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5-Hydroxymethylfurfural and Furfural Chemistry Toward Biobased Surfactants

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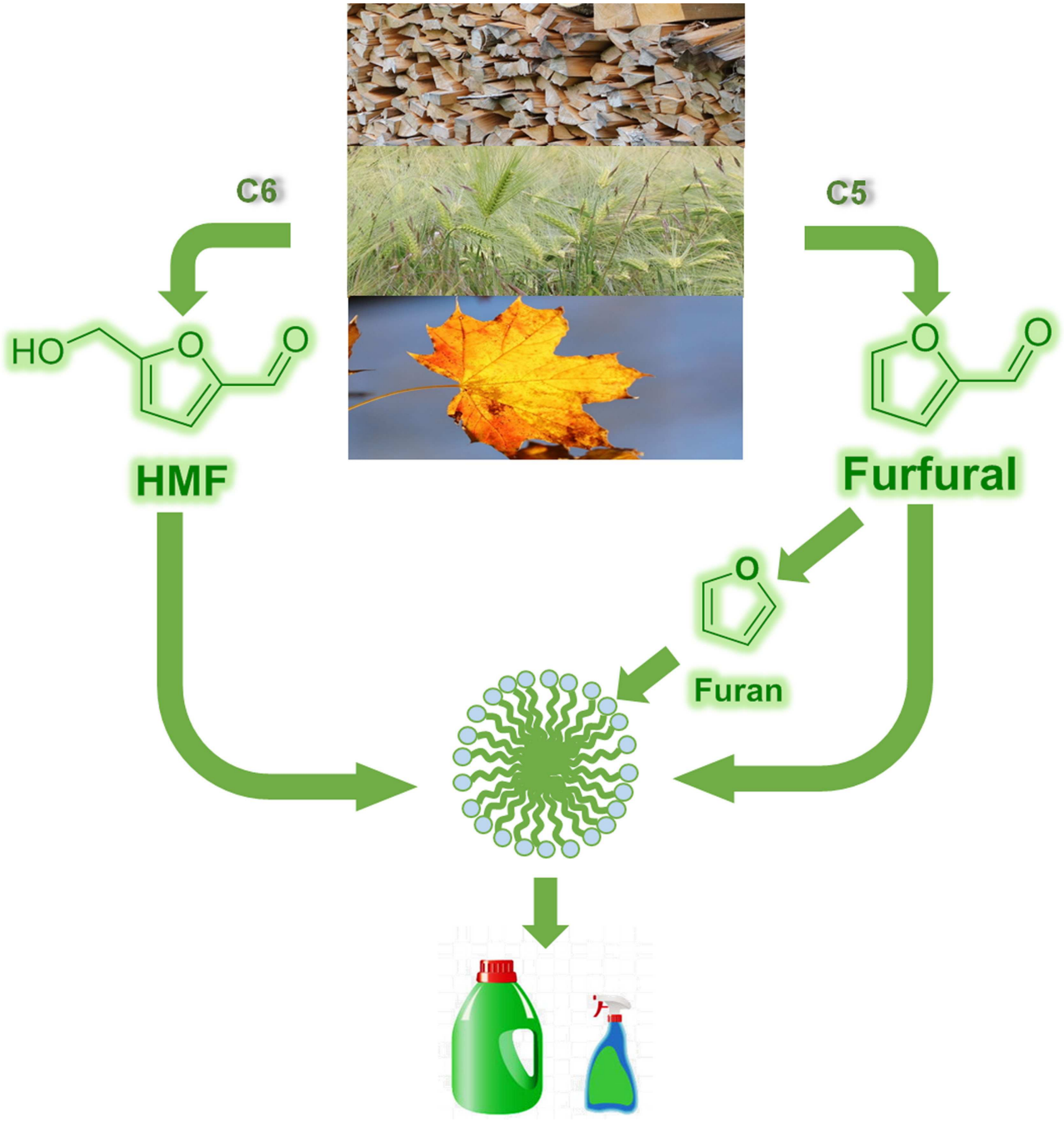

The use of 5-hydroxymethylfurfural (HMF), furfural, and furan as scaffolds for designing alternative surfactants is a rapidly developing research area. This Review gathers recent examples highlighting the variety of methods for grafting the necessary polar and non-polar appendages, exploiting the specific chemical reactivity of each of these platform molecules. While the furan (or tetrahydrofuran) backbone is maintained in some targeted amphiphiles, alternatives using rearranged HMF or furfural such as cyclopentanols or furanones have also been reported. This topic is an illustration of the diversification of the use of HMF and other biobased furanic platform molecules in the field of fine and specialty chemicals. The surfactants sector, which concerns some of the most largely consumed chemicals in everyday life, and still mostly produced from fossil resources, will benefit from such alternatives enabling increased renewable carbon content and structural innovation.

1. Introduction

Biomass, including lipids, carbohydrates, lignin, and proteins, is abundant and renewable and offers incommensurable opportunities for chemical transformations. In the context of green chemistry,[1–7] biobased chemistry is nowadays a scientific field in itself, and benefits from the contributions of all parts of the chemical sciences.[8–18]

Furanic platform molecules are easily available from biomass and ready for further functionalization for applications as intermediates in fine chemical industries. 5-Hydroxymethylfurfural (HMF) is the acid-catalyzed triple dehydration product of hexoses, fructose being the substrate of choice. A large choice of catalysts and processes have now widened its availability from cruder and cheaper resources, such as cellulose or C_6 sugar-containing agricultural by-products and wastes.[19–22] The rich chemistry of its hydroxy, aldehyde, and furan moieties offers a vast scope of possible accesses towards daughter platforms, such as 2,5-bis(hydroxymethyl)furan (BHMF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), 2,5-furandicarboxylic acid (FDCA), 2,5-dimethylfuran (DMF), 2,5-diformylfuran (DFF), and levulinic acid, which can be successfully produced from HMF through various catalytic routes (oxidation and reduction processes) with high yields and selectivities. The scope of applications is widening constantly, in particular in the field of polymers.[23–35]

Furfural, produced by dehydration of C_5 carbohydrates such as xylose, is also an interesting platform. Owing to its aldehyde group and its furan ring, furfural can undergo many reactions, such as acetalization, acylation, aldolization, reduction, oxidation, amination, alkylation, halogenation, and nitration reactions. Among major applications of furfural in sustainable chemistry, we can mention several biobased solvents, such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), γ-valerolactone, and others.[36–41] Furan, which can be produced by decarbonylation of furfural, can therefore also be seen as a biobased platform molecule.[42–44] The increasing availability of biobased furanic platforms, benefiting from recent improved processes, makes them more pertinent than ever for being used as industrial raw materials for fine chemical industries.[20]

Surfactants, compounds that accumulate at the interface between different media in order to decrease the surface tension, are among the most commonly used chemical compounds in the everyday life. They are widely applied as detergents, foaming agents, emulsifiers, and dispersants in home and personal life and in industries. The sector still relies essentially on petroleum feedstocks, even though the share of synthetic surfactants manufactured from renewable resources is regularly increasing, occupying 24% of the surfactant market in 2019 figures.[45–48]

Carbohydrates, accounting for the biggest part of biomass, have been widely utilized for serving as the polar building block of surfactants owing to their polyhydroxylated structures.[49–54] Their combination with fat derivatives led to the development, several decades ago, of 100% biobased surfactants such as sugar esters or alkyl glycosides, among others, in strategies aiming at giving more value to some agricultural crops. Their production scale kept increasing in recent years. Polyols, such as itols obtained by hydrogenation of sugars (e.g., sorbitol) or other biobased highly polar platform molecules (e.g., glycerol, lactic acid, citric acid, glutamic acid, etc.), have also been successfully used to produce surfactants.[48,55–57]

In the global context of limiting the dependence of the chemical industry on fossil resources, there is room for renewed originality in strategies applying renewable resources to the manufacture of new surfactants. In this regard, the use of HMF, furfural, and other furanic compounds is still at an early stage in their contribution to the innovation in surfactant design. After early interesting examples, which were not specifically motivated by the renewability issue, the field has recently benefited from the "biobased chemistry" impetus with very pertinent approaches from several research groups.

The purpose of this Review is to illustrate this emerging topic by depicting interesting strategies developed toward furanic surfactants using HMF, furfural, and furan as feedstocks, respectively. For each of these starting resources, examples depict the different strategies for building and connecting the polar and non-polar moieties onto the furan (or tetrahydrofuran) scaffold, thus assembling the final amphiphilic structure. Other examples relying on intermediate platforms involving rearrangement products of the furan ring are also mentioned.

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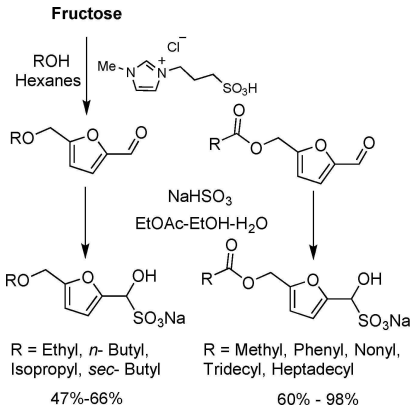
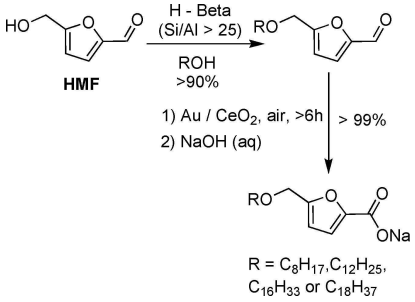
2. HMF-Based Amphiphiles

Several strategies have been reported for designing amphiphilic compounds starting from HMF. Both the CH_2OH moiety and the aldehyde can be envisaged as precursors of the future polar or non-polar appendages of the target product. They are classified herein, first with compounds relying on a fatty ether or ester, then compounds exhibiting an acetal function, before finishing with designs based on a carbon–carbon bond connection.

The etherification of the CH_2OH group of HMF by reaction with a fatty alcohol has been used as initial step in several sequences. Kraus et al. reported in 2013 the preparation of sulfonated HMF ethers by simple treatment with sodium bisulfite based on an efficient initial one-pot conversion of fructose using a task-specific ionic liquid (Scheme 1).[58,59] The direct sulfonation of the aldehyde group is a simple and effective pathway to graft a highly hydrophilic moiety on the HMF fatty ethers. Such products can be considered as alternatives to linear alkylbenzene sulfonates (LAS), which are the most commonly used sulfonates surfactants,[60] but characterized by harsh synthesis conditions and their fossil origin. HMF fatty esters can also undergo the same sequence. Most of these sulfonates exhibited high solubility in H_2O at room temperature, while the longer-chain esters required to heat up to 80 °C for reaching the Krafft temperatures. However, the poor stability under basic conditions of these systems limits their possible usages to only acidic or neutral formulations.



Scheme 1. Amphiphilic sulfonated HMF ethers and esters.[58,59]



Scheme 2. Oxidation of HMF fatty ethers to amphiphilic carboxylates.[61]

In 2014, Iborra and co-workers reported another family of biobased anionic surfactants, namely 5-alkoxymethyl furoic acid salts, prepared from HMF ethers through a strategy consisting of two catalytic steps (Scheme 2).[61] For the initial HMF etherification, the use of a H-Beta zeolite (Si/Al > 25) led to a high selectivity towards the desired alkoxymethyl furfurals, while limiting both the self-etherification of HMF to its dimer and the formation of dialkylacetals, benefiting from the ability of the intermediate to form self-organized assemblies. Subsequently, the polar part was provided by the oxidation of the aldehyde group to a carboxylate salt using Au/CeO_2 as catalyst, already reported for the oxidation of HMF to FDCA, in which the 5-hydroxymethylfuran carboxylic acid is the primary intermediate.[62] The properties of these 5-alkoxymethyl furoic acid sodium salts were characterized and showed comparable surface tension reducing ability to that of the commercial surfactant sodium dodecylbenzene sulfonate (SDBS).

The hydrophilic part can also arise from the sulfatation of the hydroxy groups. This has been applied in sequences starting from BHMF and bishydroxymethyltetrahydrofuran (BHMTHF), both easily obtained from HMF.[63–68] First, a selective etherification of only one of the two hydroxy groups was performed, either by Williamson reaction with a haloalkane using sodium *tert*-butoxide as the base, or by addition on olefins promoted by an acidic zeolite catalyst.[69–72] The hydro-

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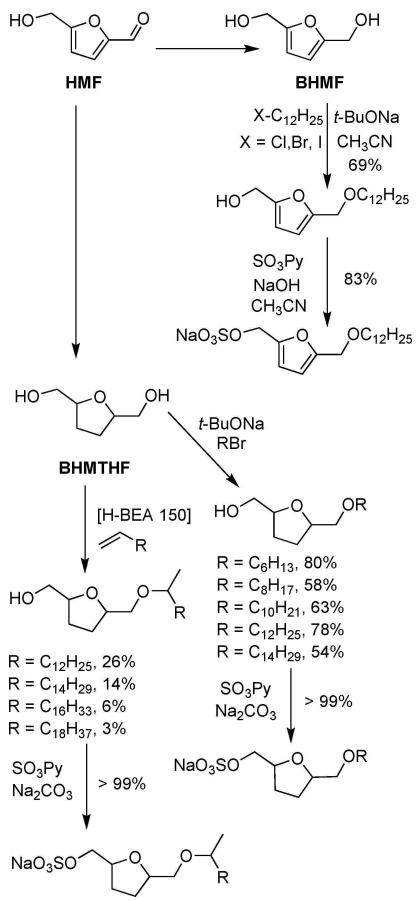
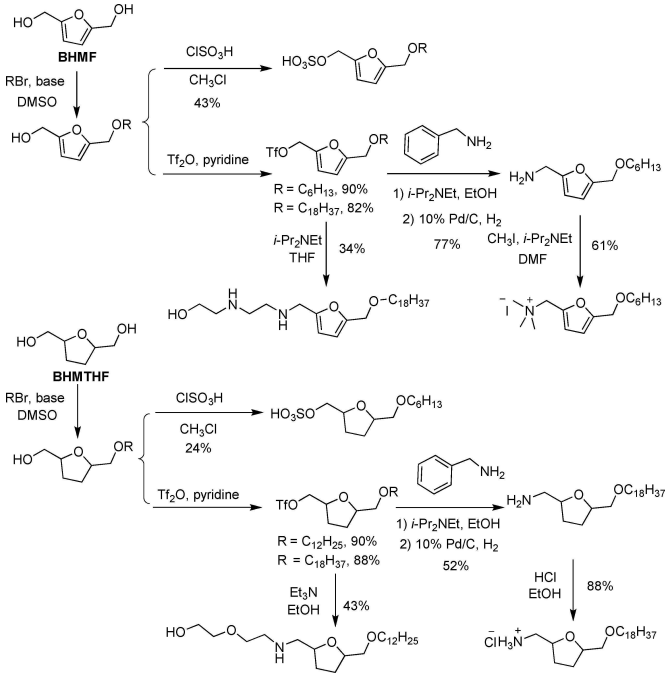
Yves Queneau is Research Director at CNRS since 1995. Born in Paris in 1960, he received his doctorate degree in chemistry with Professor André Lubineau from the University of Paris-Sud (Orsay) and was postdoctoral fellow with Professor Samuel J. Danishefsky in New York. In Lyon since 1995, he developed his projects in glycosciences, first in a mixed CNRS-industrial research facility dedicated to biobased chemistry from sugars, before joining the Institute for Molecular and Supramolecular Chemistry and Biochemistry (ICBMS) in 2003, where he leads the Organic and Bioorganic Chemistry team, working on the biological and sustainable sides of carbohydrate chemistry.



Scheme 3. Synthesis of BHMF-based and BHMTHF-based ether-sulfate surfactants.[73]



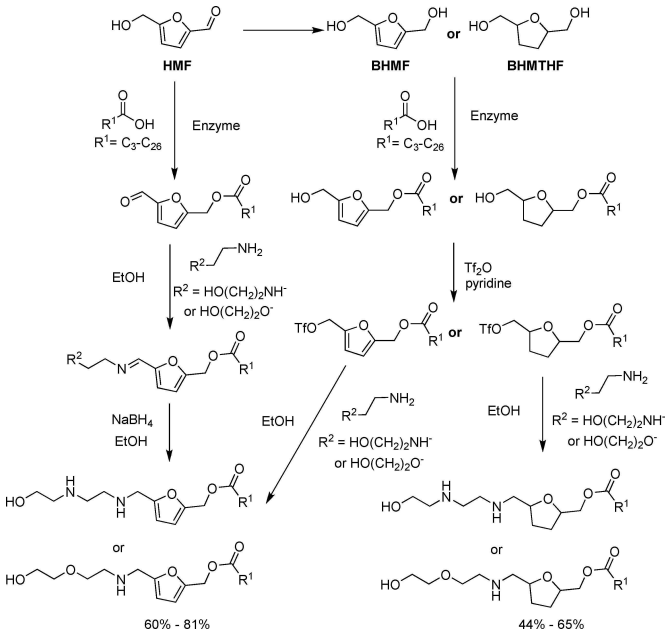
Scheme 4. Anionic, non-ionic, and cationic amphiphiles from HMF ethers.[74]

philic part was then provided by sulfatation with the SO_3·Py-complex (Scheme 3). In terms of properties, the BHMTHF-derived surfactants with C_{12}, C_{14}, and C_{16} fatty chains exhibited a comparable surface tension reduction ability to that of the commercial surfactants LAS and ethoxylate-based fatty alkyl ether sulfates (FAES), although at a lower critical micelle concentration (CMC).[73]

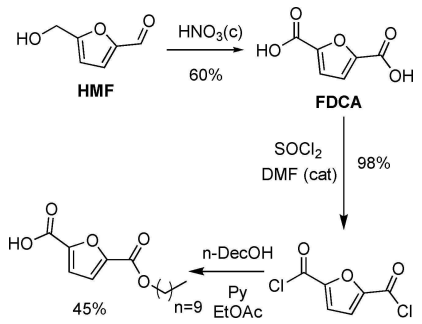
Other amphiphilic fatty ethers based on the BHMF, BHMTHF, or tetrahydrofurfurylamine backbones have been reported by Stensrud in a 2015 patent (Scheme 4). Cationic, anionic, and nonionic amphiphiles were prepared by grafting either ammonium ions, sulfates, and hydroxyethylaminoethylamino or hydroxyethyloxyethylamino polar moieties, respectively. Sulfates were obtained directly from the HMF-ethers, while furfurylamine derivatives were prepared by substitution of an intermediate triflate.[74]

A similar strategy from the same group was applied to a series of fatty esters of HMF, BHMF, or BHMTHF. An initial enzymatic esterification step using a lipase provided selectively monoesters when two hydroxy groups were present in the substrate. From HMF, the polar hydroxyethylaminoethylamino or hydroxyethyloxyethylamino moieties were introduced through the formation of an imine from the aldehyde group, followed by reduction using sodium borohydride, while the BHMF- or BHTHF-derived systems require the displacement of a triflate by the corresponding amine (Scheme 5).[75]

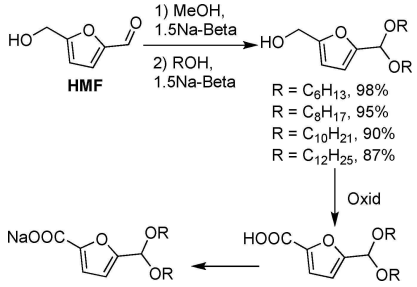
Apart from the examples shown in the Schemes 1 and 5,[59,75] a few more examples of amphiphilic systems derived from HMF esters have been described. One starts from FDCA. The simple hemiester of this diacid with decanol was found by Estrine and co-workers to be a useful additive in a preparation of APGs from decanol and D-glucose (Scheme 6). This monoester of FDCA possesses an amphiphilic structure, in which the



Scheme 5. Non-ionic surfactants from HMF fatty esters.[75]



Scheme 6. Amphiphilic FDCA hemiesters.[76]



Scheme 8. HMF acetals of fatty alcohol.[81]

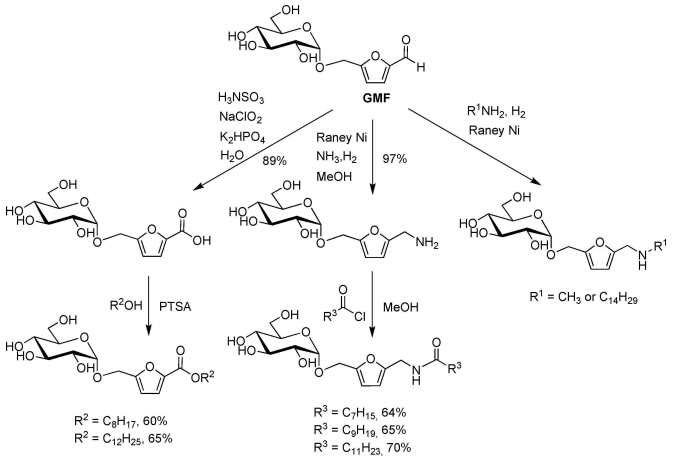
carboxylic acid function group is the hydrophilic part. When added to polyglycosides, the mixture exhibited a reduced wetting time and satisfactory biodegradation based on the EU norm (monosodium form, 68% after 28 days).[76]

The glucosylated analogue of HMF, α-D-glucosyloxymethylfurfural (GMF, obtained by dehydration of isomaltulose, the glucosyl-6-*O*-fructose isomer of sucrose),[77–79] was used to design amphiphilic systems in which the glucose moiety brings the non-ionic polar part. Reaction of GMF-derived carboxylic acid with fatty alcohols led to fatty esters, while the reaction of GMF-furfurylamine with acyl chloride led to amides, introducing the non-polar part. Alternatively, amphiphilic secondary amines were obtained via a reductive amination sequence. In terms of self-assembling properties, the mesomorphic behavior of some of these products confirmed their ability to exist at the state of liquid crystal (Scheme 7).[77,80]

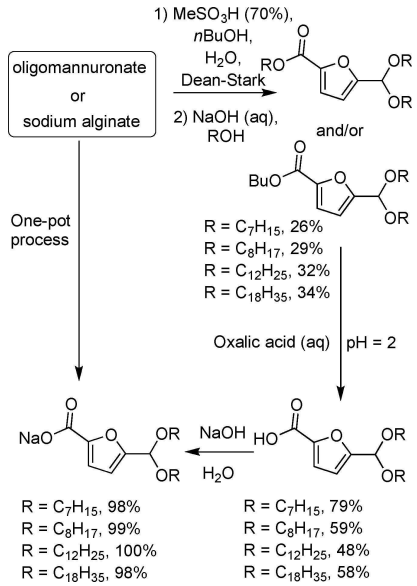
The acetal linkage can also be found in a few examples of HMF derivatives. This confers to the products increased sensitivity to acidic conditions. A straightforward route reported by Iborra and co-workers is an acetalization–oxidation sequence (Scheme 8). Using Na-exchanged Beta zeolites for the generation of the dimethyl acetal and its transacetalization with a fatty alcohol, higher selectivity and shorter reaction time was observed, while avoiding the undesired side etherification of the CH_2OH group. Further oxidation to the carboxylic acid and neutralization of this latter would provide the polar part of the surfactant.[81]

A very recent alternative sequence towards acetal-carboxylates has been reported by Benvegnu and co-workers, who developed the direct conversion of oligo-alginates or alginate into butyl-5-(dibutoxymethyl)-2-furoate. This latter can be then transesterified and/or transacetalized with long-chain alcohols. Saponification of the intermediate esters led to the target acetals-carboxylates (Scheme 9). These surfactants were found to reduce the water surface tension down to 25 mN m^{-1} and exhibited high foaming ability. In addition to the satisfactory eco-design, these compounds were readily biodegradable (96% biodegradation after 28 days) and found non-toxic for the aquatic organisms.[82]

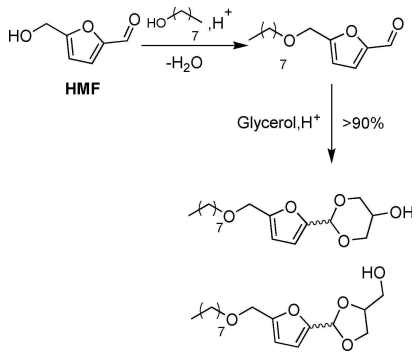
A last example of acetal, developed by Iborra and co-workers from HMF fatty ethers, relies on the acetalization of the aldehyde group with glycerol, thus targeting non-ionic systems (Scheme 10). The order of the two steps could be inverted while leading to the same molecules, thanks to the specificity of each acidic catalyst. Since three reacting hydroxy groups are present



Scheme 7. Amphiphiles from GMF via esterification, amination, and amidation.[77,80]



Scheme 9. Synthesis of non-ecotoxic anionic furanic surfactants from alginate oligo- or polysaccharides.[82]



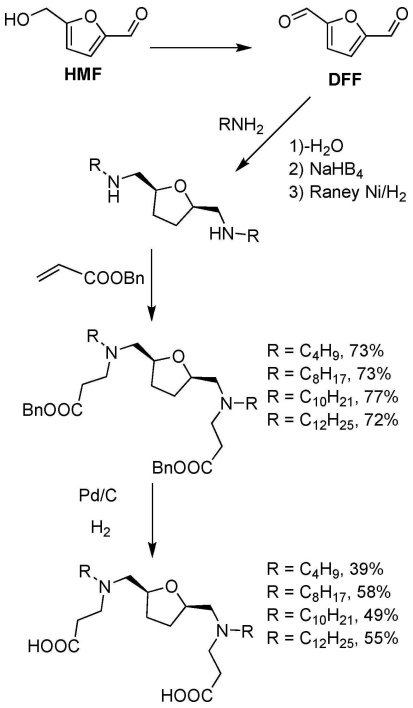
Scheme 10. Non-ionic glycerol acetals from HMF ethers.[83]

in glycerol, two different compounds can be formed.[83] These compounds exhibited hydrophilic–lipophilic balance (HLB) values ranging from 4.9 to 6.6, which are consistent with applications as humectants or emulsifiers. Their stability in water was excellent, with no change over 50 h, as well as their thermal stability with no degradation before 200 °C.

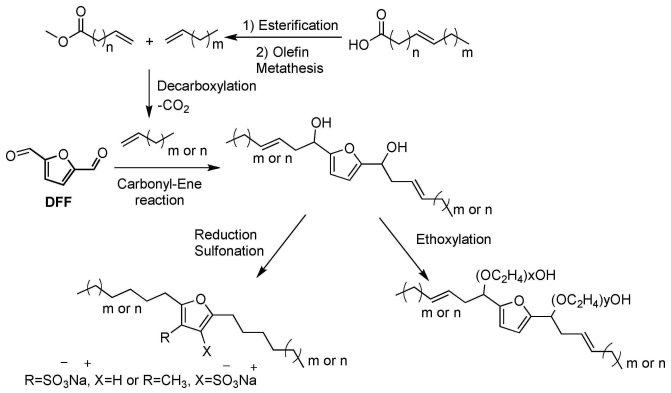
HMF can be oxidized to the bis aldehydic product DFF. A series of gemini surfactants were synthesized from DFF by Muzart and co-workers.[84] Gemini surfactants are known to exhibit very specific properties, notably self-assembling ability at significantly lower concentrations.[85] Condensation of DFF with alkyl amines, followed by the reduction to secondary amines with $NaHB_4$ and further reduction of the furan moiety led to tetrahydrofuran secondary amines. These bis-amines were carboxyethylated in two steps, firstly with a Michael addition on benzyl acrylate, followed by catalytic hydrogenation to the final amphoteric bis-aminocarboxylates (Scheme 11). These surfactants exhibited remarkable ability to reduce water surface tension (down to 30 $mN\,m^{-1}$) at an extremely low CMC ($\approx$1.5 $\mu mol\,L^{-1}$). Being amphoteric, a strong influence of pH on the properties was observed. In addition to the physicochemical properties, the compounds behaved as antifungal agents against *Fusarium graminearum*.

After the above examples all relying on carbon-heteroatom chemistry, a handful of carbon–carbon bond formation strategies should be also mentioned. One example is a sequence using the carbonyl-ene reaction of an unsaturated fatty acid as the key step, reported in a recent patent by Krumm and co-workers. This process starts from unsaturated fatty acids, which are esterified to their methyl esters, then subjected to an olefin metathesis reaction generating two new unsaturated olefins, among which one is a carboxylic ester which can be decarboxylated. The resulting mixture of two fatty unsaturated olefins can then undergo a carbonyl-ene reaction with DFF. After hydrogenation, a sulfonation or ethoxylation step introduced the polarity in the targeted amphiphiles (Scheme 12).[86]

Queneau and co-workers have investigated the application of the atom economical Morita–Baylis–Hillman (MBH) C—C bond formation reaction to furanic aldehydes.[87,88] Queneau and co-workers further applied the strategy to HMF, its glucosylated analogue GMF[77–79] and its succinic hemiester (SMF, prepared

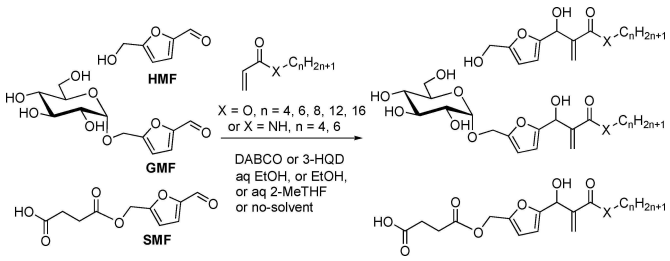


Scheme 11. Synthesis of gemini surfactants from DFF.[84]



Scheme 12. Synthesis of oleo-furan surfactants from DFF with unsaturated fatty acid.[86]

by reaction with succinic anhydride)[89] used as aldehydes, and fatty acrylates or acrylamides as activated alkenes.[90] Thus, a new family of biobased amphiphilic derivatives, prepared in clean aqueous or biobased solvents and under mild conditions, was designed (Scheme 13). They demonstrated that the GMF derivatives exhibited lower CMC values than the corresponding alkyl β-D-glucopyranosides. Hydrogenation of the acrylic linkage led to a less hydrophilic behavior, as seen by phase inversion temperature (PIT) -slope values, an interesting method for quantifying and comparing the amphiphilicity of surfactants.[91,92] HMF short-chain amphiphilic acrylamides were more hydrophilic than the corresponding acrylic esters. The C_{12} GMF compounds were found to stabilize oil-in-water-emulsions,



Scheme 13. The Morita–Baylis–Hillman route to furanic surfactants.[90]

while the more lipophilic C_{16}-SMF adduct under the acidic form could be used to formulate water-in-oil-emulsions.

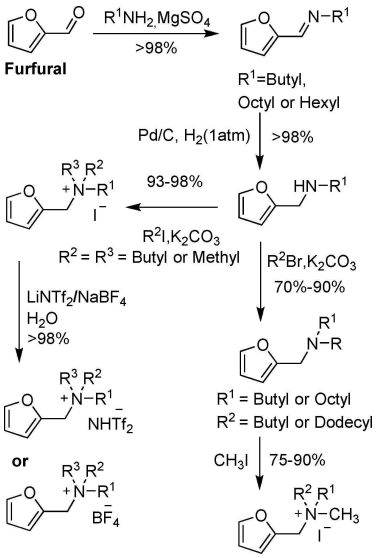
3. Furfural-Based Amphiphiles

Several quaternary ammonium salts were synthesized from furfural by Galletti et al.[93] Solvent-free condensation of furfural with amines (butylamine, octylamine, or hexylamine) using $MgSO_4$ as catalyst generated the corresponding imines. Subsequent catalytic hydrogenation led to the alkyl-substituted furfural-based amines, which could be further substituted to the tertiary amines with bromoalkanes, then quaternized to the ammonium iodide using iodomethane. Alternatively, the secondary amines could be directly treated by iodoalkanes, leading to the quaternary ammonium iodides. Further anion exchange allowed to vary the counter anion, for example as bis(trifluoromethane)sulfonimides and tetrafluoroborates (Scheme 14). The solubility of these quaternary ammonium salts was investigated, showing high solubility in polar solvents with variations depending on the alkyl chain length and on the counter anion. Satisfactory chemical stability was found under basic, neutral, and weak acidic conditions, whereas quick decomposition was observed in strongly acidic media. The compounds were found thermally stable until 165 °C or higher. The high thermal stability, the low melting point, and the low viscosity of the NTf_2 salts are consistent with their use as ionic liquid solvents. The acute ecotoxicity of the furanic salts was comparable to that of tetrabutylammonium iodide (TBAI) and benzyltributylammonium iodide (BTBAI), suggesting possible uses as alternative biocides.

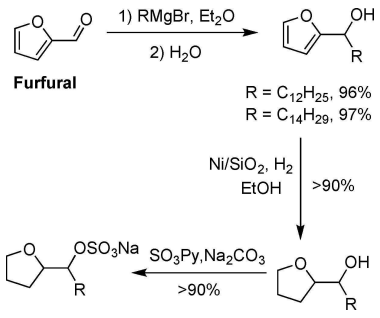
Grignard reactions targeting the aldehyde group of furfural have been used as a key step towards amphiphilic furans. This has been well illustrated by Palkovits and co-workers, who reported anionic surfactants prepared by this route.[73] The alkylated molecules they obtained could be fully hydrogenated using Ni/SiO_2 as catalyst, and the subsequent sulfatation of the hydroxy group by action of the SO_3·Py complex and neutralization with Na_2CO_3 (Scheme 15) led to the targeted amphiphilic compounds. The CMC and interfacial tension between water and isopropyl myristate at pH 8.5 of the C_{12} (0.24 g L^{-1}, 3.5 mN m^{-1}) and C_{14} (0.01 g L^{-1}, 2.9 mN m^{-1}) compounds was compared to LAS (0.08 g L^{-1}, 0.9 mN m^{-1}) and ethoxylate-based FAES (0.05 g L^{-1}, 3.9 mN m^{-1}).

Earlier, two families of such 2,5-dialkylfurans and 2,5-dialkyltetrahydrofurans were reported by Krauss et al. for being used as antibacterial agents. The reaction of furfural with dodecylmagnesium bromide generated an alcohol, which could be lithiated with *n*-BuLi, then added onto pent-4-enal to give a 2,5-disubstituted furan. Systems bearing either one hydroxy group and one alkyl chain or two hydroxy groups and two alkyl chains could thus be obtained, while subsequent hydrogenation provided the corresponding tetrahydrofuryl derivatives. Alternatively, Grignard reaction of furfural with pent-4-enylmagnesium bromide and lithiation with *n*-BuLi followed by reaction with dodecylaldehyde led to other disubstituted furans, and tetrahydrofurans after hydrogenation (Scheme 16).[94] While no expected antibacterial activity was observed, the compounds exhibited significant cytotoxicity against the HL 60 cell line.

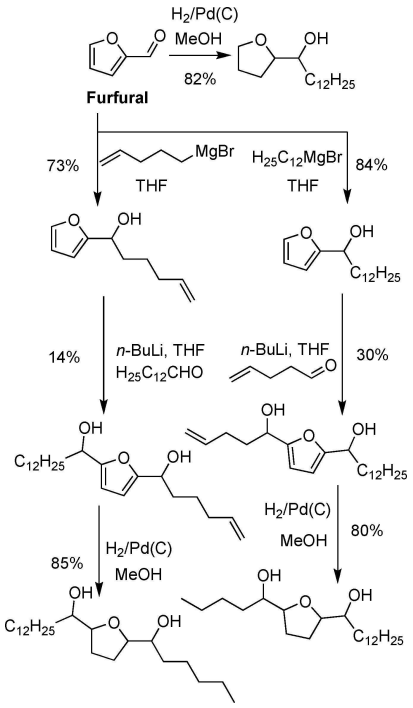
The patent of Krumm and co-workers[86] also included the preparation of surfactants by via carbonyl-ene reaction of furfural and alkyl furfurals with olefins generated from the metathesis of unsaturated fatty esters. The hydrophilic moiety was introduced either via a reduction/sulfonation sequence or by ethoxylation (Scheme 17).



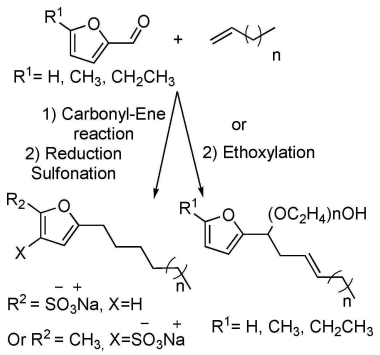
Scheme 14. Synthesis of quaternary ammonium salts from furfural.[93]



Scheme 15. Synthesis of amphiphilic alkylated furfural sulfates.[73]

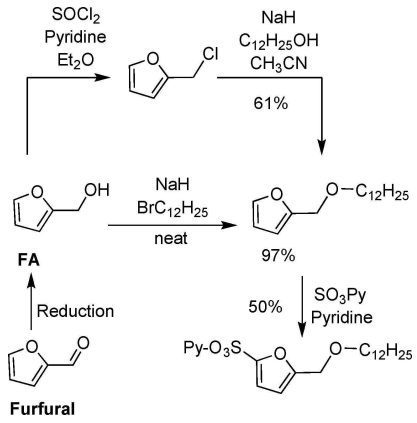


Scheme 16. Synthesis of 2,5-dialkylfurans and tetrahydrofurans from furfural.[94]



Scheme 17. Synthesis of oleo-furan surfactants from furfurals with unsaturated fatty acid.[86]

FA, easily obtained from furfural by reduction, could also serve as precursors towards amphiphiles. In their work targeting different families of amphiphilic products from furfural and furan, Palkovits and co-workers extended the scope of possible products using FA as substrate in an alkylation/sulfonation sequence (Scheme 18).[73] Alkylated FA were prepared by Williamson etherification of alkyl bromides or iodides; however, competitive E_2-elimination gave side *n*-olefins in variable extent depending on the haloalkane and the solvent. The best selectivities were observed using alkyl iodides under solvent-free condition. The alternative two-step sequence involving the furfurylation of dodecanol by furfuryl chloride suffered from degradation during the distillation process. The SO_3·Py-complex-mediated sulfonation on the furan moiety of the furfurylether was found to occur with concomitant ether cleavage, thus producing dodecylsulfate as side product.

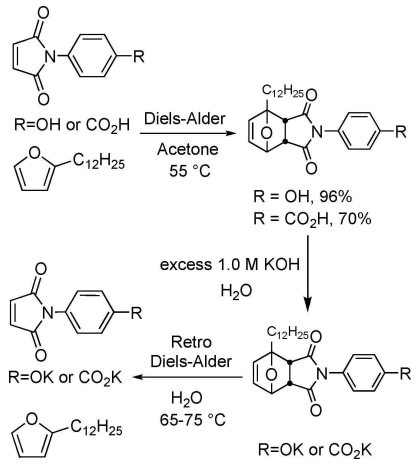


Scheme 18. Synthesis of surfactant furfuryl alcohol ethers sulfonates.[73]

4. Furan-Based Amphiphiles

Furan can be prepared by decarbonylation of furfural.[42–44] It can therefore be considered as a pertinent biobased platform among furanic scaffolds, as well as 2-alkylfurans, which can be obtained from various precursors, including furan itself, or furfural as exemplified in the previous section.

Furans or alkylfurans, thanks to their dienic nature, can undergo Diels–Alder (DA) cycloaddition, a reaction showing two interesting characteristics, firstly to be an atom economical reaction, and secondly to be reversible at higher temperature. This offers a possibility to design thermally cleavable products. This has been exploited to reach surfactants in a study reported in 2005 by Simmons and co-workers.[95] As depicted in Scheme 19, the DA reaction of dodecylfuran with maleimides was utilized as a key step to synthesize two series of



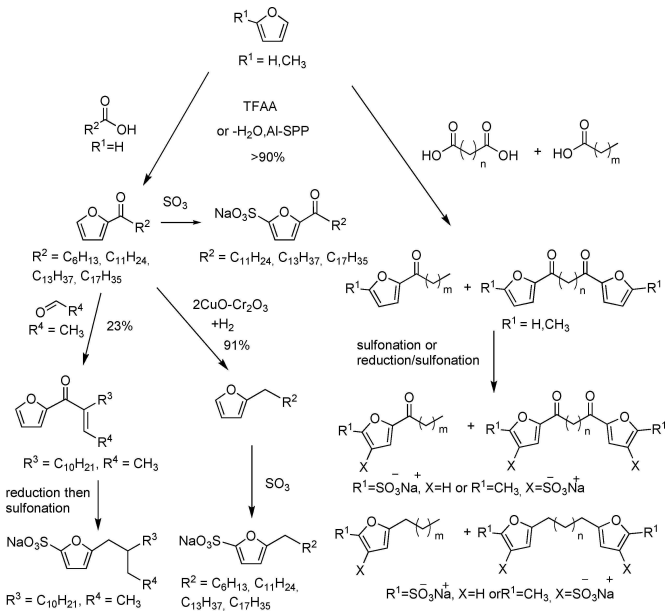
Scheme 19. Synthesis of thermally cleavable surfactants from alkyl furans by DA reaction.[95]

amphiphiles. The non-polar character is provided by the alkylated furanic substrate, while the polar one is an anionic group, either a potassium phenolate or a potassium carboxylate, arising from the maleimide dienophile substitution. The resulting DA adducts were found to exhibit interesting surfactants properties, with CMC values in the mM range and good ability to form micelles as demonstrated by small-angle neutron scattering experiments. As expected from their design, they exhibited the interesting property to be thermally cleavable, with reversion of the reaction when exposed to temperatures above 50 °C leading to smaller and non-amphiphilic degradation products. Such a behavior can be useful in sol–gel syntheses of mesoporous materials, in which the surfactant must be removed at the end of the process.[95]

More recently, Dauenhauer and co-workers reported the design of 2,5-disusbtituted furanic amphiphiles starting from furan itself. The strategy relies on grafting a non-polar moiety through a Friedel–Crafts acylation reaction of a fatty acyl chain onto the furan α position, and on a late sulfonation at the α′ position providing the polar group.[96] The name of "oleofurans" gives a clear indication of the biomass origin of these compounds.

The Friedel–Crafts acylation step could be performed with long-chain alkyl anhydrides using heterogeneous catalysts, such as Al-SPP; however, one equivalent of fatty acid is also formed in this sequence. A more atom-economical route was preferred, directly using the fatty acids in presence of trifluoroacetic anhydride (TFAA) or the H-ZSM-5 zeolite.[97] The ketone of the intermediate acylfuran could be reduced selectively in presence of copper chromite, retaining the complete furan structure, leading to alkyl analogues. The scope of oleofurans was extended further to branched systems through an intermediate aldol condensation of the furanic ketones with acetaldehyde (Scheme 20). A mixture of fatty carboxylic acids or diacids arising from an olefin metathesis/alkene oxidation sequence could also be used in the Friedel–Craft acylation step of furan (or methyl furan) leading to additional alkylfurans including symmetrical bis furanic systems.[86] An alternative clean and atom economical route to the acylfurans using the cross-ketonization reaction of 2-furoic acid and lauric acid under heterogeneous catalysis only giving H_2O and CO_2 as side products was also recently proposed by Vlachos and co-workers.[98] Other approaches towards long-chain alkylfurans lubricants reported recently by Vlachos and co-workers,[99–101] prepared by coupling alkylfurans with fatty aldehydes or ketones leading to di-furanic products, or by conjugate addition of alkyl furans onto unsaturated aldehydes, might be also considered for extending the scope of possible amphiphilic targets.

The remnant α carbon of the acyl or alkyl furans could be sulfonated through two strategies: one is sulfur trioxide sulfonation, and the other is sulfur trioxide-pyridine complex sulfonation (Scheme 20). These oleo-furan sulfonates (OFSs) surfactants exhibit same performances as LAS in terms of interfacial properties, however, at lower CMC and Krafft temperatures (T_k) due to a favorable effect of the furan moiety on the solubility, consistent with better detergency ability. Faster wetting capacity and same foaming behavior were found as compared to LAS. Interestingly, the OFS surfactants exhibited improved stability in hard water, suggesting applications in which the utilization of additional chelating agents can be avoided.



Scheme 20. Furan acylation to renewable oleo-furansulfonates.[86,96]

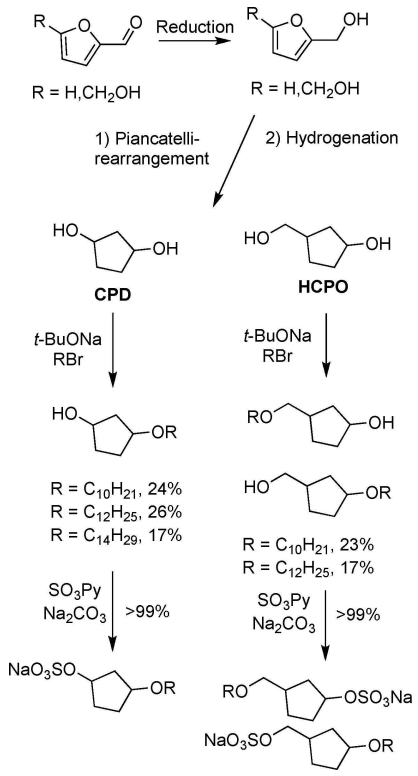
5. Alternative Approaches via Rearranged Furans

5.1. Amphiphiles via the Piancatelli cyclopentanol platform

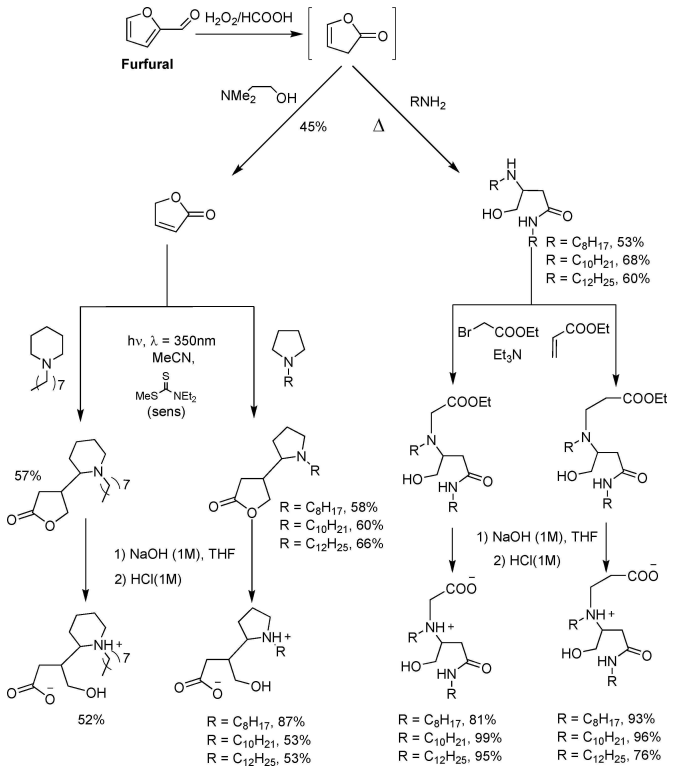
The Piancatelli reagarrangement, a way to transform furfuryl alcohols to cyclopentenones, has become a popular strategy in biobased chemistry.[102] Therefore, when applied to HMF or furfural, biobased 5-membered carbocylic diols, such as 3-(hydroxymethyl)cyclopentanol (HCPO), and 1,3-cyclopentanediol (CPD) can be reached from a hydrogenation/Piancatelli rearrangement/hydrogenation sequence, respectively.[103–105] New surfactants derived from these diols have been prepared by selective Williamson monoetherification of one of the hydroxy groups, followed by sulfatation of the remaining one (Scheme 21). Physicochemical evaluation in this series (CMC, interfacial tension) compared to LAS and FAES showed interesting values for the C_{10} product (0.13 g L^{-1}, 3.5 mN m^{-1}).[73]

5.2. Amphiphiles via the 2[*5H*]-furanone platform

Hoffmann and co-workers have exploited two different 2[5*H*]-furanone platforms obtained from furfural by oxidation of furfural, for designing amphiphilic compounds. 2[5*H*]-Furanone was generated from the oxidation of furfural by H_2O_2/formic



Scheme 21. Synthesis of HCPO-based and CPD-based surfactants.[73]



Scheme 22. Synthesis of surfactants from 2[5*H*]-furanone.[106,107]

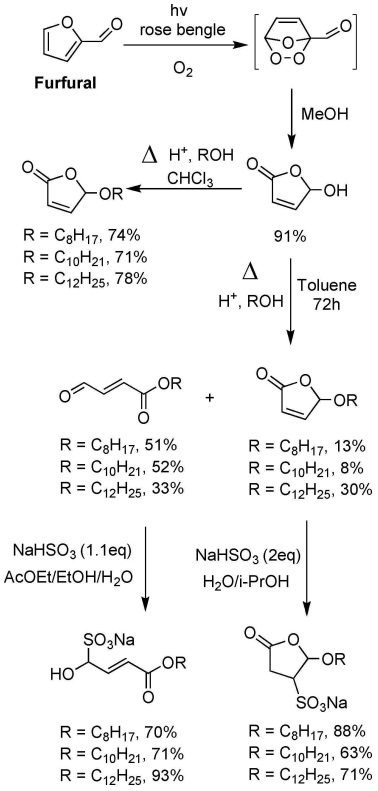
acid, followed by isomerization in presence of *N,N*-dimethylethanolamine. Radical addition of cyclic tertiary amines carrying long fatty chains under photochemical induction by catalytic amounts of 4,4′-dimethoxybenzophenone as sensitizers led to the Michael adducts, which could then be transformed to the amphiphilic ammonium/carboxylates by lactone opening and amine protonation (Scheme 22).[106]

The same 2[5*H*]-furanone could also react with two equivalents of fatty amine with concomitant Michael addition and amide transformation of the lactone, grafting simultaneously two hydrophobic chains. Selective carboxymethylation or carboxyethylation of the secondary amine either by reaction with ethyl bromoacetate or methyl acrylate, respectively, followed by saponification to the carboxylate and propotonation to the ammonium, led to a second family of amphiphilic ammonium/carboxylates (Scheme 22).[107] Interesting surfactant properties for the cyclic systems were observed at pH 10, where the anionic form is favored. The acyclic ones exhibited lower CMC than the conventional single-alkyl-chain surfactants (carboxylate, sulfate, or sulfonate) and similar to other gemini surfactants. Water surface tensions as low as 30 mN m^{-1} were measured, suggesting potential application as wetting agents, especially under basic conditions (pH = 10). The acyclic systems could be classified as potentially biodegradable under the E.U. directive standard[108] with 30–40% degradation after 28 days.[107]

A photooxygenation reaction of furfural gives access to a hemiacetalic type of 2[5*H*]-furanone platform, namely 5-hydroxy-2[5*H*]-furanone. Its acetalization with fatty alcohols under azeotropic distillation generated the corresponding 5-alkoxy-2[5*H*]-furanones. Prolonged reaction time led to the transesterification of the lactone group to the corresponding fatty esters, while the remaining enol rearranged into an α,β-unsaturated aldehyde. The furanone acetal and the linear α,β-unsaturated aldehyde could both be sulfonated with $NaHSO_3$ to provide a polar part, achieving the surfactant design, among which the cyclic systems exhibited chemical stability consistent with potential uses as surfactants (Scheme 23). For the furanone sulfonates, the higher lipophilicity of the furan moiety led to lower CMC as compared to alkylsulfate and alkylsulfonate surfactants with same fatty chain length, while similar to that of LAS surfactants. The furanone surfactants were classified as biodegradable (70% after 28 days), which is better than LAS (26–50% after 28 days).[109]

6. Recapitulative Structural Scope of Furanic Amphiphiles, Conclusion and Perspectives

Though still in its infancy, the furanic route toward biobased amphiphiles is already rich of several examples that demonstrate interesting novelty and variability in structural design, which can derive from 5-hydroxymethylfurfural (HMF), furfural, and furan and their derivatives. All types of possible surfactants [anionic, cationic, amphoteric (Figure 1), and non-ionic (Figure 2)] have been shown to be reachable, using different ways



Scheme 23. Synthesis of alkoxyfuranone-based surfactants.[109]

for grafting the polar and non-polar moieties, either retaining the furan or tetrahydrofuran rings in the targets, or resulting from an initial reduction or oxidation transformation and rearranged architectures such as the Piancatelli cyclopentanols or the 2[5*H*]-furanones.

Breakthrough innovation in properties (applicative and environmental) of chemicals can only result from new molecular design. Among directions towards a renewed portfolio of chemical compounds, the use of biobased furanic platforms will contribute to this design renewal and to the efforts aiming at the limiting the dependence of chemistry on fossil resources. Remaining challenges reside in the complexity of some of the processes, which will require the commitment of all facets of chemistry, in particular chemical and enzymatic catalysis and chemical engineering adapted to the specificities of biobased furans chemistry. One-pot processes, which can start from the crude carbohydrate biomass by encompassing the initial dehydration step, would be also valuable alternatives. Besides such improvements in the feasibility and economic viability of the processes, studies focusing on the understanding of the contribution of the furanic backbone to the physicochemical and environmental properties will help defining the structures with the most promising applicability.

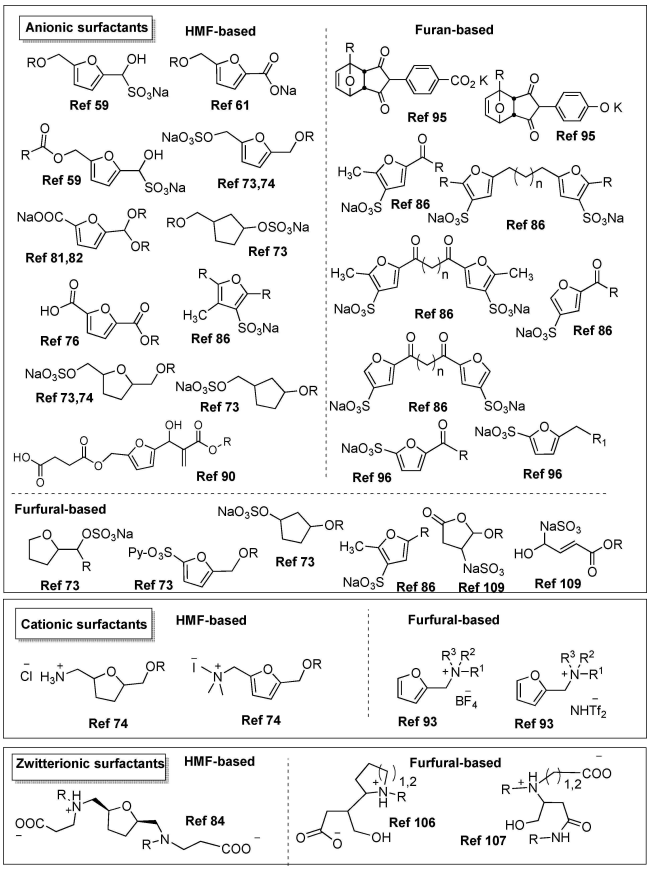


Figure 1. Structural scope of ionic amphiphiles derived from biobased furans.

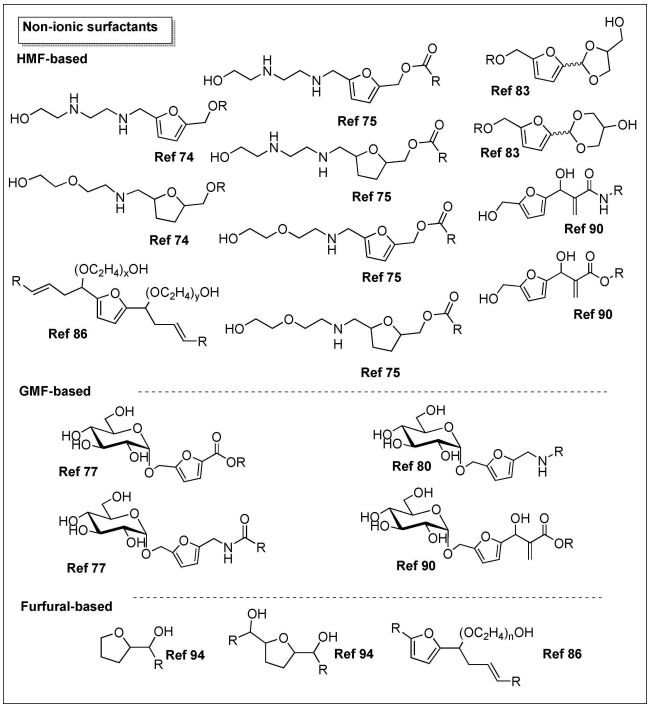


Figure 2. Structural scope of ionic amphiphiles derived from biobased furans.

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Conflict of Interest

There are no conflicts of interest to declare.

Keywords: 5-hydroxymethylfurfural · biomass · furfural · furans · surfactants

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