Design and properties of a novel family of nonionic biobased furanic hydroxyester and amide surfactants

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Abstract. A series of original amphiphiles prepared by Morita-Baylis Hillman (MBH) coupling biobased furanic aldehydes with hydrophobic alkenes is explored. Structural variations result from the level of polarity on the furanic substrate, the type of activated alkenes (ester of amide),

the alkyl chain length and the presence of an unsaturation. The physicochemical properties such as the Krafft point, critical micellar concentration (CMC) and hydrophilic lipophilic behavior determined with the PIT-slope method have been explored. The glucosyloxymethyl furfural (GMF) derivatives exhibit higher water-solubility than the succinyl hydroxymethyl furfural (SMF) and the HMF-derived ones. Saturation of the acrylic linkage results in slightly lower CMC for GMF derived compounds by the enhanced solvation of the unsaturation. As expected, increasing the alkyl chain length diminishes the water-solubility, the CMC and the hydrophilicity. The decreasing hydrophilic behavior of surfactants is as follows: **G$_i$** > **G$_i$H** > **HS$_i$**. For the shorter HMF amphiphiles, the order is: **H$_i$N** > **H$_i$** ≈ **H$_i$H**. These surfactants cover a wide range of HLB values. The dodecyl GMF -G_{12}- is as hydrophilic as $C_{12}E_6$ and the hexadecyl SMF -HS16- is much more hydrophobic than SPAN 40. Formation of stable emulsions with two cosmetic oils of different polarity is very encouraging for a possible application of this new family of biobased surfactants.

Keywords: Furans; Hydroxymethylfurfural (HMF) ; Glucosyloxymethyl furfural (GMF) ; Morita-Baylis-Hillman ; Surfactants ; PIT-slope ; Emulsion.

Introduction

The use of the furanic scaffold for designing novel biobased amphiphilic compounds and exploring their physicochemical properties in the future is a rapidly developing field. This area is supported by the increasingly popular use of biobased furanic platform molecules towards a wide scope of potential applications, outside their already established usefulness in the biobased solvents and biobased polymers fields.[1–12]

Considering their wide range of applications and the very large quantities used in the everyday life,[13,14] surfactants are the object of intense academic and industrial research. In a longer term research strategy, it is crucial to diversify their molecular design and exploring novel resources offering the opportunity for introducing more renewable carbon in the final products. [15–19] These approaches are complementary to the development of more classical systems derived from the etherification or esterification of polyols (carbohydrates, glycerol, sorbitan, isosorbide, erythritol, etc.).[20–29]

With respect to furanic platform molecules, seminal studies have reported surfactants built on a furanic scaffold (either furan, furfural or HMF), including recent ones by Dauenhauer, Corma and Climent, and Hausoul and Palkovits.[30–41] Among reported examples, a few keep the furan architecture in the final design, with representative examples shown in **Figure 1**. Oleofurans of type A-C, prepared by Friedel-Crafts acylation of furans, exhibit interesting ability to suppress the effects of hard water and simultaneously capability to form micelles.[30] Amphiphilic furfural glyceryl acetal of type D prepared by etherification of HMF with fatty alcohols followed by acetalization with glycerol show good ability to stabilize emulsions.[31]

Other acetals of type E were reported by Climent et al. using a two-step acetalization-oxidation

sequence.[33] The Benvegnu group found that the same systems could be prepared in one step from oligo-alginates or alginates alginate, and were able to reduce water surface tension and were readily biodegradable with absence of aquatic ecotoxicity.[42] Sulfonate esters of type F, showing satisfactory stability in acidic or neutral media, have been also reported.[34] Original polycyclic systems of type G were prepared by Diels-Alder reactions of alkylfurans with maleimides, which behave as surface active agents, forming spherical micelles, with an interesting property to be thermally labile, through a retro-Diels-Alder process occurring at 50 °C leading to a complete loss of surfactant behavior.[35] Anionic furanic surfactants such as type H and I compounds prepared from furfural of HMF, respectively, exhibit promising critical micelle concentrations and surface tension lowering abilities.[36] Systems of type J, K and L, reported in patents, have been prepared *via* reductive amination-esterification, or bis-Friedel-Crafts sequences, respectively.[37,38] Monoesters of furandicarboxylic acid of type M were found to improve the efficiency of fatty glucoside synthesis,[39] while systems of type N obtained by reductive amination and further amine quaternisation were designed as novel cationic surfactants or ionic liquids.[40,43] Other systems, arising from furanic platforms, but not showing the furan ring in the final design, have also been reported.[44–48]

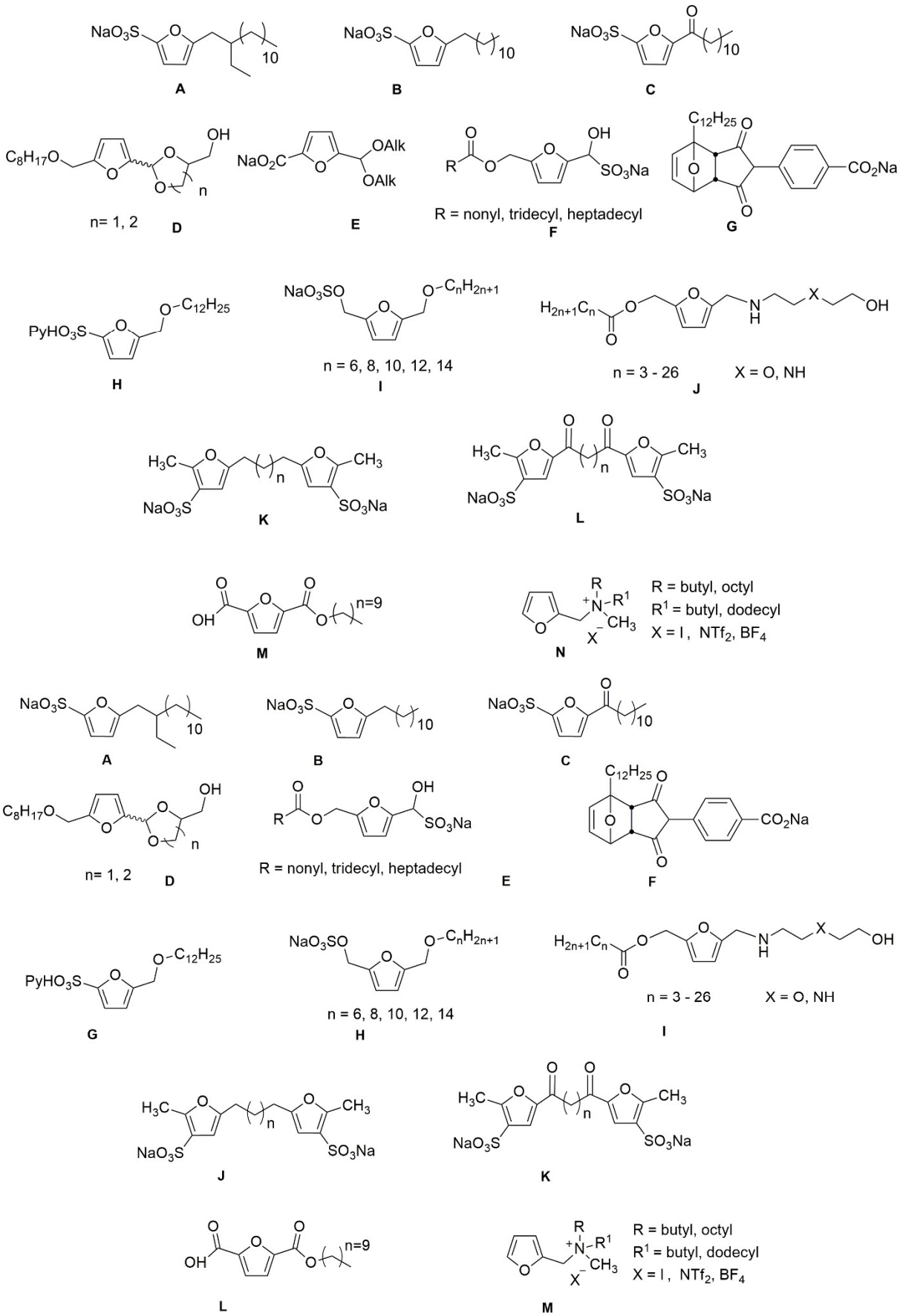


Figure 1. Examples of reported surfactants with a furan-containing design.

In order to contribute to this exploration of novel designs of amphiphilic compounds based on a furanic scaffold, the work reported herein relies on the use of the Morita-Baylis-Hillman (MBH) reaction enabling a carbon-carbon bond extension by reaction of the C-1 aldehyde group of HMF with lipophilic acrylic substrates. The MBH reaction is an attractive one-step reaction with high atom-economy and broad structural scope,[49–53] shown to be readily applicable to HMF, and analogues under mild and clean conditions.[54,55] Thanks to the presence of the hydroxymethyl group, HMF offers opportunities for structural modulation of the hydrophilic moiety, while the activated alkene chain length allows the modulation of the hydrophobic side. Hydrogenation of the acrylic double bond in the MBH adducts has also been envisaged. The purpose of the work is to reach, by this original route, novel amphiphilic systems in order to explore their physicochemical properties. The study covers a family of 16 compounds with high variability in their hydrophilic and hydrophobic structure (**Scheme 1**). Their aqueous behaviour through their water-solubility as a function of temperature was first studied, as well as their capacity to reduce the water/air surface tension and their self-aggregation as a function of concentration (CMC). Then, their hydrophilic-lipophilic balance has been quantified using the PIT-slope method[56,57] that allows a direct comparison with a large number of known polyethoxylated and bio-based surfactants. Finally, the emulsifying properties of the compounds with an alkyl chain bearing more than 10 carbon atoms have been studied using two technical grade oils commonly used in cosmetic applications.

Materials and methods

Chemicals.

Reagents were purchased at the highest quality from commercial company like Aldrich, Alfa Aesar, or TCI and used without further purification, unless otherwise noted. HMF was purchased from Carbosynth, GMF was prepared as previously reported[58] from isomaltulose which was a gift from Cargill. SMF was obtained from the esterification of HMF with succinic anhydride *N*-monoalkyl acrylamides was prepared from previous reported reaction between acyl chloride and *N*-alkyl amines.[59,60] Solvents and eluents (EtOH, MeOH, pentane, EtOAc, CH_2Cl_2, MeOH) were purchased from Carlo Erba reagents in high purity. Water used as solvent or co-solvent was ultrapure water (18 MΩ).

Pure tetraethyleneglycol monodecyl ether ($C_{10}E_4$) was synthesized according to a method described elsewhere.[61,62] Its purity was assessed by NMR and GC analyses (> 99%) and by comparing its cloud point temperature (20.4 °C at 2.6 wt.%) with the reference value (20.56 °C at 2.6 wt.%)[63]. *n*-Octane (> 99%) was obtained from Sigma-Aldrich. Sodium chloride NaCl (≥ 99.5%) was supplied by Acros Organics. All these chemicals were used without further purification.

Analyses and purifications.

Reactions were monitored by thin-layer chromatography (TLC), using aluminum-backed plates pre-coated 0.2 mm silica gel 60. TLC plates were visualized using either 5% (w/w) ethanolic sulfuric acid or 1% (w/w) aqueous potassium permanganate containing 1% (w/w) $NaHCO_3$. Flash chromatographies were performed on Merck Si 60 silica gel (40–63 μm). NMR spectra

(^{1}H and ^{13}C) were recorded on Bruker DRX 300, 400 or 500 spectrometers and high-resolution mass spectra (HRMS) were recorded on Bruker MicrOTOF-Q II XL spectrometer using ESI as ionization source. All data and spectra are presented in supplementary information.

Syntheses.

MBH reactions of HMF, GMF and SMF were performed using the following procedure. A mixture of HMF (17.4 mmol) and DABCO (17.4 mmol) in 34 mL EtOH/H_2O (1:1) and butyl or hexyl acrylate (34.8 mmol) was stirred at room temperature for approximately 2 days. Upon completion (TLC), solvent was removed under vacuum and the crude mixture was purified by flash chromatography using pentane/EtOAc (1:1) as eluent, leading to adducts **H4** and **H6** in 62 and 56 % yields respectively. Alternatively, solvent free conditions were used for the synthesis of **H6** using 1.5 equiv. of acrylate and 0.8 equiv of DABCO, room temperature, 7 hrs, chromatography eluent DCM/ether = 2/1, giving **H6** in 49 % yield. GMF-derived **G6** adducts was obtained using no-solvent conditions with 3 equiv of acrylate, 5 days, whereas for **G8**, **G12** and **G16**, the reaction of GMF was conducted in ethanol with 0.8 equiv of DABCO, and 1.1 equiv of acrylate. Removal of the solvent and further purification of the residue by flash chromatography using CH_2Cl_2/MeOH (9:1) as eluent, lead to **G6**, **G8**, **G12** and **G16** in 58, 56, 53 and 57 % yields respectively. SMF adducts were obtained under no-solvent conditions using 2.4 equiv of DABCO and 2 equiv of alkyl acrylate which were stirred vigorously at room temperature. After 64 h, addition of 5mL HCl (1M) and extraction by EtOAc, the organic phase was dried over Na_2SO_4 and concentrated under vacuum, before column chromatography purification using EtOAc/pentane = 1/1 containing 0.5 % acetic acid as eluent, leading to **HS8**,

HS12 and **HS16** in 91, 93 and 72 % yields respectively. HMF acrylamide adducts were obtained from HMF using butyl or hexyl acrylamide (2 equiv), 3-HQD (1 equiv) in 1:1 2-MeTHF/H_2O at room temperature. After 3 days, the solvent was evaporated and the concentrated crude mixture was purified by column chromatography using EtOAc/pentane (1:1) as eluent leading to **H4N** and **H6N** in 53 % and 60 % yields respectively.

The hydrogenation of MBH adducts towards **H4H**, **H6H**, **G8H**, **G12H** and **G16H** was performed using following the procedure. The MBH adduct was mixed with $Pd(OH)_2/C$ (1 mmol %), pyridine (1.5 eq) in MeOH (0.1 M) under H_2 (p = 1 atm) at room temperature for about 2 hours. Upon completion, the mixture was filtered on celite, and the solvent was removed under vacuum. The crude product was purified by flash column chromatography on silica gel using EtOAc/pentane (1:1) as eluent for HMF adducts and CH_2Cl_2/MeOH (9:1) as eluent for GMF adducts, in yields ranging from 93 to 97 %.

Tensiometry measurements.

The surface tensions were measured at 25 °C with a K100MK2 Krüss tensiometer using a platinum rod as probe. Measurements were made on 2 mL samples. The surface tension of pure water was first measured for calibration and then different concentrations of the same sample were measured. When the surface tension was stable (standard deviation of the 5 final measurements lower than 0.15 $mN \cdot m^{-1}$), the average value was recorded.

PIT-slope method.

10 mL of the $C_{10}E_4$/*n*-Octane/0.01M NaCl system were prepared and hand-shaken and left to

pre-equilibrate at room temperature. A first heating-cooling cycle was performed and then the second surfactant S_2 was added (mass m_{S2}). The amount of $C_{10}E_4$ was then adjusted to m_{S1} so that the proportion of S_1 surfactant remains constant at 3 wt. % in all experiments. Equation 1 defines S_2 surfactant molar fraction in the surfactant mixture.

$$x_2 = \frac{m_{S2}/MW_2}{m_{S1}/MW_1 + m_{S2}/MW_2} \quad (1)$$

The water weight fraction f_w defined by equation 2 is 0.5 in all systems.

$$f_w = \frac{m_w}{m_w + m_o} \quad (2)$$

m_w and m_o are the weight of 0.01M NaCl solution and octane, respectively. The system was kept under continuous stirring at 500 rpm. The sample was then subjected to two heating-cooling cycles at a rate of 1 °C/min. The reported value is the average for the four phase inversion temperature measurements. Other technical details of the experimental procedure are explained in literature.[57]

Emulsion tests.

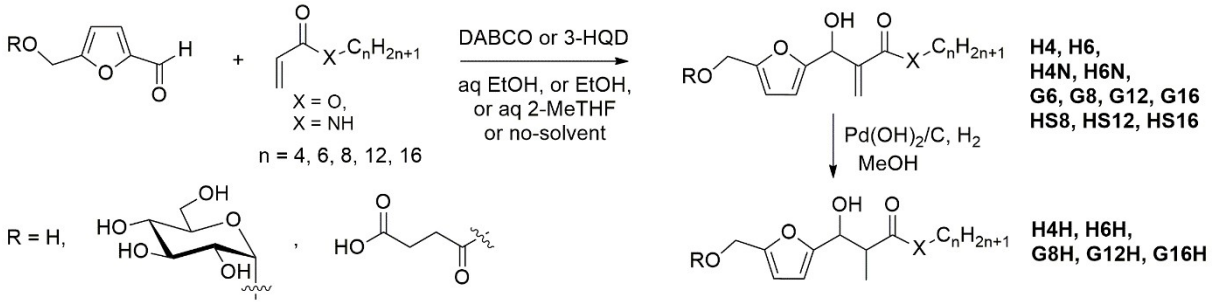
2 mL of emulsion was prepared in 4 mL vials by weighing successively the compounds. Isopropyl myristate (IPM) and Creasil IH CG (isohexadecane) were used as the oily phases. NaCl aqueous solution and the oil (octane or Creasil IH CG) had the same volume in each sample. The 1 wt.% surfactant/oil/0.01 M $NaCl_{(aq)}$ resulting system was gently mixed to enhance the partitioning of the surfactant between the oil and water phases. All systems were prepared and left to equilibrate at least for 18h. The samples were then emulsified using an Ultra-Turrax at speed 3 for 20s and their conductivity was measured simultaneously.

Results and Discussion

Synthesis of the furanic hydroxyester and amide surfactants.

Considering the known applicability of the MBH reaction to HMF and analogues in mild and clean conditions,[54,55] the scope of the reaction was extended to the design of original amphiphilic systems in order to explore their physicochemical behavior. The 5-CH_2OH appendage in HMF offers the opportunity to modulate the polarity on the furanic building block, using either HMF itself, bearing the unsubstituted CH_2OH group, glucosyloxymethyl furfural (GMF, prepared from isomaltulose),[58] bearing a full glucosyl substituent,[58,64–66] or succinyl-HMF (SMF), the hemiester of HMF and succinic acid (prepared by reaction following known procedures with succinic anhydride at room temperature in the presence of DMAP in DCM),[59,60] bearing a carboxylic group. Regarding the hydrophobic side, the variability relies on the use of activated alkenes in the MBH reaction, namely alkyl acrylates of various chain lengths, from 4 to 16 carbon atoms, or alkylacrylamides. The reaction design involves the formation of an hydroxyacrylic linkage in the adducts, an additional lever by subsequent hydrogenation of the double bond can be envisaged and the influence of the saturation (hydrophobicity and rigidity) of the chain can be estimated by comparing some hydrogenated derivatives in which only the acrylic part is reduced, not the furan. Based on this design, the 16 hydroxy esters or amides, shown in **Scheme 1** and **Figure 2** in the series allow to compare all features at least between two compounds while keeping all other structural parameters identical. The synthesis of the hydroxyacrylates was achieved using DABCO as promoter, according to reported procedures for MBH reaction of HMF,[54] and performed for all cases in harmless media, either in aqueous ethanol, pure ethanol or without any solvent depending on the relative

miscibility of HMF, GMF or SMF with the acrylate as a function of the alkyl chain length. Adducts **H4**, **H6**, **H12**, **G6**, **G8**, **G12**, **G16**, **HS8**, **HS12**, **HS16** were obtained in yields ranging from 31 to 93 %. *N*-Butyl or *N*-hexyl acrylamide, known to be less reactive substrates in MBH reactions, required the use of 3-hydroxyquinuclidine (3-HQD) leading to targeted adducts **H4N** and **H6N** in 53 and 60 % yields.[67] The glucose moiety being chiral, the MBH adducts **G6**, **G8**, **G12** and **G16** derived from GMF are therefore mixtures of two diastereoisomers at the newly created CHOH position, in 1 to 1 ratio seen by NMR and as already reported for other examples. Selective palladium catalyzed hydrogenation of the acrylic group of a selection of these MBH adducts was performed using $Pd(OH)_2$ as catalyst in MeOH containing trace quantities of pyridine providing in nearly quantitative yields compounds **H4H**, **H6H**, **G8H**, **G12H** and **G16H** (as mixtures of diastereoisomers in the CHOH-CHMe relationship). All 16 compounds were fully characterized through NMR and mass spectrometry analyses leading to unambiguous identification. Overall, a family of 16 compounds structurally differing in level of polarity of the polar moiety, level of hydrophobicity of the non-polar moiety, and structure of the connecting systems (acrylate/acrylamide/saturated ester) could be subjected to physicochemical measurements.



Scheme 1. Synthesis of studied furanic surfactants.

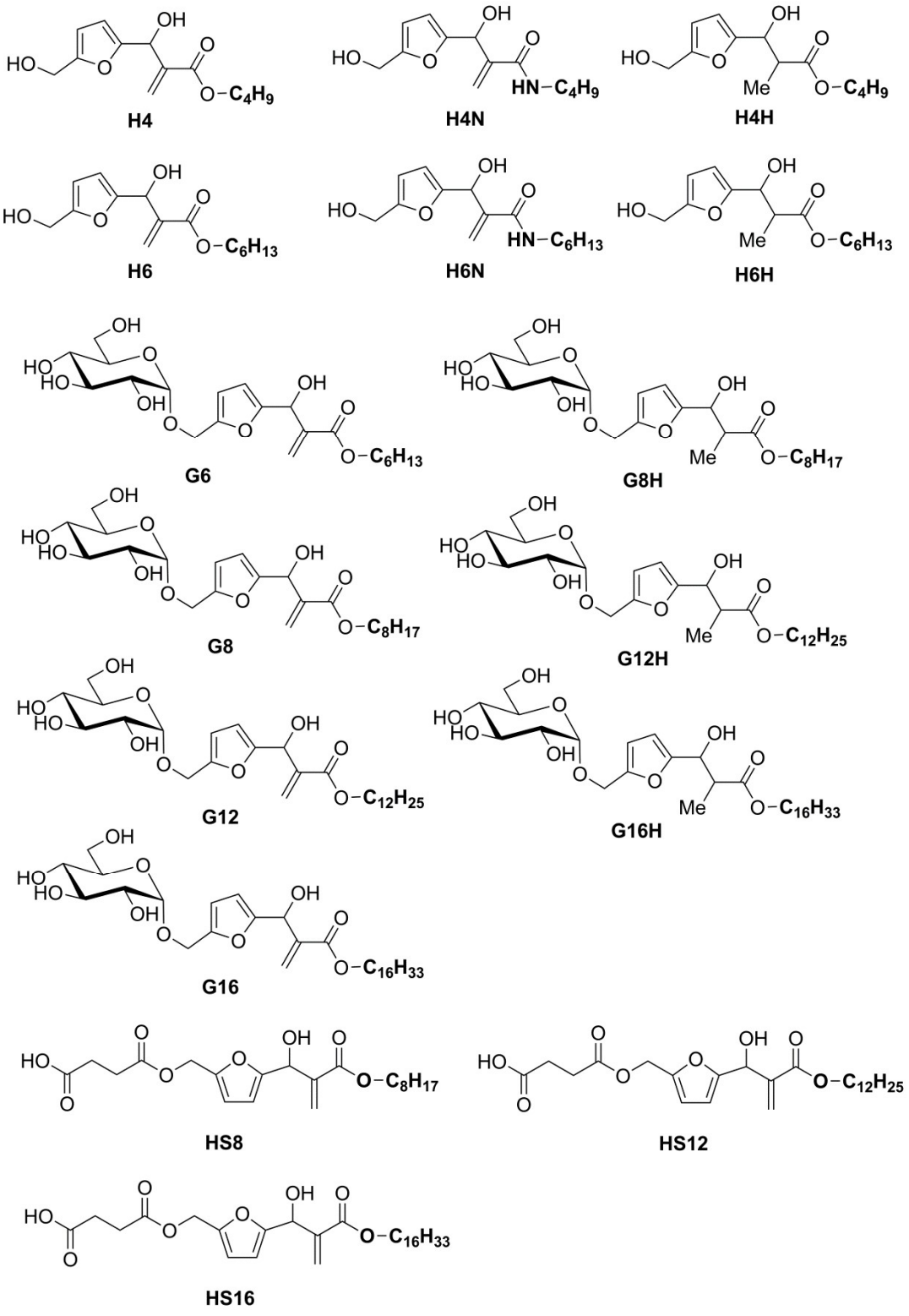
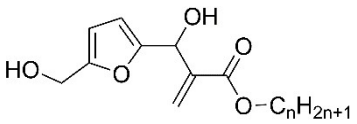
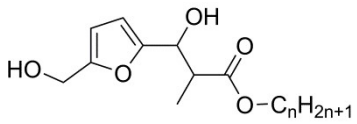
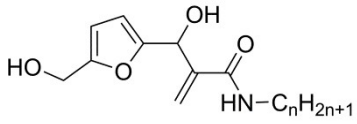
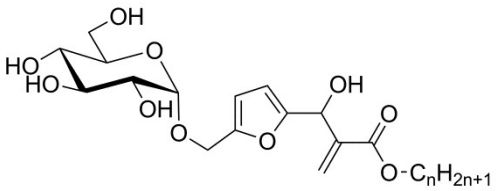
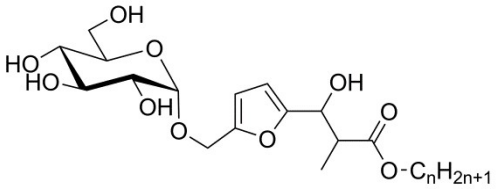
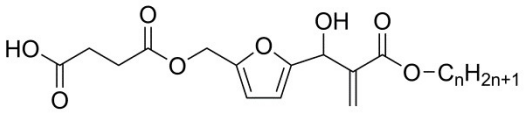


Figure 2. Structural scope arising from variable polar and hydrophobic blocks.

Physicochemical properties of the compounds.

The main surfactant properties of the 16 compounds in water, namely the critical micelle concentration (CMC), the reduction of surface tension at CMC (γ_{CMC} and γ at 10^{-4} M) and HLB, determined with the PIT-slope method, have been investigated. The results are gathered in **Table 1**. As the compounds have different water-solubility, the effect of temperature was studied with solutions at 0.1 wt.% instead of 1 wt.% as for the classical determination of the Krafft or Cloud points[68] in order to have comparative values for the whole series.

Table 1. Temperature to solubilize 0.1 wt.% of compound, critical micelle concentration CMC (at 25 °C), surface tension at CMC (γ_{CMC}) and at 10^{-4} M ($\gamma_{10-4\,M}$) and PIT-slope (mass dPIT/dC and molar fraction dPIT/dx_2) of bio-based furanic surfactants.

Entry	Chemical structure	$T_{0.1wt.\%}$ (°C)	CMC (mM)	γ_{CMC} (mN/m)	$\gamma_{10^{-4}\,M}$ (mN/m)	dPIT/dC (°C/wt.%)	dPIT/dx_2 (°C)
HMF derivatives							
H4		> 75	-	-	56.9	-6.7	-20.4
H6		> 75	-	-	61.3	-14.4	-49.7
H4H		50	-	-	62.4	-4.0	-13.8
H6H		60	-	-	58.6	-13.4	-47.6
H4N		35	-	-	71.2	3.4	11.7
H6N		40	-	-	70.1	0.23	1.3
GMF derivatives							
G6		< 25	4.6	32.5	-	23.9	113.4
G8		< 25	0.10	31.1	-	19.1	94.9
G12		< 25	0.018	35.2	-	5.8	34.5
G16		> 75	*n.d*	*n.d*	58.1	2.5	15.8
G8H		< 25	0.077	30.7	-	14.4	73.6
G12H		< 25	0.010	31.3	-	4.2	24.3
G16H		> 75	*n.d*	*n.d*	57.5	-3.2	-19.2
SMF derivatives							
HS8		> 75	-	-	44.7	-19.9	-90.3
HS12		> 75	-	-	47.8	-19.4	-96.4
HS16		> 75	-	-	50.35	-19.9	-108.1

Though nonionic, these compounds behave as ionic amphiphiles with an increase of water-solubility with temperature increase and do not show any cloud point like the nonionic polyethoxylated fatty alcohols. This is similar to what is known for other

carbohydrate-based surfactants, which are less sensitive to the effect of temperature on the hydration shell of the polyhydroxylated polar groups as compared to poly ethers. As expected, the HMF compounds show a decrease of solubility when the alkyl chain increases and the temperature required to reach solubilization is therefore higher. Also, despite their short alkyl chains, **H4** and **H6** compounds have a poor solubility and they are not entirely soluble in the studied interval of temperatures while hydrogenation of the double bond significantly improves their water-solubility (compare **H4** with **H4H** and **H6** with **H6N**). Besides, the presence of the amide function in **H4N** and **H6N** leads to the most soluble compounds within the HMF series thanks to the capacity of making hydrogen bonding (accept and donate) with water molecules. Among a series of linear amides, esters, carbonates and ethers with the same alkyl chain and four ethylene oxide units, Stjerndahl and Holmberg[69] have shown that the amide surfactants have the higher CMC and the higher cloud point.

Low water-solubility was also observed for the succinic derivatives (SMF) at neutral pH. On the other hand, introducing a glucose moiety as a hydrophilic head notably improves the solubility of the furfural biobased amphiphiles except for the hexadecyl GMF compounds which remain insoluble.

The surface tension of furanic surfactants in aqueous solutions was measured by the Wilhelmy plate method using a platinum rod as probe. For HMF and SMF compounds, the high temperatures needed to solubilize 0.1 wt.% do not allow the CMC determination at 25 °C. In most of these cases, at 10^{-4} M, a dispersion was obtained even for the short alkyl chains of HMF (n = 4). However, the solubilized fraction for most of these

compounds reduces the surface tension of water except for **H4N** and **H6N** (see **Table 1**). The surface tension profiles for the alkyl glycosyloxymethyl furfural compounds are shown in **Figure 3**.

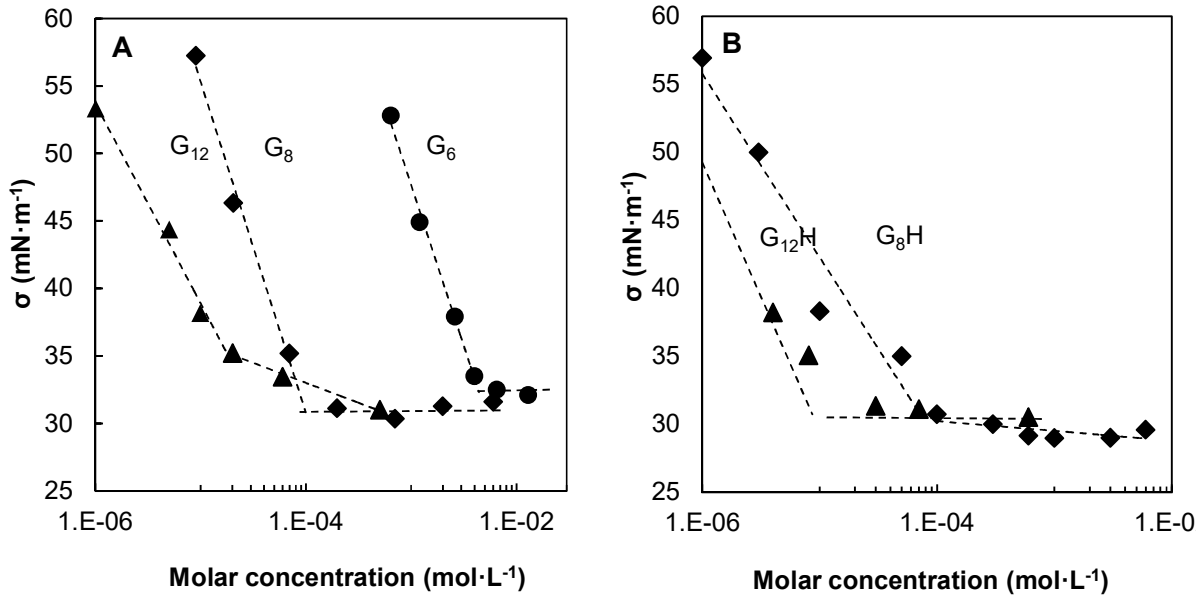


Figure 3. Surface tension *versus* concentration of alkyl glycosyloxymethyl furfural (GMF) surfactants. (●) hexyl, (◆) octyl and (▲) dodecyl. (A) unsaturated GMF (B) saturated GMF.

All soluble GMF compounds decrease the surface tension of water and the plateau value is reached around 30-35 $mN.m^{-1}$, except for **G12** whose surface tension continues to decrease in the studied range of concentrations. As this behavior is sometimes found when there is a vesicle to micelles transition,[70,71] DLS measurements were carried out at several concentrations after the break point estimated as the CMC. The average size of the structures evolves from 152 to 107 nm when increasing the concentration from 0.03 to 0.36 mM. This finding suggests the presence of bigger aggregates like vesicles.

The "hydrophobic contribution" of the double bound is lower than the saturated one and for same alkyl chain lengths, the CMC of **GiH** is lower than that of **Gi**, as reported for

sodium 10-undecenoate and sodium undecanoate.[72] Even if the difference in the CMC values is not the double as reported by Sprague et al.[72] and Yokoyama et al.[73], the CMC of unsaturated **Gi** is between 1.3 and 1.8 times the CMC of saturated **GiH**. This discrepancy can be accounted for by the solvation of the double bond which could be less favorable energetically in the formation of the micelles. In addition, the surface tension at the CMC is slightly higher for unsaturated **Gi** compared to **GiH** as also pointed out by Gaudin et al.[74] with some unsaturated sugar based surfactants.

For saturated and unsaturated GMF compounds, the concentrations of some solutions used in the CMC determination are quite low (< 10^{-6} M). Indeed, for hexadecyl compounds, the determination of the CMC at 25 °C was not possible due to not only their low water-solubility but also the relatively long times of equilibration needed to get a representative value of the surface tension when solutions are in this range of low concentrations.

Comparing the CMC values of both GMF derivatives with those of the corresponding alkyl β-D-glucosides (i.e. 25 mM and 0.19 mM[75] for the C_8 and C_{12} β–D-glucoside, respectively), we can note that it is significantly reduced. It is noteworthy that there is a 20 °C of difference in the Krafft point between the two isomers α and β for pure alkyl glucopyranosides.[76] The lower CMC value found for the new GMF derivatives can also be ascribed to the presence of two isomers (at the CHOH junction) in the **Gi** compounds. The surface tension at the CMC remains higher for the GMF derivatives (> 30 $mN.m^{-1}$) than for the alkyl β-D-glucosides (28 $mN.m^{-1}$).[75] **G12** and **G12H** can also be compared to other typical dodecyl nonionic surfactants as dodecyl diglycerol (CMC = 0.031 mM;

γ_{cmc} = 27 mN·m^{-1})[77] or diethylene glycol monododecyl ether (CMC = 0.033 mM; γ_{cmc} = 26 mN·m^{-1})[78]; in both cases, the GMFs show a lower CMC and a slightly higher surface tension.

The HLB of the compounds were determined by the PIT-slope method[56,57] which is based on the perturbation of the phase inversion temperature (PIT) of the reference 3% $C_{10}E_4$/*n*-octane/0.01M $NaCl_{(aq)}$ system at f_w = 0.5 through addition of the surfactant. The PIT is determined by conductivity monitoring and linearly changes as a function of the added surfactant. Consequently, the behavior of each surfactant can be quantified by the value of the slope, dPIT/dC (mass concentration) or dPIT/dx_2 (molar fraction) (see **Table 1**). Positive values indicate a more hydrophilic surfactant than $C_{10}E_4$ while negative values indicate a more lipophilic behavior when using temperature as a formulation variable.

Figures 4A and 4B show the conductivity *versus* temperature profiles for **G12H** and **HS16**, respectively. These profiles exhibit the classical shape of a transitional phase inversion. The morphology of the emulsion evolves from O/W (high conductivity) to W/O (almost zero conductivity) when increasing the temperature. The temperature range in which the conductivity drastically falls indicates the phase inversion. By adding increasing amounts of **G12H** to the reference system, the phase inversion temperature (PIT) gradually increases. Indeed, the system requires more energy to change the affinity of the ($C_{10}E_4$ + $G_{12}H$) surfactant system into the oily phase. From these results, it is possible to conclude that **G12H** is more hydrophilic than $C_{10}E_4$. When the temperature

required to inverse the entire system ($C_{10}E_4$+ HS16) decreases, as shown in **Figure 4B**, the surfactant is less hydrophilic than $C_{10}E_4$, as in the case of the **HS16**.

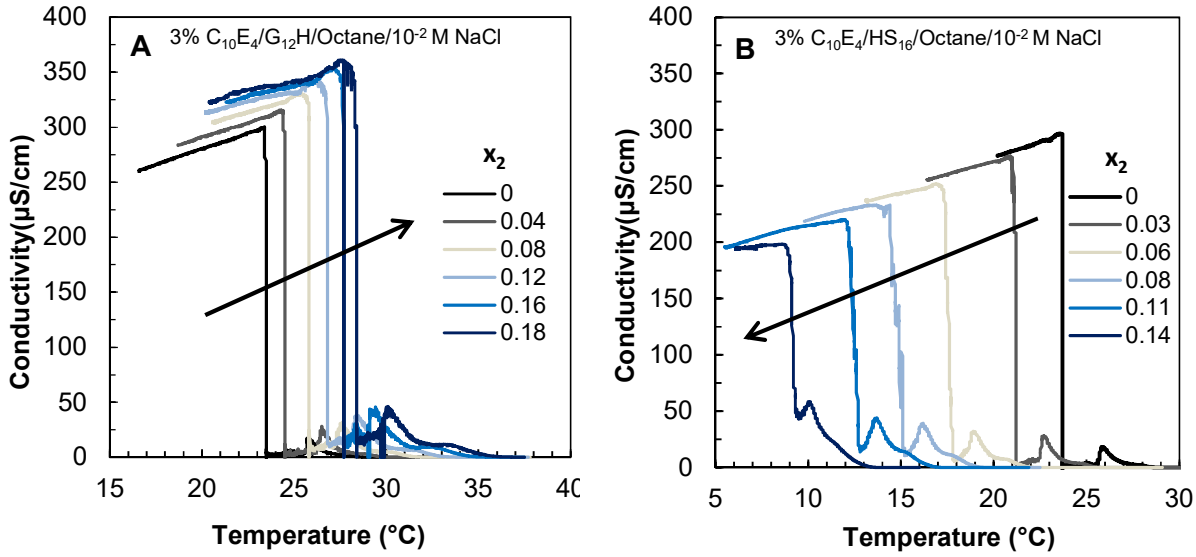


Figure 4. Conductivity-temperature profiles for the system 3% $C_{10}E_4$/*n*-octane/10^{-2} M NaCl + S_2 (f_w = 0.5) at different molar fractions of the second surfactant. (A) S_2 = **G12H**. (B) S_2 = **HS16**.

As pointed out in **Figure 4**, addition of the surfactant results in a small or greater increase or decrease of the PIT value. A linear regression fits well the points of the PIT with the molar fraction x_2 or the weight concentration of the added surfactant. **Figure 5** shows in blue the values of the GMF derived compounds and in black some results for typical polyethoxylated surfactants (data for the other families of furanic derivatives are given in the Supporting Information - **Figure S1**). The linearity of the PIT with the molar fraction diminishes when comparing the longer true surfactants (n = 16 or 12) with the shorter amphiphiles (n = 6 or 8), due to their higher solubility in aqueous phase.

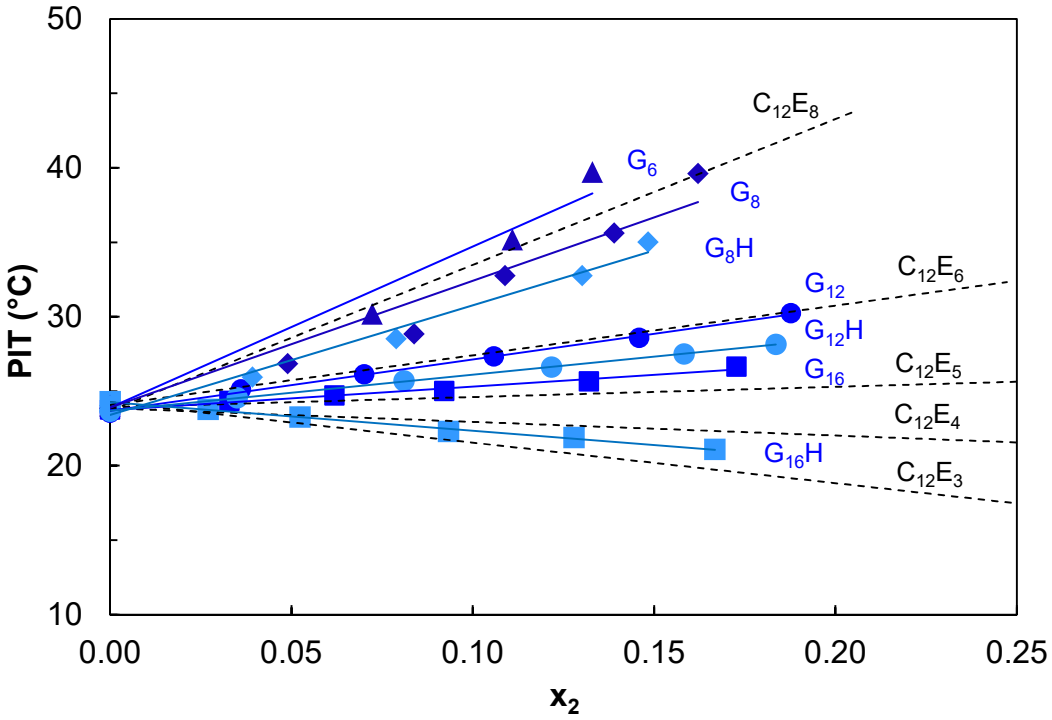


Figure 5. Phase Inversion Temperature (PIT) vs. molar fraction x_2 for the system 3% $C_{10}E_4/S_2$/*n*-octane/10^{-2}M NaCl at f_w = 0.5. S_2 = **G6** (▲); **G8** (◆); **G12** (●); **G16** (■); **G8H** (◆); **G12H** (●); **G16H** (■). Lines indicate linear fitting leading to $dPIT/dx_2$. Black dotted lines indicate the PIT-slope for several $C_{12}E_j$ surfactants.

Figure 6 represents the PIT-slope values with respect to the alkyl chain length for each family of the furanic-based surfactants. It provides useful information on the novel furanic-based surfactants. As reported in the literature for other nonionic surfactants,[57] when the carbon chain of GMF derivatives increases from 6 to 16, their interactions with the oil side of the interfacial palisade increases and also the "affinity" for the oil phase, diminishing the PIT-slope value. Comparison of saturated compounds **GiH** with unsaturated ones **Gi** indicates that the latter are slightly more hydrophilic, probably due to the solvation of double bond that decreases the hydrophobicity of these surfactants.

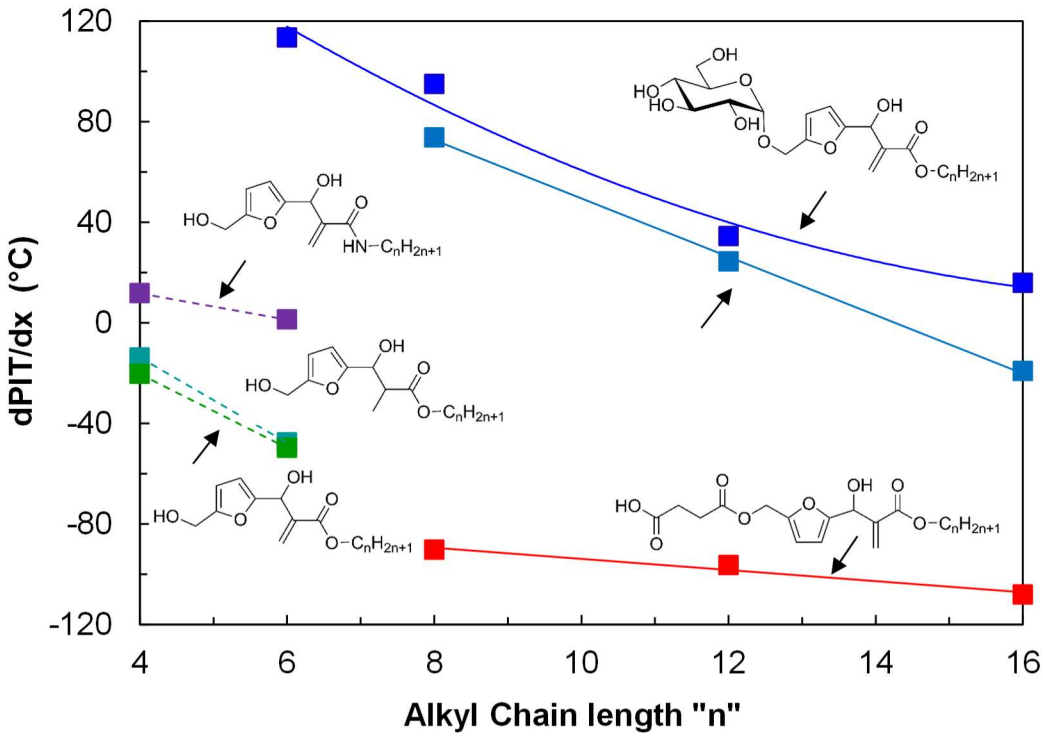


Figure 6. Evolution of $dPIT/dx_2$ (°C) with increasing alkyl chain length of different families of furanic surfactants for the system 3% $C_{10}E_4$ + S_2/*n*-octane/0.01M NaCl at $f_w = 0.5$.

With regard to the hydrophilic polar head group, glucose (GMF) provides the most polar surfactants (higher $dPIT/dx_2$ values), followed by alcohol (HMF) and then succinic acid (SMF) for which the surfactants are clearly lipophilic (negative $dPIT/dx_2$ values). The amides **HiN** are more hydrophilic than esters **Hi**, because both O and N are able to form hydrogen bond with water and their PIT-slope are higher.

The influence of the saturated/unsaturated chain is more complex. For the GMF compounds, the glucose group gives the hydrophilic character to the molecule while the furan and ester groups are intermediate between the glucose and the hydrophobic chain. The structure of these surfactants can be assimilated to the extended surfactants described by Salager et al.[79]. In this family of surfactants there is a transition between the hydrophobicity of the alkyl chain and the

hydrophilicity of the polar head that enhances some properties as solubilization capacity. Alkyl propoxy-ethoxylated surfactants are an example of this compounds in which the transition is done by the propoxy groups. In our case, the unsaturation slightly increases the hydrophilic character of the compound. However, for HMF compounds, the single alcohol function cannot be considered as the polar head and the ester (or amide), the furan and the terminal alcohol are all part of the hydrophilic group and the unsaturation has no influence, compared to the effect of the amide already discussed.

Figure 7 compares the HLB of the furanic surfactants with that of other nonionic well-defined surfactants. **G12** has a $dPIT/dx_2$ similar to that of $C_{12}E_6$ and slightly higher than that of **C_{12}βGlu** (dodecyl-ß-D-glucopyranoside). **G12H** is slightly less hydrophilic than **C_{12}βGlu**. The difference between **G12**, **C_{12}βGlu** and **G12H** indicates that the nature of the "linker" between the glucose polar head and the alkyl chain modifies the hydrophilic character of the surfactant and confirms that the higher hydrophilicity of **G12H** is due to the unsaturation. This tendency is also confirmed by comparing **G8**, **C_8βGlu** and **G8H.** There is no pure well-defined polyethoxylated surfactant to compare with **HSi** which are much more lipophilic than $C_{12}E_2$. Indeed, comparing the PIT-slope of each HSi with the carboxylic acid having the same alkyl chain (-51.1,-54.1 and -58.5°C for octanoic, dodecanoic and hexadecanoic acid, respectively)[80] indicates that the presence of the second carboxylic function (less polar than the acid terminal group) does not compensate the lipophilic contribution of the furanic group and drastically diminishes their hydrophilicity. This family can be also compared to technical grade surfactants and in this case, we can estimate that **HS12** (dPIT/dC = -96.4 °C/wt.%) is more lipophilic than sorbitan monolaurate or SPAN® 20 (dPIT/dC = -12.1 °C/wt.%) while **HS16** is more lipophilic

than corresponding sorbitan monopalmitate or SPAN® 40 (dPIT/dC = -13.5 °C/wt.%).[56] These two commercial surfactants are well-known as lipophilic emulsifiers.

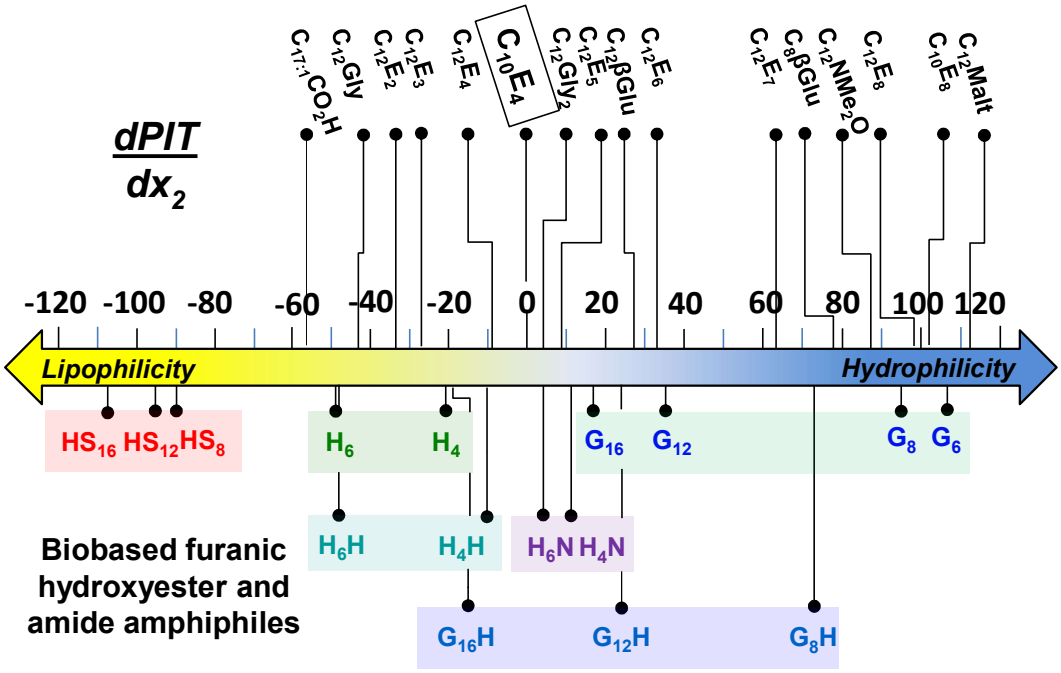


Figure 7. Classification of biobased furanic hydroxyester and amide amphiphiles and comparison with other well-defined nonionic surfactants[62,78] according to their dPIT/dx_2.

Emulsifying properties

One of the important properties of surfactants is their ability to stabilize liquid-liquid dispersions. To study the emulsifying properties of the furanic surfactants, emulsions of two cosmetic oils, i.e. isopropyl myristate (IPM) and Creasil IH CG (a mixture of hexadecane isomers) were prepared with the compounds having more than 10 carbon atoms in their alkyl chain. The surfactant was introduced at 1 wt.% and the water-to-oil volume ratio (WOR) was equal to 1. The type of the emulsion was determined by conductivity, the aqueous phase was a 0.01 M NaCl solution. **Table 2** shows the systems after emulsification.

Table 2. Photographs of the surfactant/oil/water systems at WOR = 1 and 1 wt.% surfactant before and after emulsification. Oils = isopropylmyristate (IPM) or Creasil.

Surfactant (dPIT/dx)	Before mixing		1h after mixing		24h after mixing	
	IPM	Creasil	IPM	Creasil	IPM	Creasil
G12 (34.5 °C)			 o/w	 o/w	 stable	 stable
G12H (24.3 °C)			 o/w	 o/w	 stable	 stable
G16 (15.8 °C)			 o/w	 o/w	 unstable	 stable
G16H (-19.2 °C)			 o/w	 o/w	 unstable	 stable
HS12 (-96.4 °C)			 o/w	 n.d.	 unstable	 unstable
HS16 (-108.1 °C)			 w/o	 w/o	 unstable	 stable

After emulsification, all systems exhibit a high conductivity indicating O/W emulsions except HS_{16} which has a zero conductivity giving thus a W/O emulsion. This surfactant is indeed the most lipophilic according to its PIT-slope. For the GMF series, the dodecyl surfactants are able to stabilize biphasic O/W emulsions with both oils showing clarification phenomenon without

no coalescence after 24 hours, making them potentially applicable as emulsifiers for cosmetic oils. The hexadecyl GMF surfactants are less soluble, as can be seen before emulsification. With IPM, **G16** and **G16H** based systems show very low stability and coalescence is almost instantaneous while a much better stability is obtained with Creasil, in particular with **G16H** which provides a total O/W emulsion. Regarding the oils, we can compare their EACN or "equivalent alkane carbon number". This descriptor defines the *n*-alkane that allows obtaining the optimal formulation at the same physicochemical conditions as the studied oil. IPM is more polar and less hydrophobic (EACN = 7.3[80]) than Creasil (EACN = 13.5[81]). Formulate emulsions with IPM is harder because a significant part of the surfactant can be solubilized in the oil phase, thus reducing its effectiveness at the interface for the emulsion stabilization. For the SHF family, more lipophilic than GMF, only the **HS16** is able to produce a W/O emulsion with both oils, even if the emulsion is stable only with Creasil. **HS12** is partially dissolved in both oily phases (see photos before the emulsification), corroborating its lipophilic affinity but, at the studied WOR, the morphology is O/W. The instability of the obtained emulsion is due to its lipophilic character and probably, by increasing the concentration of the surfactant or the oil proportion, this surfactant could be used to formulate W/O emulsions. The wide range of PIT-slope values for these biobased surfactants and the stable O/W or W/O emulsions obtained with some of them with only 1 wt.% indicate that these surfactants can be used as emulsifying agents with both polar oils or alkanes.

Conclusions

Sixteen novel bio-based amphiphiles were synthesized by coupling furanic aldehydes with alkyl

acrylate or acrylamide using the straightforward Morita-Baylis-Hillman (MBH) addition reaction under mild and clean conditions. A heterogeneous family of compounds was obtained by modulating both the furanic block and the alkyl chain: HMF (with amide or ester acrylates), glucosyloxymethyl furfural (GMF) and succinyl hydroxymethyl furfural (SMF). The glucose-based derivatives (GMF) have a good water-solubility unlike the succinic acid-based derivatives (SMF). The CMC of the GMF amphiphiles is lower than that of the corresponding alkyl β–D-glucopyranosides. The hydrophilic-lipophilic behavior of these amphiphiles was quantified using the PIT-slope method and their decreasing hydrophilic behavior (for same alkyl chain length) is as follows: **Gi** > **GiH** > **HiS**. For the shorter HMF amphiphiles, the decreasing hydrophilic order is: **HiN** > **Hi** ≈ **HiH**. Saturated **GiH** are less hydrophilic than unsaturated **Gi** as a consequence of the solvation of the double bound that increases the hydrophilicity of **Gi** even when compared with corresponding alkyl β-D-glucopyranosides. The **HiS** surfactants are more lipophilic than pure $C_{12}E_2$ and technical-grade alkyl esters of sorbitan (SPAN). Increasing the alkyl chain length lowers the PIT-slope value of the surfactants, as expected. Preliminary tests of cosmetic oil emulsification with 1 wt.% surfactant and a water-to-oil ratio equal to 1 indicates that most GMF compounds (**G12, G12H**) are able to stabilize O/W emulsions. SMF are more lipophilic and W/O emulsions can be formulated with **H16S**. All these results show that this new series of biobased surfactants that can emulsify both polar and apolar oils providing both W/O and O/W emulsions are relevant alternatives to the conventional petroleum-based polyethoxylated surfactants, opening avenues for their applications in various domains like in detergents, cosmetics or paints. Further research is needed to study their solubilizing, foaming and wetting properties.

Supporting Information

The Supporting Information is available free of charge on line. PIT-slope data for SMF and HMF amphiphiles, NMR characterization data of all new products, NMR Spectra.

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Synopsis

Here, we investigate a new and original family of biobased nonionic surfactants prepared by Morita-Baylis Hillman coupling furanic aldehydes with hydrophobic alkenes.

TOC Graphical abstract