

NEW PERACETYLATED SUGAR-BASED SURFACTANTS FOR SUPERCRITICAL CARBON DIOXIDE

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In this work we describe the synthesis and the first phase and interfacial characterizations of three novel fluorine-free sugar-based amphiphiles, designed to be used in supercritical carbon dioxide (sc-CO₂). They contain peracetylated chains as CO₂-philic parts and unprotected hydroxyl groups as CO₂-phobic ones. The first measurements suggest these new molecules present solubility in sc-CO₂ and activity at water-CO₂ (W/C) interface, which points toward promising applications in chemical processes using sc-CO₂.

INTRODUCTION

The application on supercritical carbon dioxide (sc-CO₂) as an alternative solvent to traditional organic ones, despite of its several desirable characteristics, is often hindered because CO₂ is non-polar, and only dissolves small and apolar molecules. One way to overcome such limitation face to polar chemical species is to introduce specially-designed surfactants in the system. The sc-CO₂-suitable surfactants are molecules composed of a CO₂-philic part (generally containing a perfluorocarbon chain) and a CO₂-phobic part (capable of solubilizing polar compounds).

The first observations of aggregation of surfactants in sc-CO₂ [1] has opened an intense research interest for surfactants capable of solubilizing polar substances in sc-CO₂ [2-5]. However, it is a well known that perfluorinated compounds, despite of high solubilities in sc-CO₂, are persistent organic pollutants. So, since observations that oxygenated compounds could serve as substitutes for fluorinated compounds [6-9], new compounds has been synthesized and tested as potential amphiphiles to be used in sc-CO₂ media. In this study we present the syntheses of three new non-ionic interfacially active molecules, containing hydroxyl groups (some of them from unprotected sugar precursors) as CO₂-phobic (hydrophilic) groups. These molecules are penta-*O*-acetyl-D-gluconamides of ethanolamine (**G1A**), N-methylglucamine (**G2A**) and D-glucosamine (**G3A**). All of them, obtained in good yields, were characterized by ¹H-NMR, FT-IR and microanalysis. Also, the first phase behavior and interfacial tension studies in sc-CO₂ are presented.

MATERIALS AND METHODS

Chemicals

Acetonitrile (Mallinckrodt, spec. grade) was distilled from P₂O₅ (Aldrich, 98%). Ethyl ether (Et₂O, Merck, spec. grade) was refluxed over metallic sodium (Vetec, analytical grade) in presence of benzophenone (Aldrich, 99%) and distilled. Toluene (Vetec, analytical grade) was refluxed over metallic sodium and distilled. Acetone (Vetec, analytical grade), chloroform (Vetec, analytical grade), anhydrous ethanol (Carlo Erba, spec. grade) and petroleum ether (Vetec, analytical grade) were used as received.

The solvents CDCl₃ (0.05% TMS), DMSO-*d*₆ (0.05% TMS) and D₂O (99,9% D) were purchased from Cambridge Isotope Laboratories and used as received in NMR analyses.

The water used in the experiments was purified by systems Elix 10 (reverse osmosis and electrodeionization) and Milli-Q Gradient (ultrafiltration), both from Millipore.

Ethanolamine (Aldrich, 99%) was distilled at 10 mbar. Anhydrous zinc chloride was obtained melting the hydrated chloride (Aldrich, 98%) at 400 °C and keeping the resulting crystals in a vacuum desiccator with P₂O₅ overnight.

Acetic anhydride (Ac₂O, Merck, spec. grade), *D*-glucono- δ -lactone (Aldrich, 99%) *D*-glucosamine hydrochloride (Aldrich, 98%), *N*-methyl-*D*-glucamine (Sigma, 99%), phosphorus pentachloride (Aldrich, 99%), silicagel (Synth, spheres, 1/4 mm) and sodium hydroxide (Merck, analytical grade) were used as received.

Apparatus

Uncorrected Melting points were determined with a MelTemp model 1102D apparatus. Microanalyses were carried out with a Perkin-Elmer model CHN 2400 equipment. FT-IR spectra were recorded with a Shimadzu IRPrestige-21 and spectra were treated with software IRSolution. The absorption signals were reported cm⁻¹ based on common attributions from the literature [10]. ¹H-NMR spectra were recorded in a Varian Gemini 200 spectrometer, operating at 200 MHz for ¹H. We used concentrations of about 10 mg of compound in 0,7 mL of deuterated solvent containing 0.05% of TMS as internal standard in Wilmad 735PP NMR tubes, 5 mm of internal diameter. Attributions were based in δ e J values from the literature and the spectra were Fourier transformed and fitted with MestReC software, version 4.8.11.

Synthesis

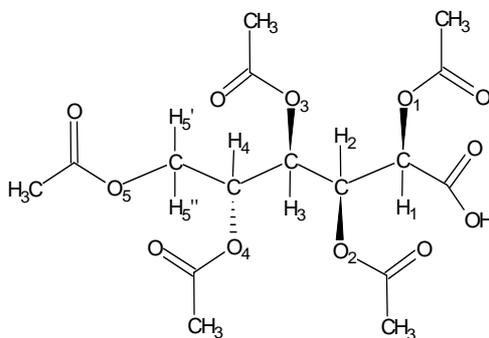
Monohydrate 2,3,4,6-tetra-*O*-acetyl-*D*-gluconic acid (1). For the first precursor, 12.0 g (88 mmol) of anhydrous zinc chloride were added to 150 mL of Ac₂O (1.68 mol, 2.5 equiv.) until most part of solid being dissolved. The system was kept at 0 °C (iced water bath) under vigorous stirring. After cooling, 30.0 g (168 mmol) of *D*-glucono- δ -lactone were added slowly in several portions. The solution was kept under stirring for 24 h at room temperature and after poured in an erlenmeyer containing 600 mL of water (hydrolysis of excess Ac₂O), which was kept under stirring for 2 h. The mixture was stored at the refrigerator at 4 °C during 48 h until the product has been cristalized. The material was filtered, washed with 20 mL of cold water and analyzed by FTIR (KBr pellet), ¹H-NMR (DMSO-*d*₆, 0.05% TMS) and elemental analysis.

Yield: 57.5%; melting point: 96-101 °C (MP^{lit.} 113-117 °C) [11]. FTIR (KBr pellet, cm⁻¹): 3438 (ν_{O-H} , carboxylic acid + alcohol), 1745 ($\nu_{C=O}$, ester, acetate-characteristic), 1716 ($\nu_{C=O}$, carboxylic acid, as a satellite of 1745 cm⁻¹, more intense), 1378 ($\delta_{O-H} + \omega_{C-H}$), 1235 ($\nu_{C(O)-O}$, saturated alcohol acetates). ¹H-NMR (25 °C in DMSO-*d*₆, δ in ppm): 2.01 (_{sap}, O_{2,3}(CO)-**CH₃**, 6H), 2.02 (s, O₅(CO)-**CH₃**, 3H), 2.09 (s, O₁(CO)-**CH₃**, 3H), 3.35 (broad, -**OH**), 3.67 (m, 1H), 3.94 (m, 2H), 5.10 (m, 2H), 5.68 (m, 2H). Microanalysis: found 43.84% C, 5.75% H (calcd. 46.16% C, 5.53% H, for C₁₄H₂₀O₁₁).

2,3,4,5,6-penta-*O*-acetyl-*D*-gluconic acid (2). 30.0 g (82 mmol) of **1** were added to a cooled solution (iced water bath) of 10.8 g (79 mmol) anhydrous zinc chloride were in 150 mL of Ac₂O (1.68 mol, 2.5 equiv.). The mixture was kept under stirring for 24 h at room temperature and after poured in an erlenmeyer containing 600 mL of water (hydrolysis of excess Ac₂O), which was kept under stirring for 2 h. The product was then extracted with four 60 mL portions of chloroform. The solution was concentrated to a 120 mL volume and 150 mL of toluene were added. The system was again concentrated and an equal amount of toluene was added. Then, the system was concentrated to a final volume of 180 mL and was kept at 4 °C during 48 h until the product has been cristalized. The material was filtered, washed with 10 mL of toluene and analyzed by FTIR (KBr pellet), ¹H-NMR (CDCl₃, 0.05% TMS) and elemental analysis.

Yield: 79.8%; melting point: 100-103 °C (MP^{lit.} 110-111 °C) [11]. FTIR (KBr pellet, cm⁻¹): 3258 (ν_{O-H}, carboxylic acid), 1744 (ν_{C=O}, ester, acetate-characteristic), 1726 (ν_{C=O}, carboxylic acid, as a satellite of 1744 cm⁻¹, more intense), 1450 (δ_{C-H} symmetric, -CH₃), 1431 (δ_{C-H} asymmetric, -CH₃), 1215 (ν_{C(O)-O}, saturated alcohol acetates). ¹H-NMR (25 °C in CDCl₃, 0.05% TMS, δ in ppm): 2.06 (s, O₂(CO)-**CH₃**, 3H), 2.09 (s_{ap}, O_{3,4,5}(CO)-**CH₃**, 12H), 2.20 (s, O₁(CO)-**CH₃**, 3H), 4.17 (dd, **H-5'**, 1H), 4.30 (dd, **H-5''**, 1H), 4.97 (broad, CO-**OH**), 5.10 (m, **H-4**, 1H), 5.32 (d, **H-1**, 1H), 5.52 (dd, **H-3**, 1H), 5.64 (dd, **H-2**, 1H). Proton numbers used in the attribution above are represented in figure 1 below. Microanalysis: found 47.11% C, 5.43% H (calcd. 47.29% C, 5.46% H, for C₁₆H₂₂O₁₂).

Figure 1: Proton numbering for NMR attribution of gluconic acid precursors.



2,3,4,5,6-penta-*O*-acetyl-*D*-gluconyl chloride (3). 10.0 g (24 mmol) of **2** were partially dissolved in 74 mL of anhydrous Et₂O followed by slow addition of 5.0 g (24 mmol) of phosphorus pentachloride. The system was kept under vigorous stirring at room temperature for 24 h in a round bottom flask with a drying tube (silicagel). The solution was concentrated to half of its initial volume and stored at -12 °C for 72 h, until the product has been cristalized. The material was rapidly filtered (in a cold büchner funnel, to avoid hydrolysis), washed with 10 mL of petroleum ether and analyzed by FTIR (KBr pellet), ¹H-NMR (CDCl₃, 0.05% TMS) and elemental analysis.

Yield: 92.2%; melting point: 61-65 °C (MP^{lit.} 68-71 °C) [11]. FTIR (KBr pellet, cm⁻¹): 1806 (ν_{C=O}, acyl chloride, as a satellite of 1745 cm⁻¹, more intense), 1745 (ν_{C=O}, ester, acetate-characteristic), 1432 (δ_{C-H} asymmetric, -CH₃), 1244 (ν_{C(O)-O}, saturated alcohol acetates). ¹H-NMR (25 °C in CDCl₃, δ in ppm): 2.07-2.25 (m, O_{1,2,3,4,5}(CO)-**CH₃**, acid chloride and hydrolysis

acid-product methyl signals are mixed), 2.78 (broad, CO-**O**H), 4.16 (dd, **H-5''**, 1H), 4.31 (dd, **H-5'**, 1H), 5.08 (m, **H-4**, 1H), 5.32-5.53 (m, **H-1** and **H-3**, 2H), 5.64-5.78 (m, **H-2**, 1H). Microanalysis: found 45.36% C, 4.76% H (calcd. 45.24% C, 4.98% H, for C₁₆H₂₁ClO₁₁).

N-(2-Hydroxyethyl)-2,3,4,5,6-penta-O-acetyl-D-gluconamide (G1A). 2.00 g (4.71 mmol) of the acyl chloride **3** (dissolved in 10 mL of acetonitrile) were slowly dropped into 0.575 g (9.42 mmol) of ethanolamine dissolved in 10 mL of acetonitrile at 0 °C. The system was kept under vigorous stirring for 24 h. The salt formed in the process (2-hydroxyethanolaminium chloride) was quantitatively filtered and the solvent was evaporated. The product was mixed with chloroform and toluene and crystallized the same way as precursor **2**. It was dried under vacuum in the presence of P₂O₅ and analyzed by FTIR (KBr pellet), ¹H-NMR (DMSO-*d*₆, 0.05% TMS) and elemental analysis.

Yield: 68%; melting point: 108-112 °C. FTIR (KBr pellet, cm⁻¹): 3234 (ν_{N-H}, secondary amide), 3258 (ν_{O-H}, alcohol), 2980 (ν_{C-H} asymmetric, -CH₃), 2950 (ν_{C-H} symmetric, -CH₃), 1749 (ν_{C=O}, ester, acetate-characteristic), 1657 (ν_{C=O}, solid secondary amide), 1579 (δ_{N-H} + ν_{C-NH}, solid secondary amide), 1440 (δ_{C-H} asymmetric, -CH₃), 1375 (δ_{C-H} symmetric, -CH₃), 1217 (ν_{C(O)-O}, saturated alcohol acetates), 1051 (ν_{C-O}, primary alcohols like RCH₂CH₂OH). The 2-hydroxyethyl methylene stretching bands are also present as little shoulders. ¹H-NMR (25 °C in CDCl₃, 0.05% TMS, δ in ppm): 1.98 (s, O₂(CO)-**CH**₃, 3H), 2.01 (s, O_{3,4}(CO)-**CH**₃, 6H), 2.05 (s, O₅(CO)-**CH**₃, 3H), 2.14 (s, O₁(CO)-**CH**₃, 3H), 3.23 (m, 2H, NH-**CH**₂-CH₂-), 3.48 (t, 2H, -CH₂-**CH**₂-OH), 4.12 (dd, **H-5''**, 1H), 4.28 (dd, **H-5'**, 1H), 5.01 (m, **H-4**, 1H), 5.19 (d, **H-1**, 1H), 5.42 (m, **H-3**, 1H), 5.60 (m, **H-2**, 1H), 6.88 (broad, **N-H**, 1H). Microanalysis: found 48.11% C, 6.06% H, 3.05% N (calcd. 47.95% C, 6.04% H, 3.05% N, for C₁₈H₂₇NO₁₂).

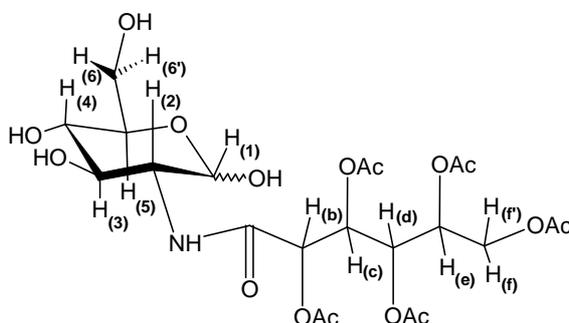
N-methyl-N'-[(2R,3S,4S,5S)-2,3,4,5,6-penta-hydroxy-hexyl]-2,3,4,5,6-penta-O-acetyl-D-gluconamide (G2A). 0.919 g (4.71 mmol) of *N*-methyl-glucamine were dissolved in 20 mL of water at -10 °C (salt-ice bath) in a three-neck round bottom flask. Then, 2.00 g (4.71 mmol) of **3** (dissolved into a small amount of acetonitrile) were slowly dropped with an addition funnel. At the same time, 4.71 mL of 1 M NaOH aqueous solution (containing, thus, 4.71 mmol of base) were dropped with a pasteur pipette. The system was kept under stirring for 24 h, the solvent was evaporated, giving a highly deliquescent white solid, which was dissolved in 20 mL of acetone (remotion of NaCl), filtered, dried with P₂O₅ under vacuum and analyzed by FTIR (KBr pellet), ¹H-NMR (DMSO-*d*₆, 0.05% TMS) and elemental analysis.

Yield: 68%; melting point: 82-86 °C. FTIR (KBr pellet, cm⁻¹): 3700-2800 (ν_{O-H}), 1749 (ν_{C=O}, ester, acetate-characteristic), 1645 (ν_{C=O}, solid tertiary amide), 1440 (δ_{C-H} asymmetric, -CH₃), 1375 (δ_{C-H} symmetric, -CH₃), 1217 (ν_{C(O)-O}, saturated alcohol acetates), 1047 (ν_{C-O}, primary alcohols like RCH₂OH). Methyl and methylene stretching bands are encumbered by a broadband between 2800 and 3700 cm⁻¹, related to several hydroxyl stretching modes (alcohol groups present and some hydration water). ¹H-NMR (25 °C in DMSO-*d*₆, δ in ppm): 1.97 (s, O₂(CO)-**CH**₃, 3H), 2.00 (s, O_{3,4}(CO)-**CH**₃, 6H), 2.06 (s, O₅(CO)-**CH**₃, 3H), 2.18 (s, O₁(CO)-**CH**₃, 3H), 2.35 (s, 3H, -N-**CH**₃), 2.72-2.80 (m, 2H, -N(CH₃)-**CH**₂-CH(OH)-), 3.40-3.81 (m, attached-to-carbon protons signals superposed), 4.10 (dd, **H-f'**, 1H), 4.25 (dd, **H-f**, 1H), 4.98 (m, **H-e**, 1H), 5.13 (d, **H-b**, 1H), 5.38 (m, **H-d**, 1H), 5.56 (m, **H-c**, 1H), 7.18 (broad, **N-H**, 1H). Microanalysis: found 46.04% C, 6.03% H, 2.21% N (calcd. 47.34% C, 6.39% H, 2.40% N, for C₂₃H₃₇NO₁₆).

2-[2,3,4,5,6-penta- O-acetyl-D-gluconamido]-2-deoxy-D-glucopyranose (G3A). 1.015 g (4.71 mmol) of *D*-glucosamine hydrochloride were dissolved in 20 mL of water containing 4.71 mmol of NaOH (as NaOH 1 M solution) at - 10 °C (salt-ice bath) in a three-neck round bottom flask. Then, 2.00 g (4.71 mmol) of **3** (dissolved into a small amount of acetonitrile) were slowly dropped with an addition funnel. At the same time, 4.71 mL of 1 M NaOH aqueous solution (containing, thus, 4.71 mmol of base) were dropped with a pasteur pipette. The system was kept under stirring for 24 h, the solvent was evaporated, giving a white solid, which was dissolved in 20 mL of acetone (remotion of NaCl), filtered, dried with P₂O₅ under vacuum and analyzed by FTIR (KBr pellet), ¹H-NMR (DMSO-*d*₆, 0.05% TMS) and elemental analysis.

Yield: 57%; melting point: 98-104 °C. FTIR (KBr pellet, cm⁻¹): 3700-3000 (ν_{O-H}), 2966 (ν_{C-H} asymmetric, -CH₃), 2943 (ν_{C-H} symmetric, -CH₃), 1749 (ν_{C=O}, ester, acetate-characteristic), 1674 (ν_{C=O}, solid secondary amide, *trans* form), 1634 (ν_{C=O}, solid secondary amide, *cis* form), 1547 (δ_{N-H} + ν_{C-NH}, solid secondary amide), 1435 (δ_{C-H} asymmetric, -CH₃), 1375 (δ_{C-H} symmetric, -CH₃), 1223 (ν_{C(O)-O}, saturated alcohol acetates), 1051 (ν_{C-O}, primary alcohols like RCH₂OH). ¹H-NMR (25 °C in DMSO-*d*₆, δ in ppm): 1.94 (s, O₂(CO)-**CH₃**, 3H), 2.09 (s, O_{3,4}(CO)-**CH₃**, 6H), 2.13 (s, O₅(CO)-**CH₃**, 3H), 2.18 (s, O₁(CO)-**CH₃**, 3H), 3.0-3.9 (m, H-2 to H-6' pyranosyl protons signals superposed), 4.18 (dd, **H-f'**, 1H), 4.31 (dd, **H-f**, 1H), 5.00 (m, **H-1**, 1H), 5.03 (m, **H-e**, 1H), 5.18 (d, **H-b**, 1H), 5.45 (m, **H-d**, 1H), 5.60 (m, **H-c**, 1H), 7.12 (broad, **N-H**, 1H). Proton numbers used in the attribution above are represented in figure 2 below. Microanalysis: found 46.36% C, 5.93% H, 2.31% N (calcd. 46.56% C, 5.86% H, 2.47% N, for C₂₂H₃₃NO₁₆).

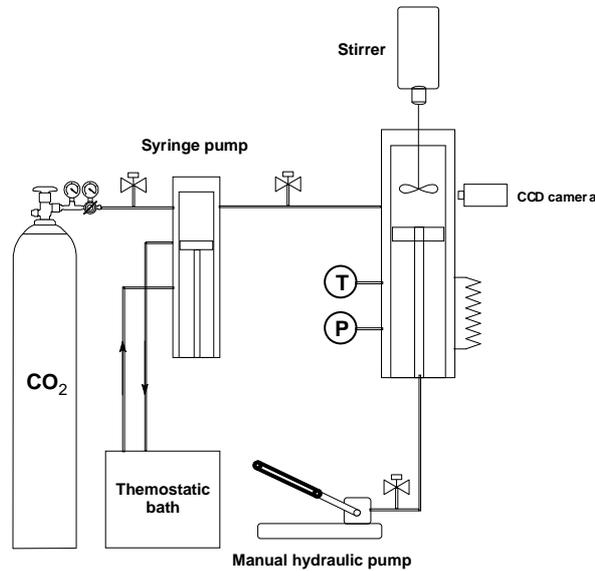
Figure 2: Proton numbering for NMR attribution of a glucose-coupled gluconic acid molecule.



2.4. Phase behavior and interfacial tension measurements

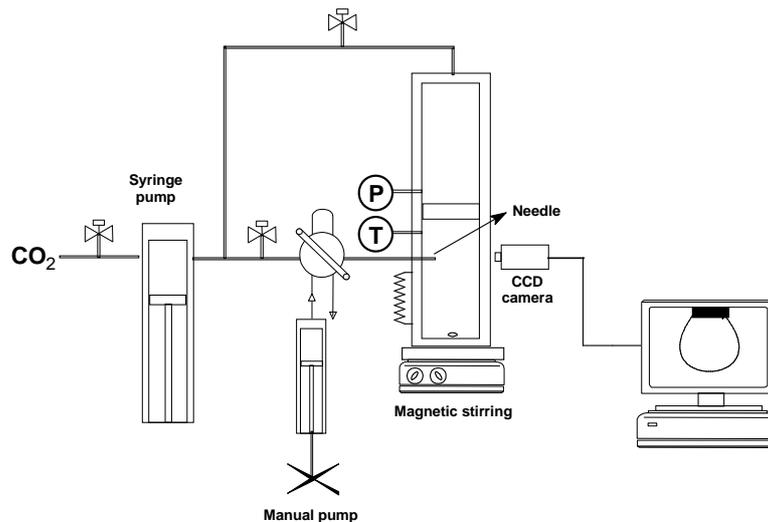
For the sc-CO₂ solubility and cloud point visual measurements we used a TharTech SPM20 phase monitor, formed by a variable volume cell (5.0 – 15.5 mL), mechanical stirring magnetically coupled, pressure transducer, heating cartridges, thermocouple and a CCD camera perpendicularly LED illuminated through sapphire windows. The CO₂ source was a liquid CO₂ line at 55 bar compressed into adequate pressures using a Teledyne Isco 260D syringe pump, cooled at -5 °C with a Julabo EB thermostatic bath (figure 3).

Figure 3: Phase behavior measurements apparatus, SPM20 phase monitor.



Interfacial tension measurements were recorded in a home-made high pressure pendant drop tensiometer formed by a variable volume cylinder equipped with a directly illuminated camera, which capture the image of the drop (figure 4). The software CAM2008 calculates the curvature radius and, solving the Young-Laplace equation, allows to measure dynamically or to calculate final (after interface equilibration) interfacial tension values. We measured saturated systems containing surfactant in the sc-CO₂ phase (light phase) against a pure water drop (heavy phase) at 2000 PSI (137.8 bar) during 10000 s. For comparison, we also measured interfacial tensions of fluorinated analogues synthesized by our group.

Figure 4: High pressure tensiometer.



RESULTS AND DISCUSSION

Synthesis

Synthetic schemes are presented at figures 5 and 6 below. The choice for a three step synthesis of the precursors [11] instead of a more straightforward one is explained by the high purity and crystallinity of the products, since the direct acylation of gluconic acid or some of its salts, as extensively found in the literature [7, 12], gave us a syrupy product, which was very difficult to work in the chlorination (carboxylic acid activation) step and, also, to chemically characterize.

Figure 5: Synthesis of the peracetylated surfactants' precursors **1** to **3**.

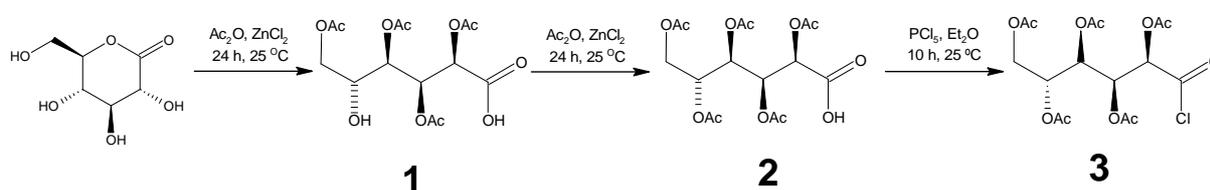
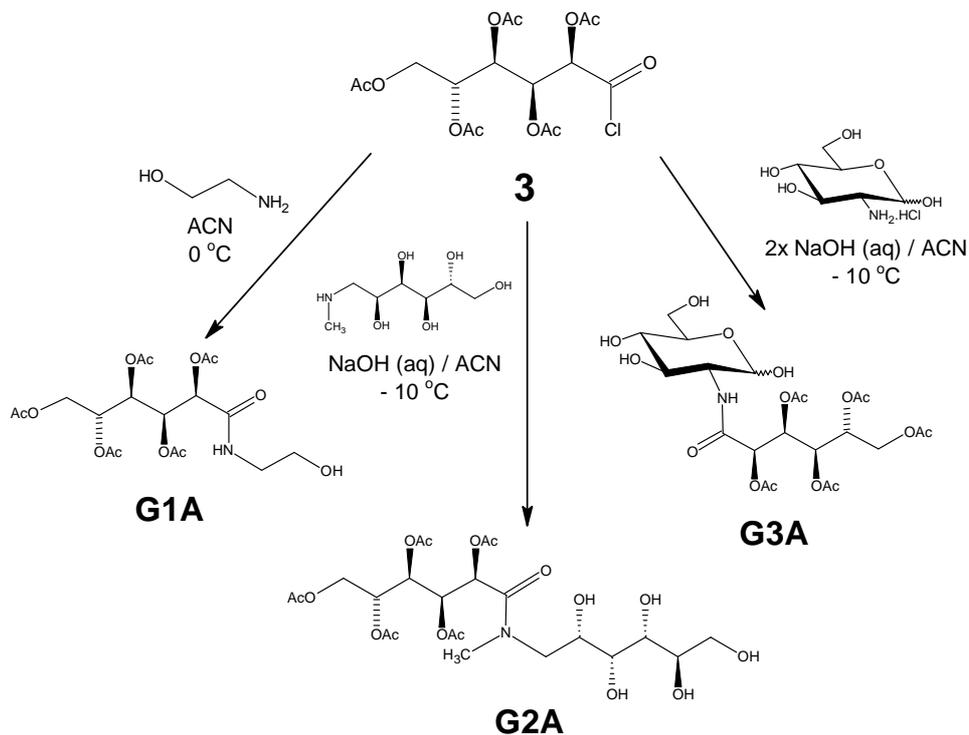


Figure 6: Synthetic scheme for the surfactants preparation.



The FTIR measurements were essential to verify the desired chemical transformations. For example, it is evident that the acyl chloride **3** was formed with total consumption of carboxylic acid **2**, as shown by disappearance of the carbonyl band in 1726 cm^{-1} with concomitant

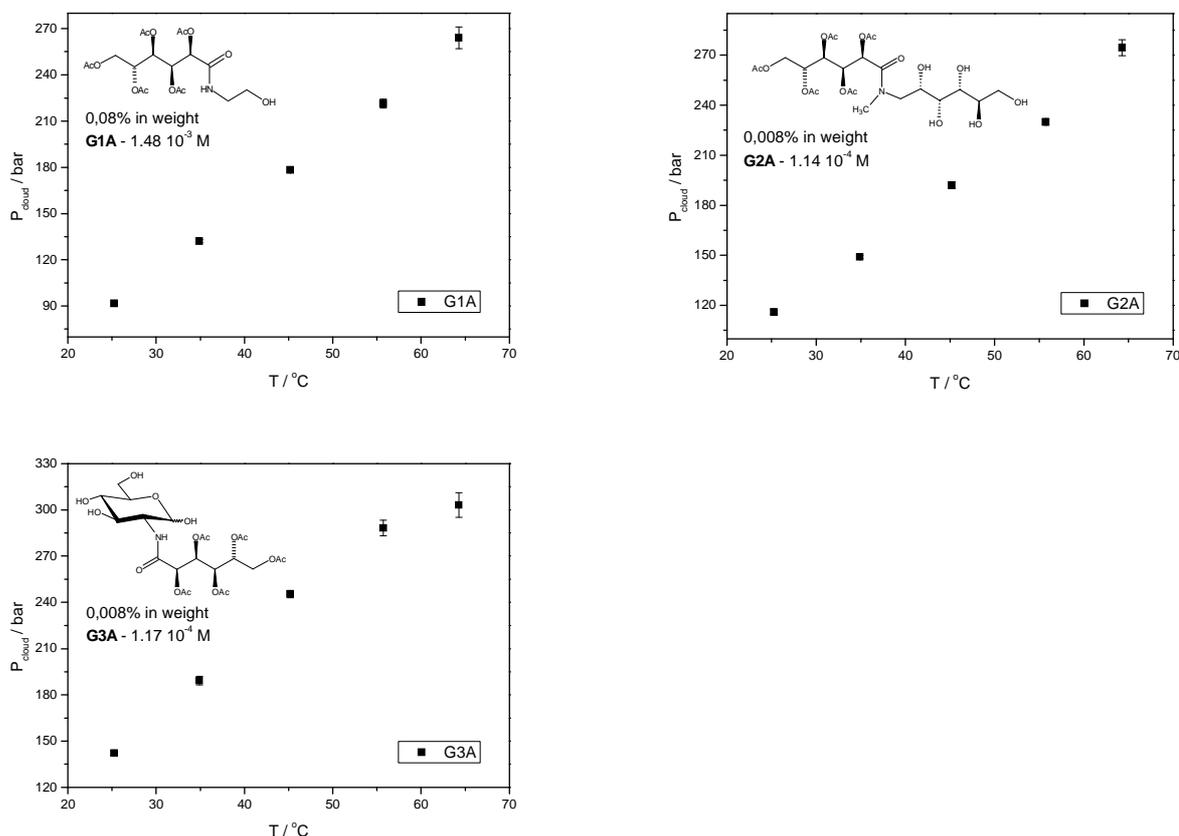
appearance of a new signal in about 1800 cm^{-1} . The surfactants' FTIR signals showed, as expected, amide I bands (carbonyl stretching) between 1675 and 1640 cm^{-1} and amide II bands for the secondary amides (**G1A** and **G3A**) at 1540 cm^{-1} .

In comparison with their fluorinated analogue, the new peracetylated surfactants (specially **G1A** and **G3A**) presented a better solubility in polar solvents, including water. This is probably due to the higher hydrophilicity of peracetylated-sugar chains, if compared with perfluorinated ones. Despite of these water-affinity differences, molecule **G1A** (like its eight-carbon perfluorinated analogue, **F1A**) was soluble in sc-CO₂.

Phase and interfacial behavior

We observed cloud point pressures of about 100 bar for surfactant **G1A**, as well as a water dispersion capability at pressures of about 150 bar. Figure 7 presents the simplified phase diagrams for binary systems sc-CO₂/surfactant.

Figure 7: Cloud point (visual) measurements for the new surfactants (saturated systems).



A simple explanation for the trend observed could be that a temperature increase promotes an increase in the sc-CO₂ solubilities of the molecules, causing a raise in the cloud pressures observed (the measurements were done in a supersaturated system). Besides, the solubilization of a particular substance in sc-CO₂ depends on the density of the fluid, and also on the agitation of the molecules. Thus, even assuming a negligible variation in the solubility, an increasing

temperature will cause increasing *agitation* and density and, that way, the necessity of greater pressures to solubilize the same amount of surfactant.

Also, the first results showed us that the peracetylated surfactants have similar solubility behavior than their fluorinated analogues, except for the range of cloud pressures – fluorinated analogues present cloud pressures typically 20% lower than the peracetylated surfactants. It is important to stress out that the solubilization of oxygenated carbonyl compounds in sc-CO₂ is explained by specific Lewis acid-base interactions between the carbon dioxide molecule (its carbon acting as an acidic species) and the acetyl group residues in the solute molecules [6-8, 13]. The acetyl methyl groups, vicinal to carbonyl, are also suggested to play a cooperative role, donating protons to form hydrogen bonds with the oxygen atoms from CO₂ [14-16]. Meanwhile, the solubility of fluorinated compounds is still subject of debate, sometimes treated as being promoted by specific interactions [17, 18], and sometimes have seen as entropically-driven processes, mediated by tail-tail interactions and minimization of sterical volumes [19].

The first interfacial tension measurements against pure water (25 °C, at 138 bar), showed that molecule **G1A** reduced interfacial tension of W/C binary system (supposed to be about 25 mN/m) to 10.26 mN/m, while its fluorinated analogues containing eight and ten carbon, resulted in interfacial tension values of 12.06 and 9.091 mN/m, respectively, which is an indication of comparable interfacial activities. The interfacial behavior of molecules **G2A** and **G3A** is now being studied in a more detailed way, taking account of pressure and temperature variations. We are also studying water uptake capabilities of these surfactants in sc-CO₂ using high pressure UV-Visible spectroscopy measurements.

CONCLUSIONS

So far, we have synthesized three new sugar-based surfactants that are potentially useful for supercritical carbon dioxide. The first solubility and interfacial studies revealed that those molecules are active at W/C interface and present a phase behavior comparable with their fluorinated analogues. This suggests that oxygenated molecules can indeed act as environmentally-friendly substitutes of fluorinated amphiphiles in sc-CO₂.

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