evolution of the ratio I_{Pc}/I_{Pa} has been studied as a function of the scan rate for GLUACO8, MALTACO8 and the non-glycosidic molecule **13**. For a scan rate of 0.1 V s^{-1} only MALTACO8 exhibits a reversible peak with $I_{Pc}/I_{Pa} = 1.92$. If the scan rate is raised to 5 V s^{-1} a small reversibility appears for GLUACO8 with $I_{Pc}/I_{Pa} = 3.81$, while that of **13** is greatly increased ($I_{Pc}/I_{Pa} = 1.95$, Fig. 5) and that of MALTACO8 remains quite stable.

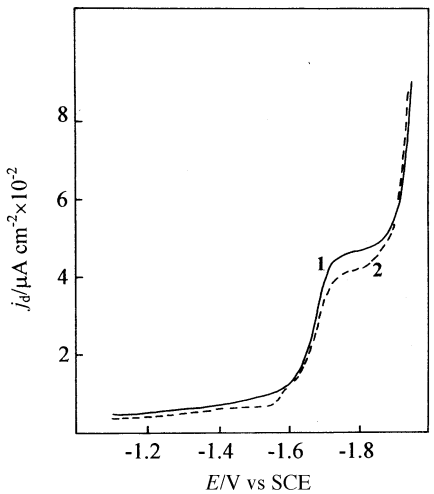


Fig. 1 Polarographic curves (T = 48 °C) at pH 10.5 of GLUACO3 (curve 1) and GLUACO8 (curve 2) at $c = 5 \times 10^{-4}$ M

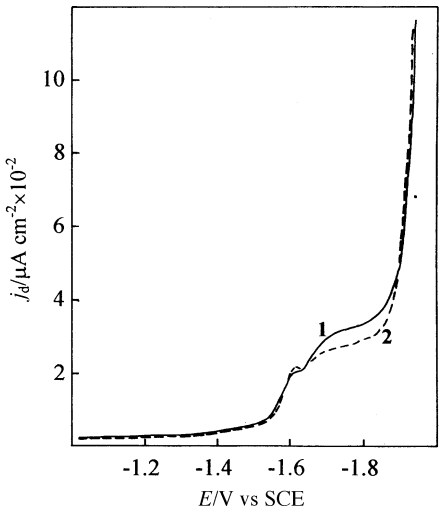


Fig. 2 Polarographic curves (T = 48 °C) at pH 10.5 of MALTACO8 (curve 1) and MALTACS8 (curve 2) at $c = 5 \times 10^{-4}$ M

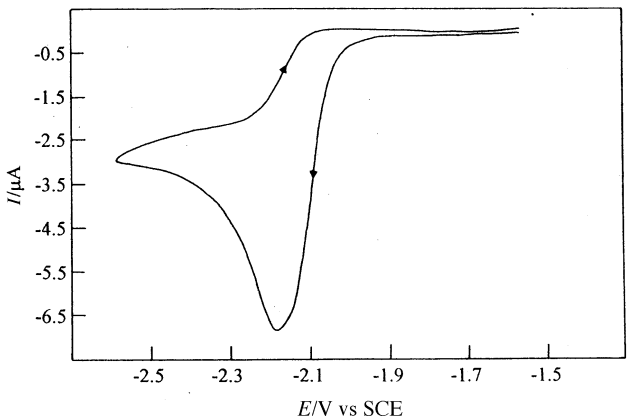


Fig. 3 Voltammetric reduction of GLUACO8 at $c = 2 \times 10^{-3}$ M, $v = 0.1$ V s^{-1} in 0.1 M DMF–Bu_4NPF_6

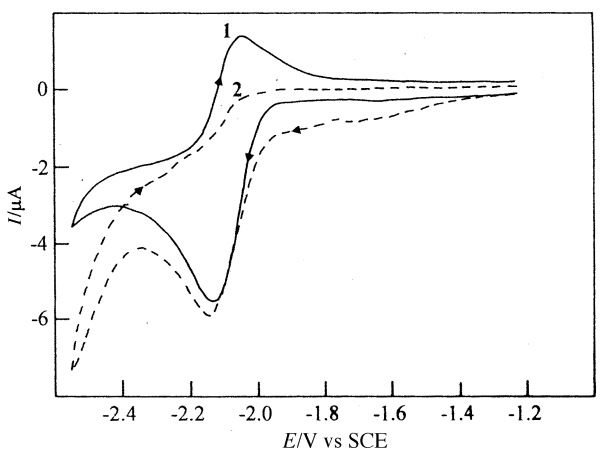


Fig. 4 Voltammetric reduction of MALTACO8 at $c = 2 \times 10^{-3}$ M, $v = 0.1$ V s^{-1} in 0.1 M DMF–Bu_4NPF_6 in the absence (curve 1) and in the presence (curve 2) of Bu_4NHSO_4 ($c = 4 \times 10^{-3}$ M)

Tensammetry

Tensammetric curves of the studied surfactants are plotted in Figs. 6–9. In the case of GLUACO3 (Fig. 6), the region of the minimum in the *C vs. E* curves becomes broader and the capacity minimum decreases as the surfactant concentration increases, reaching a value of 8.4 μF cm^{-2} for $c = 1 \times 10^{-2}$ M. At the same time, the height of the bell-shaped cathodic peak increases while shifting towards more negative potentials. The increase of the chain length causes a very low solubility of GLUACO8 in water compared to GLUACO3. For this reason, the tensammetric measurement of GLUACO8 was only performed at a concentration of 1×10^{-4} M (Fig. 7). In this case, the tensammetric curve presents a broad hump located between −0.4 and −1.05 V *vs.* SCE, leading to two capacity minima with a lower value for the second. The bell-shaped peak is located at −1.57 V *vs.* SCE.

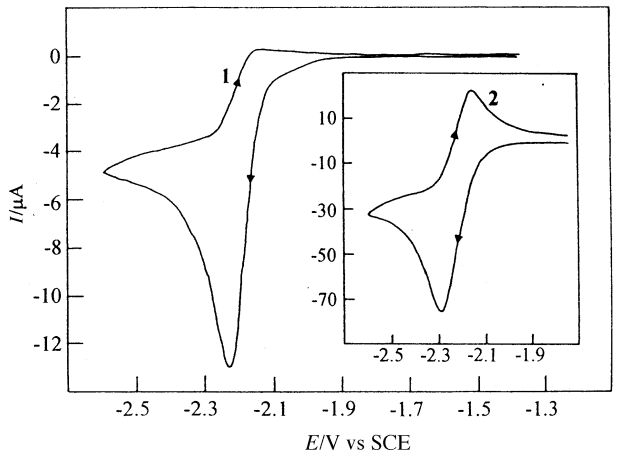


Fig. 5 Voltammetric reduction of **13** at $c = 2 \times 10^{-3}$ M, $v = 0.1$ V s^{-1} (curve 1) and 5 V s^{-1} (curve 2), in 0.1 M DMF–Bu_4NPF_6

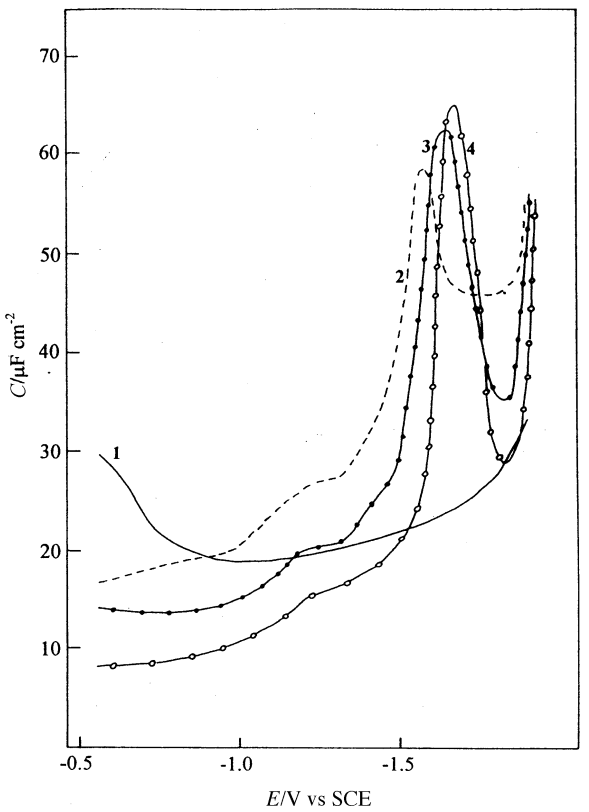


Fig. 6 Tensammetric curves at a DME ($T = 30$ °C) at pH 9.1 of GLUACO3 in increasing concentration: (curve 1) 0 (curve 2) 2×10^{-3}, (curve 3) 4×10^{-3}, (curve 4) 1×10^{-2} M

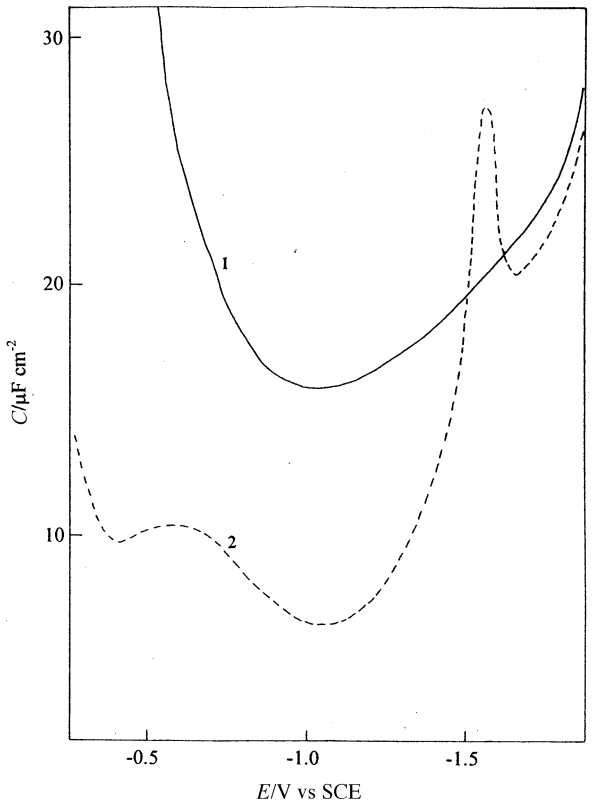


Fig. 7 Tensammetric curves at a DME ($T = 30$ °C) at pH 9.1 of GLUACO8: (curve 1) 0, (curve 2) 1×10^{-4} M

Tensammetric curves of MALTACO8 and MALTACS8 are shown in Figs. 8 and 9, respectively. In the case of MALTACO8 we observed: (*i*) a first broad peak located in the region of the capacity minimum as already observed with GLUACO8. This peak is shifted towards higher negative potentials as the surfactant concentration increases from $c = 1 \times 10^{-4}$ to 1×10^{-3} M; (*ii*) a second peak located at a

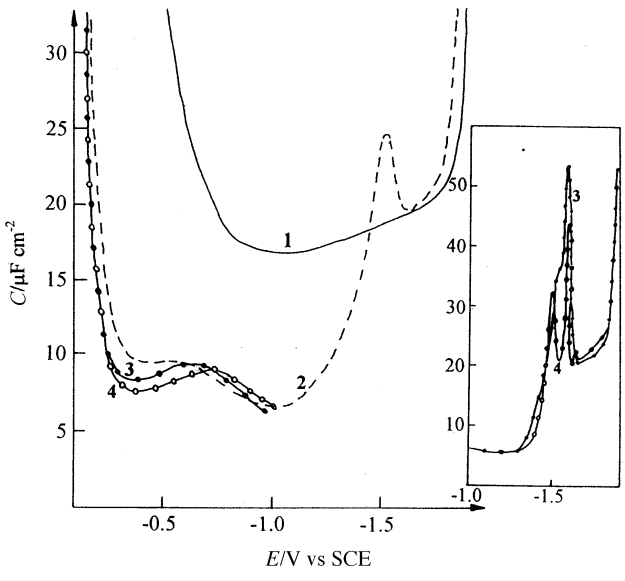


Fig. 8 Tensammetric curves at a DME ($T = 48$ °C) at pH 10.5 of MALTACO8 in increasing concentration: (curve 1) 0, (curve 2) 1×10^{-4}, (curve 3) 5×10^{-4}, (curve 4) 1×10^{-3} M

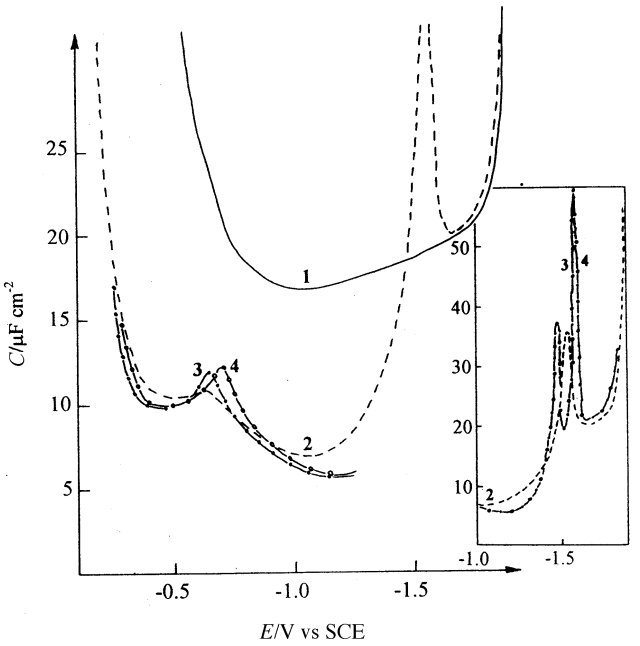


Fig. 9 Tensammetric curves at a DME ($T = 48\,°C$) at pH 10.5 of MALTACS8 in increasing concentration: (curve 1) 0, (curve 2) 1×10^{-4}, (curve 3) 5×10^{-4}, (curve 4) 1×10^{-3} M

potential around -1.5 V *vs.* SCE. At $c = 5 \times 10^{-4}$ M it becomes sharp on the more negative potential side while a hump appears on the more positive potential side. Finally it splits at $c = 1 \times 10^{-3}$ M, leading to a new peak at higher positive potential.

In the case of MALTACS8 the evolution of the tensammetric curves (Fig. 9) is similar. However, the first peak at -0.65 V *vs.* SCE is sharper and the second at -1.5 V *vs.* SCE splits at a lower concentration ($c = 5 \times 10^{-4}$ M).

Discussion

The voltammograms of the two types of glycosidic surfactants in non-aqueous medium (DMF) are different. The electrochemical reduction of the glucose derivatives yields an irreversible peak while that of the corresponding maltose disaccharides is reversible for the same scan rate. This can be interpreted as a better stability of the anion radical of the latter. Unprotected mono- or disaccharides possess free hydroxyl groups that can induce the formation of hydrogen bonds with negatively charged intermediates or favour particular conformations implying more important steric hindrance to the molecule. These two factors can play a role in protonation or dimerization reactions of the electrogenerated anion radicals. As a support of this hypothesis, it has been shown[29] that, even in aprotic polar medium, some disaccharides, in particular those derived from maltose, can develop strong hydrogen bonds between the OH(2) and OH(3′) of the sugar units. Under these conditions, the molecule can present a bent conformation in which the other hydroxyl groups associated with the solvent molecules constitute a more compact "solvent-cage" structure making the protonation reactions towards the anion radical and the dimerization process less efficient than for the glucose monosaccharides.

We have realized a molecular dynamics calculation with the MALTACO8, **5**, molecule in the solvent DMF. One of the structures of lowest energy ($E = -1445.3$ kcal mol^{-1}) stocked during the dynamic process is shown in Fig. 10. Both intramolecular hydrogen bonds observed in the vapour phase are maintained: $C_2—O—H_{12}\cdots O_{24}—C_{3'}$ and $C_4—O—H\cdots O—C_6$. Two intermolecular hydrogen bonds with DMF molecules appear during the solvation: $C_{3'}—O—H\cdots$(DMF) and $C_{6'}—O—H\cdots$(DMF). The temporal evolution of the intramolecular $H_{12}\cdots O_{24}$ hydrogen bond is presented in Fig. 11. We consider that this hydrogen bond is maintained for at least 28 ps because in the various structures, the $H_{12}\cdots O_{24}$ bond has a length between 1.6 and 2.6 Å for most of that time.

In aqueous solution, the polarographic curves of the studied compounds are perturbed by adsorption phenomena. These perturbations are more noticeable with compounds bearing a long alkyl chain ($n = 8$) and/or maltose as a polar head group (GLUACO8, MALTACO8 and MALTACS8). In previous work, we have shown that the adsorption mode at the mercury electrode of electroreducible surfactants derived from the 4-acetyl-1-phenoxyalkyl group depends on their chain lengths and/or their micellar properties.[17–19]

As previously observed with 4-acetyl-1-phenoxyalkyl sulfates,[19] when the alkyl chain length of the studied electroreducible saccharidic surfactants increases, the tensammetric curves present two adsorption regions, which can be associated with a change in the nature of the adsorption mode on passing to a more negatively charged surface. In the potential

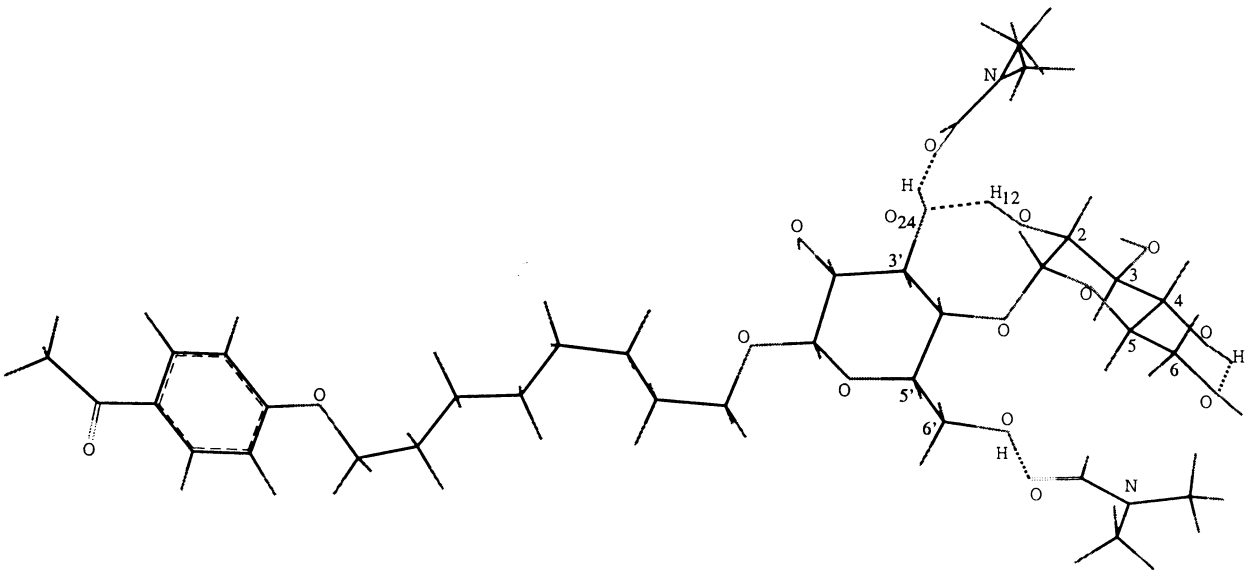


Fig. 10 Molecular drawing of MALTACO8 and the DMF molecules with intermolecular hydrogen bonds, $E = -1445.3$ kcal mol^{-1}

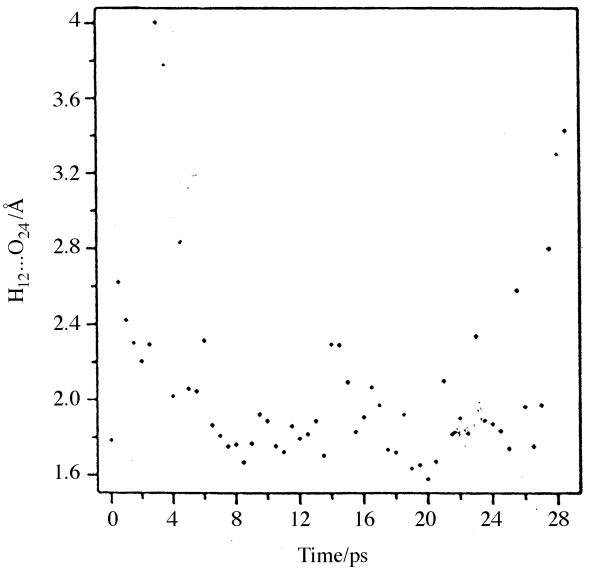


Fig. 11 Temporal evolution of the $H_{12}\cdots O_{24}$ hydrogen bond in the molecular dynamics simulation

range $0 \geqslant E \geqslant -0.5$ V *vs.* SCE behind the potential of zero charge (PZC), the minimum capacity value is around 10 μF cm^{-2}, and when the potential becomes more negative the capacity decreases to a minimum value of 6 μF cm^{-2}. The first minimum capacity value equal to 10 μF cm^{-2} is similar to that obtained with acetophenone, suggesting that, in this potential range, the adsorption is determined predominantly by a π-electron interaction of the benzoyl group with the mercury electrode. When the potential becomes more negative, an adsorption increase (lowest value of the minimum capacity) should be associated with a conformation of the surfactants perpendicular to the electrode surface, leading to the formation of hemi-micelles or micelles at the electrode surface. This assumption is confirmed by the cathodic peak shape. In the case of GLUACO3, the small humps observed at −1.25 V *vs.* SCE, just before the cathodic peak, can probably be assigned to the same phenomenon. However, as previously observed with 4-acetyl-1-phenoxyalkyl sulfates,[19] hydrophobic interactions are less efficient between short alkyl chains, which hinder the progressive turnover of molecules to more negative potentials.

Indeed, the evolution of the cathodic peak, situated for compounds **5**, **7**, **12a** and **12b** between −1.52 and −1.57 V *vs.* SCE, as a function of the concentration and the nature of the polar head group is in agreement with the behaviour that we had previously observed with non-reducible saccharidic surfactants.[15] In the case of monosaccharidic surfactants (GLUACO3 and GLUACO8), a broad and bell-shaped peak is observed in the tensammetric curves. Adsorption of such surfactants depends on the concentration of the monomers in solution, leading to the formation of a monolayer called hemi-micelles at the mercury electrode. However, the poor solubility of GLUACO8 does not allow the determination of the critical micellar concentration following the criteria of Vollhard and colleagues, as we have previously done with non-reducible monosaccharidic surfactants.[20]

For disaccharidic compounds, a split of the capacity peak is observed at $c = 1 \times 10^{-3}$ M for MALTACO8 and $c = 5 \times 10^{-4}$ M for MALTACS8. As proposed by Nikitas *et al.*,[30,31] this splitting, which appears above the CMC, is related to the formation of multilayers of micelles on the electrode surface. According to our previous observations with non-reducible disaccharidic surfactants,[20] these concentrations should approach the value of the CMC of MALTACO8 and MALTACS8. This seems to be confirmed by the fact that the CMC of MALTACS8 should be lower than that of MALTACO8. Indeed, replacement of the oxygen atom by a sulfur in the alkyl maltosides causes a drastic decrease of the CMC.[32] The measurement of surface tension as a function of the concentration of surfactant has been made in the case of the thiomaltoside MALTACS8. The curve $\gamma = f(c)$ exhibits a characteristic breakpoint for a concentration $c = 5 \times 10^{-4}$ M, similar to that obtained by the tensammetric method.

Conclusion

The electrochemical behaviour of these new electroreducible amphiphilic compounds bearing a sugar head group is influenced by their particular conformation in an aprotic solvent and by the micellar and adsorption properties in aqueous solutions. Intramolecular hydrogen bonds, postulated in the case of the maltoside and thiomaltoside derivatives, may explain the reversible one-electron reduction step observed in DMF. The difference in the adsorption behaviour between the mono- (GLUACO3 and GLUACO8) and the disaccharidic (MALTACO8 and MALTACS8) surfactants confirms our previous results concerning the non-electroreducible glycosidic surfactants[20] and their CMC values can be estimated by AC polarography (tensammetry). Furthermore, we are investigating the stereochemical outcome of the electrochemical reductions in connection with the micellar properties. One could expect a stereocontrol due to the chiral saccharide moiety in the organized surfactant layer on the electrode surface. Results concerning this part will be published in the near future.

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