Impact of the chemical structure on amphiphilic properties of sugar-based surfactants: A literature overview

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Théophile Gaudin[1,2,✉], Huiling Lu[1,3], Guillaume Fayet[2], Audrey Drelich[1], Patricia Rotureau[2], Gwladys Pourceau[3], Anne Wadouachi[3], Elizabeth Van Hecke[1], Alla Nesterenko[1], Isabelle Pezron[1,✉]

1)   Sorbonne University, Université de technologie de Compiègne, ESCOM, EA 4297 TIMR, Centre de recherche Royallieu, CS 60319, 60203 Compiègne cedex, France

2)   INERIS, Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France

3)   Laboratoire de Glycochimie des Antimicrobiens et des Agroressources (LG2A), UMR CNRS 7378, Institut de Chimie de Picardie FR 3085, Université de Picardie Jules Verne, 33 rue St Leu, FR-80039 Amiens Cedex, France

✉ gaudin.theophile@gmail.com, isabelle.pezron@utc.fr

Abstract

In this review, structure-property trends are systematically analyzed for four amphiphilic properties of sugar-based surfactants: critical micelle concentration (CMC), its associated surface tension (γ_{CMC}), efficiency (pC_{20}) and Krafft temperature (T_K). First, the impact on amphiphilic properties of the alkyl chain size and the presence of branching and/or unsaturation is investigated. Then, various polar head parameters are explored, such as the degree of polymerization of the sugar unit (mono- or oligosaccharides), the chemical nature of the linker and the sugar configuration. Some systematic comparisons between ethoxylated surfactants and sugar-based surfactants are also carried out. While some structural trends with the impact of alkyl chain length or the polar head size are now well understood, this analysis points out that systematic studies of more specific effects of alkyl chain (*e.g.* branching, unsaturation, presence of rings, position on the polar head) and polar head (*e.g.* linker, anomeric configuration, internal stereochemistry, cyclic vs. acyclic sugar residues) were scarcer or not available to date. This work encourages the use of these structural trends in the perspective of developing new bio-based surfactants and their consideration in predictive models. It also highlights the need of further experimental tests to fill remaining gaps notably to explore some specific structural features (such as the introduction of rings in the alkyl chain or the position of the alkyl chain on the polar head) and towards applicative properties (like foaming capacity or wettability).

Keywords: sugar-based surfactants, structure-property trends, amphiphilic properties, biorefinery, renewable materials

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Contents

1   Introduction

Surfactants on the market are nowadays mostly produced from crude oil [1], i.e. from non-renewable resources [2]. In order to reduce the carbon footprint of surfactant production, and since crude oil reserves may be depleted in this century, efforts are engaged to replace such petroleum-based compounds by bio-based alternatives. Facilities aiming at production of valuable materials from biomass, called biorefineries, have emerged [3]. Among other products, biomass containing sugars and fatty acid esters [3] can be used to produce sugar-based surfactants [4]. These latter represent good renewable alternatives to conventional petroleum-based surfactants [5, 6].

Many different carbohydrates and fatty molecules can be obtained from biorefineries [3], and even more, sugar-based surfactants can be synthesized from these biorefinery-derived building blocks [7]. Anticipating trends between renewable sugar-based surfactant structures and properties represents an important challenge from fundamental but also applicative points of views, which can help research and industrial efforts towards the production of greener surfactant-containing products with equivalent or even better properties [8]. Besides, such an understanding can direct synthesis effort towards suitable surfactants for a dedicated industrial application, which limits synthesis efforts, also leading to both cost and environmental benefits. Ideally, an understanding of structure-property relationships for surfactant blends would provide the best help in this respect. However, a consolidated understanding of the properties of pure surfactant solutions can help rationalize the behavior of blends with mixing rules reflecting the underlying physical phenomena. For complex molecules like sugar-based surfactants, such consolidation is still challenging. To overcome this challenge, we realized a first step towards a better understanding of structure-property trends by collecting the largest possible database for amphiphilic properties of sugar-based surfactants [9]. This new database, considering 24 amphiphilic properties, 659 sugar-based surfactants and 2626 property values, allowed us to perform an extended analysis of structure-property trends of sugar-based surfactants.

Indeed, several books [4, 10, 11], book chapters [6, 12-15], and reviews [16-18] have been published about sugar-based surfactants, but they are mostly focused on the specific family of alkyl(poly)glycosides. Marchant et al. [19] reviewed surface-active properties of polysaccharide surfactants. Von Rybinski et al. [11] and Nickel et al. [20] focused on alkyl(poly)glycosides, Laughlin et al. [12] on *N*-alkanoyl-*N*-alkyl glycamines (with an amide linker) and Razafindralambo et al. [21] on various uronic acid derivatives. These studies generally covered synthetic methods, properties, and applications of specific subclasses of sugar-based surfactants, but an extensive and systematic investigation of structure-property relationship remained to be conducted.

This review focuses on four amphiphilic properties for which a large amount of data is available, thus enabling some quantitative comparison: critical micelle concentration (CMC), surface tension at CMC (γ_{CMC}), efficiency of adsorption at air-water interface (pC_{20}), and Krafft temperature (T_K). These

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properties are at the same time fundamentally defined from a thermodynamic point of view and related to the performances of surfactants in various applications, notably in detergent and cosmetic formulation, or for enhanced oil recovery [5]. It can be noticed that properties relevant to Hydrophilic Lipophilic Deviation – Net Average Curvature (HLD-NAC) theory [22] such as characteristic curvature or characteristic surfactant length in various oils would be even more directly helpful to develop industrial formulations, but unfortunately, no database as large and systematic as for the four mentioned properties could be found in literature for sugar-based surfactants.

In this article, structural trends were analyzed for CMC, γ_{CMC}, pC_{20} and T_K by comparing the data for homologous series of compounds for which only one structural parameter changed in order to derive structure-property trends. Of course, this review takes into account existing literature. It also benefits from Quantitative Structure-Property Relationship (QSPR) models recently developed by our team for these four properties in which some structural trends were particularly pointed out [23-26].

2 Investigated properties

2.1 *Definitions and applications*

Amphiphilic molecules, and, among them, sugar-based surfactants, exhibit two specific behaviors in solution: self-association and adsorption at interfaces. In this review, we studied two properties reflecting self-association (critical micelle concentration (CMC), Krafft point (T_K)) and two properties reflecting adsorption at interfaces (surface tension at CMC (γ_{CMC}) and the adsorption efficiency (pC_{20})).

Most of the studied properties can be defined by analyzing the surface tension of aqueous solutions as a function of the surfactant concentration. At very low concentrations of surfactant, the surface tension of the aqueous solution is close to that of pure water. As surfactant concentration increases, surface tension starts to decrease, at first slowly and, then, more strongly, until reaching a linear slope with respect to the logarithm of concentration (log C). The onset of this linear relationship with log C is usually observed before surface tension has decreased by 20 mN/m. For this reason, this concentration is usually used, in negative logarithm (pC_{20}), as an indicator of the efficiency of a surfactant to reduce surface tension. Then, the concentration reaches a critical limit after which the surface tension remains almost constant when surfactant concentration increases. In the case of surfactants soluble in water, this critical point corresponds to the CMC, which is the concentration at which micelles (self-associated surfactant structures) start to form in solution, and the associated surface tension is denoted γ_{CMC}. In the case of non-water-soluble surfactants, the concentration at the critical point corresponds to the solubility limit.

CMC is one of the simplest means to characterize the colloid and surface behavior of a surfactant solutes that yet can help evaluating its industrial or pharmaceutical usefulness [27]. In some cases, surfactants with low CMC are desired, for instance to solubilize hydrophobic drugs within micellar

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cores with a minimal amount of surfactants [28]. Furthermore, in many applications, like foaming, wetting and hard surface cleaning (where a low surface tension of the product is often desired), above CMC, micelles act as surfactant reservoirs such that the product can be diluted without significant modification of its surface tension. In some other cases, a high CMC is desired, like for membrane protein extraction, where the extraction efficiency generally stops increasing with surfactant concentration at about four times the CMC value of the surfactant due to self-association [29]

γ_{CMC} measures the effectiveness of surface tension lowering, which can be useful for applications such as hard surface cleaning [30]. Indeed, with a lower surface tension (or lower γ_{CMC}), the same amount of cleaning solution can wash larger surfaces, allowing cost reduction. pC_{20} characterizes the efficiency of surfactant adsorption. Therefore, it represents a complementary information with respect to γ_{CMC}: while γ_{CMC} indicates the maximal surface tension lowering, pC_{20} indicates how much surfactant is needed to reach a certain surface tension lowering. These properties are known to be influenced by temperature, salts, organic substances, and molecular structure of the surfactants.

To evidence whether a solid surfactant dissolves or not at a given temperature, the Krafft point T_K is used. T_K is the temperature at which the solubility limit is equal to CMC. Below T_K, surfactants precipitate before reaching a concentration at which they can form micelles. Since most available T_K have been measured for water solutions, the present analysis focuses on T_K in water. This property has practical interest because below T_K, surfactant molecules are not soluble and therefore cannot be optimally used, for example in industrial processes. T_K is commonly observed for ionic surfactants [5], but non-ionic sugar-based surfactants sometimes exhibit T_K. T_K is affected by the structure of the surfactant as well as by the presence of salts and other organic substances [5].

3   Challenges of the data analysis

Since the experimental data available in open literature can be subject to high uncertainties, or even be erroneous, any chemical data collection should be analyzed with caution. For example, a recent study [31] highlighted that the Carbbank, a database of complex carbohydrates and their properties, contained 35% of errors. Accordingly, a deep analysis of the 2626 data was conducted to check the purity and reproducibility of the experimental data used in this survey [9].

Regarding purity, most of the data gathered were collected for molecules that were both synthesized and characterized in the same original study. Authors mostly characterized the purity of compounds by Nuclear Magnetic Resonance (NMR) spectrometry and neither provided the proportion of impurities nor the chemical structures of impurities, while these latter could strongly impact the physico-chemical properties, as pointed out by Lorber et al. [32]. Moreover, Stubenrauch et al. [17] also identified some reproducibility issues in an earlier review. Accordingly, while for some well-known molecules, such as octyl-β-D-glucoside, good agreement was observed between the property values proposed by different investigators, lack of reproducibility was observed for some other molecules,

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e.g. for dodecyl-β-D-glucoside (γ_{CMC} of 27.3 mN/m [33] and 39.3 mN/m [34]) or *N*-decyl-D-lactobionamide (CMC of 1.32 mM [35] and 3.40 mM [36]). Presence of unknown impurities and potential lack of reproducibility can explain, in some cases, exceptional reported data for one molecule (*i.e.* with large differences when compared to other similar molecules).

Another challenge in this survey relates to the large structural diversity of sugar-based surfactants, leading to less systematically comparable structures than for simpler surfactants like polyoxyethylenes, as also noted in Stubenrauch et al. study [17]. Figure 1 illustrates the diversity of structural modifications that can change one sugar-based surfactant into another, considering the octyl-β-D-glucoside, one of the simplest and most studied sugar-based surfactants, as a reference system. For some of the structural parameters (alkyl chain length, branching and unsaturation; number, anomeric configuration of the sugar units; nature of the linker), collected data from literature allowed systematic analysis on homologous series, raised in this article. Unfortunately, for all other modifications (like cyclization of alkyl chain or position of alkyl chain on the polar head), available data did not allow elucidation of structure-property trends and further experimental investigations should be encouraged.

<mark>FIGURE 1 HERE</mark>

4   Structure-property trends

The influence of the various structural parameters of sugar-based surfactants on their amphiphilic properties were investigated systematically depending on the availability of experimental data allowing direct comparison. The investigated parameters are presented successively from those related to the alkyl chain to the ones related to the polar head.

4.1   *Influence of the alkyl chain*

In most sugar based-surfactants, the hydrophobic part of the molecule is an alkyl chain. Because it has low affinity with aqueous solutions, this lipophilic moiety is the main driving force of surfactant behavior [8, 30]. Three structural features related to the alkyl chain were investigated: the alkyl chain length, branching and unsaturation degree.

4.1.1   Alkyl chain length

An alkyl chain is primarily characterized by its size, which is commonly considered through its number of carbon atoms. Many authors [35, 37-40] investigated homologous series of sugar-based surfactants, in which only the number of CH_2 units in the alkyl chain changed.

An exponential decrease of CMC with alkyl chain length is observed for most surfactants, including sugar-based surfactants [4, 5, 8, 11-13, 19, 30, 41-48]. This influence of the alkyl chain on the CMC was confirmed for glucoside, maltoside and glucuronate-based surfactants [49-51]. Indeed, in Figure 2 (a), log CMC linearly decreases with respect to the number of carbon atoms in the alkyl chain (up to

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15-16 atoms) for four homologous series of sugar-based surfactants. Besides, our recent QSPR analysis of sugar-based surfactants also evidenced this main structural feature influencing log CMC of sugar-based surfactants [23]. Indeed, the most significant descriptors of the three fragment-based models developed in this study were directly related to the alkyl chain length (e.g. the molecular weight of the alkyl chain in the best fragment-based model).

Hydrophobic effect [52] explains such behavior. This effect is defined as the entropy loss induced by water structuring around alkyl chains that leads to a positive Gibbs free energy of solvation of CH_x groups of the alkyl chain. Thus, upon increasing surfactant concentration, longer alkyl chains tend to avoid unfavorable water structuring by forming micelles at lower concentrations.

Some authors [53, 54] also pointed out that chain entanglement (also named coiling) can occur for long chains, resulting in a less favorable micellar free energy and therefore effectively increasing CMC with respect to what it would be if entanglement would not occur. This seems confirmed from our database for lactobionamide- and raffinose-based surfactants exhibiting long alkyl chains when the number of C atoms becomes higher than 15 (as shown in Supporting Information, Figure S1).)

FIGURE 2 HERE

Contradictory trends are claimed in literature regarding the influence of the alkyl chain on γ_{CMC}. Indeed, Molina-Bolivar et al. [55] found a decrease of γ_{CMC} for methyl glucamines (MEGA-n) series. This trend was recently confirmed by Lu et al. [40, 49] for three homologous series of sugar-based surfactants with a ester or an ether linker. But Marchant et al. [19], reviewing four studies [56-59], did not conclude to any significant impact based on the five homologous series in these studies. Our analysis of available data [33, 39, 41-45, 47-50, 60-62] evidenced a globally decreasing trend of γ_{CMC} with alkyl chain length (as shown in Figure 2 (b) for four homologous series and Figure S2 (a) for complementary data for 9 other series). The data also indicate that in many cases (such as alkyl-β-D-glucosides, alkyl-(1-α-methyl)glucuronates, alkyl-α-D-galactosides or alkyl-β-D-maltosides), the decrease becomes lower with larger alkyl chains.

The decrease of γ_{CMC} with the alkyl chain length may be interpreted as follows. If alkyl chains are longer, the surface, once saturated in surfactants, is expected to be more nonpolar (because surfactants are more nonpolar). Nonpolar surfaces exhibit lower surface tensions [63]. Thus, γ_{CMC} is expected to decrease with longer alkyl chains up to a limiting value (corresponding to a pure alkane surface).

Such interpretation is also in agreement with the lower decrease of γ_{CMC} observed for the longest alkyl chains. For example, the γ_{CMC} difference between hexyl-β-D-glucoside (n_C = 6) and heptyl-β-D-glucoside (n_C = 7) is 3.2 mN/m, whereas it is only 0.5 mN/m between decyl-β-D-glucoside (n_C = 10) and dodecyl-β-D-glucoside (n_C = 12) [49].

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The discrepancy between the conclusions of Marchant et al. [19] and the trends observed in the present study may be due to the low magnitude of the decrease that can be, in some cases, comparable to the variability of γ_{CMC} measurements observed for a single molecule (about 1-2 mN/m). For example, in the case of dodecyl-β-D-maltoside in water at 25°C, Varga et al. [50] measured γ_{CMC} of 35.0 mN/m whereas Drummond et al. [64] measured γ_{CMC} of 36.3 mN/m. The data cited by Marchant et al. [19] indicated a decrease with alkyl chain length for three of the five homologous series cited (cf. Figure S2 (b)), while the two other homologous series (alkyl maltonamides and glucosyl alkanes) show almost flat curve of γ_{CMC} with respect to the alkyl chain length. Since γ_{CMC} are already relatively low for these two series, a possible cause might be surface-active impurities keeping surface tension low at short alkyl chain lengths.

By definition [30], efficiency is linearly linked to the free energy of transfer of the surfactant from the bulk of the liquid phase to the interface of the liquid (ΔG_{ads}). According to Rosen's hypothesis [30, 65], each functional group of the molecule contributes independently to ΔG_{ads}, and notably CH_2 groups. So, efficiency may be linearly dependent on the alkyl chain length.

This is also found in the literature survey [37, 41, 48, 60, 66] which reveals such linear increase with the number of C atoms in alkyl chain, as shown in Figure 2 (c). This trend was already identified by Rosen for other families of surfactants [67] and by Holmberg et al. [68] for a few sugar-based surfactants. Besides, recent QSPR modeling [25] confirms the alkyl chain length as the main structural impact on pC_{20} for sugar-based surfactants. Indeed, the molecular weight of the alkyl chain appears as the most significant descriptor of the best QSPR model to predict pC_{20} of sugar-based surfactants in this study.

Within the investigated database, two exceptions are found: 6'-*O*-alkanoyl-maltoses and 6-*O*-alkanoyl-maltotrioses [66] (see Supporting Information, Figure S3). For these molecules, efficiency seems to decrease with alkyl chain length from 15 C atoms and 17 C atoms in alkyl chain onwards, respectively. Since chain entanglement in micellar cores could explain CMC anomaly of long chains [53, 54], it may also explain this pC_{20} anomaly. Indeed, we could expect entanglement at a surfactant saturated interface, making saturation less favorable due to entropic effects [69] and thus increasing C_{20} (interpreted as the concentration required to saturate the interface [65]), resulting in a decrease of pC_{20}.

Surfactant dissolution capacity, characterized by T_K, is also influenced by alkyl chain length. Some authors [19, 55] proposed that surfactants with alkyl chains containing less than 12 C atoms are generally soluble. However, recent QSPR modeling study pointed out that many sugar-based surfactants with 9-10 C atoms in the alkyl chain may already exhibit dissolution issues [26] (like for alkyl-D-xylitols [37] in the collected data) and, as a consequence, that the water solubility of sugar-based surfactants seems lower than initially assumed. Among the data collected, T_K reveals to globally

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but not regularly increase with the number of C atoms in alkyl chain (as illustrated in Figure 3 for alkyl-α-D-glucosides [18] and *N*-alkanoyl-*N*-methylglucamines [70-72]).

As already evidenced by Van Doren et al. [71] for other homologous series of sugar-based surfactants, an odd-even effect is observed, with surfactants with odd numbers of C atoms in alkyl chain having similar T_K than next surfactants with even numbers of C atoms in alkyl chain. Such behavior is analogous to the relationship between melting point and number of C atoms of linear paraffins [73]. Besides, the analogy between T_K and melting point has already been pointed out in literature [74, 75]. Shinoda [76] even proposed to define the Krafft point as the melting point of a hydrated surfactant. Since solid-state behaviors are recognized difficult to quantify and correlate with molecular structure [77], it may explain difficulties in anticipating T_K based on molecular structure [71].

FIGURE 3 HERE

4.1.2   Branching

Another structural feature of alkyl chain is branching. Branched alkyl chains are constituted of non-linear alkyl moieties (cf. Figure 4). Branching can be analyzed from two perspectives [30]. The first one consists in comparing different types of branched chains at constant number of C atoms with the corresponding linear alkyl chain, and the second one consists in measuring the impact of adding C atoms within branched side chain. Available data led us to follow the first perspective. Three types of branched alkyl chains were identified for the collected data on sugar-based surfactants: branching at the first C of the alkyl chain [78], at the second C of the alkyl chain [79], or isoprene-like branching [80]. It may be noticed that the carbon at branching position is chiral in all identified studies. Therefore, the measured properties are related to mixtures of diastereoisomers.

FIGURE 4 HERE

In literature, CMC has been observed to increase with branching (*i.e.* branched alkyl chains compared to a linear alkyl chain with the same number of C atoms) for different classes of surfactants [30]. This seems to be also valid for a series of *sec*-decyl-β-D-glucosides (with branching at the 1st C of the alkyl chain, cf. Figure 5) [78]. The effect is consistent with a physical interpretation. Indeed, an increase of CMC with branching can be related to the unfavorable packing of branched alkyl chains into spherical or cylindrical micelles [30, 55].

FIGURE 5 HERE

On the contrary, a decrease of γ_{CMC} with respect to branching (as represented by the number of C atoms in a side chain at constant number of C atoms in alkyl chain) is evidenced for the same series of *sec*-decyl-β-D-glucosides (Figure 5) [78]. This trend was already observed for other classes of surfactants.

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Rosen [30] interpreted it as stemming from a lower affinity of the branched surfactants for micelles while affinity for surfaces was unchanged, when compared to surfactants with linear alkyl chains (as characterized by higher CMC/C_{20} ratios). Unfortunately, no C_{20} value is available to validate this hypothesis for *sec*-decyl-β-D-glucosides.

Nevertheless, based on Sierra et al. [81] and Minamikawa et al. [80] measurements, CMC/C_{20} were calculated for n-decyl-β-D-glucoside and 3,7-dimethyloctyl-β-D-glucoside and revealed lower for the surfactant with a linear alkyl chain, in line with Rosen's interpretation (cf. Figure 6). No clear conclusion could be obtained regarding the relationship of pC_{20} itself with branching due to the limited amount of available and comparable data.

FIGURE 6 HERE

To the end, a decrease of T_K is noticed when introducing branching in the alkyl chains of carboxylate, sulfonate and sulfate anionic surfactants [30]. However, such conclusions appeared as not applicable for sugar-based surfactants in the collected data, where branching can either increase or decrease T_K depending on the sugar head as shown in Table 1.

TABLE 1 HERE

4.1.3 Unsaturation

Among the collected data on sugar-based surfactants presenting an unsaturated chain, some were measured below the T_K. If further experimental campaigns at temperatures higher than T_K are encouraged, first trends were interestingly found.

Most of the identified sugar-based surfactants presenting an unsaturated chain from the literature survey include the oleyl chain [38, 60], with one *cis* double bond at the ninth position of a chain containing 18 carbons. Satgé et al. [82] synthesized galactose-based surfactants with an undecenyl chain (having the double-bond located at the end of the alkyl chain) and with the undecyl chain. Another study from Sun et al. [46] compared trehalose esters at various degrees of unsaturation. If Razafindralambo et al. [21] did not find significant effects of unsaturation by comparing undecanoyl glucuronate and undecenoyl glucuronate, looking at the global available data (summarized in Table 2) seems to exhibit some trends.

TABLE 2 HERE

At first, the presence of an unsaturation appears to increase CMC. It even seems to increase with the number of double bonds. This trend has been identified in our QSPR analysis [23], where the relative number of single bonds appeared in two models as a decreasing factor for log CMC. This trend is probably due to steric hindrance in micelle formation. Indeed, a *cis* double bond is not linear, more rigid and thus less easy to pack into a micelle than a saturated alkyl chain, according to general

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knowledge about surfactants [30]. It may also be associated to the solvation of the double bond in the micellar core which could be less favorable, since less hydrophobic than saturated alkyl group [73].

Regarding γ_{CMC}, a slight increase is observed for three of the four available examples. Undecenyl-α-D-galactoside is the only molecule for which no increase of γ_{CMC} is observed. However, the γ_{CMC} of undecenyl-α-D-galactoside and undecyl-α-D-galactoside were measured below their T_K. So, solubility issues may explain this exception. This trend is in agreement with experimental knowledge for other families of surfactants [30], but the magnitude of the variation (1-2 mN/m) is small, and comparable to experimental uncertainty, and thus this trend remains to be confirmed.

No direct comparison of homologous surfactants was possible among available pC_{20} data to investigate the impact of double bonds in the alkyl chain on this property. However, QSPR models pointed out that double bonds may decrease pC_{20} [25]. Indeed, the relative number of single bonds in the alkyl chain again appeared in the best QSPR model for pC_{20}, this time with a positive coefficient. Like for CMC, this may be related to the decreased hydrophobicity of unsaturated alkyl chains, which leads to a lower affinity of the surfactant for the surface.

At last, T_K appears to decrease with the introduction of unsaturation for all provided examples, in line with observations for ionic surfactants [30] and in agreement with Burczyk et al. [13] for alkyl-*N*-methyl gluconamides and lactonamides. Decrease observed when a double bond is present at the end of the alkyl chain of galactose-based surfactants may be due to the lower hydrophobicity of the unsaturated alkyl chains. All remaining surfactants with unsaturated alkyl chains contain oleyl alkyl chains, and thus *cis* double bonds. In these cases, by analogy to *cis*-unsaturated fatty acids [83], the bent in the alkyl chain caused by the *cis* double bond may disfavor the molecular packing. Thus, it may disfavor crystallization and decrease T_K.

4.2   *Influence of the polar head*

The analysis of the structural trends related to the polar head is complex (cf. Figure 1) notably due to the large number of functional groups that constitute them. Various structural features of the polar head of sugar-based surfactants were highlighted from this data collection: the size of the polar head, the nature of the linker and the stereochemistry of the carbohydrate residue (notably the anomeric carbon but also the configuration of the sugar itself). Unfortunately, further experimental data (that could be collected in the future) would be required to clarify the impact of other features like cyclic vs. acyclic sugar units or the introduction of different chemical moieties on polar head (*e.g.* amide vs. alcohol).

4.2.1   Polar head size

The polar head size is the most obvious structural feature related to the polar head. Besides, steric hindrance was proposed to explain the influence of the polar head size on the behavior of surfactants at interfaces and the micelles [30]. For sugar-based surfactants, the size of the polar head can be

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characterized at two different levels: the size of sugar residues (*e.g.* pentose *vs* hexose) and the number of sugar residues in the polar head (*e.g.* monosaccharides *vs* disaccharides). So, if for a global quantitative analysis, the number of atoms in the polar head can represent a good indicator, as a first approximation, the number of sugar residues can also be analyzed. For acyclic polar heads, the number of CHOH units is also a good parameter to characterize the size of the polar head.

At first, increasing the size of the polar head, directly related to the number of sugar units, tends to slightly increase the CMC (cf. Supporting Information, Table S1) [84, 85]. The impact is lower than in the case of alkyl chain length. Indeed, doubling the alkyl chain length would have a much larger impact on CMC than adding one sugar unit to a glucoside surfactant. This trend was expected from the available literature [30, 86] indicating that, in general, oligosaccharidic heads should perturb micelle formation due to sterical hindrance and higher hydrophilicity, and therefore, lead to larger CMC. QSPR analyses were also in agreement with this trend [23]. Indeed, different descriptors directly related to the size of the polar head for sugar-based surfactants (*e.g.* the number of oxygen atoms or the number of rings) were included in the developed models with a positive contribution to log CMC (*i.e.* increasing CMC). However, in some cases (3,7-dimethyloctyl-β-D-glycosides and octyl-β-D-glycosides in Supporting Information, Table S1), polar head size (here in terms of number of sugar residues) does not noticeably impact CMC [80, 87]. This was already observed by Bogdan et al. [13] (comparing three *N*-alkyl-*N*-methyl aldonamides) and Marchant et al. [19] (comparing two *N*-alkyl aldonamides). It can be noticed that, in one study [88], a slight decrease of CMC was even observed with addition of one sugar unit, with 70 mM for *N*-octanoyl-β-D-glucosylamine and 55 mM for *N*-octanoyl-β-D-maltosylamine. These observations suggest that the impact of the number of saccharidic residues of the polar head on micelle formation is more complex than increasing sterical hindrance or hydrophilicity. Indeed, oligosaccharidic polar heads may, in some cases, adopt a favorable shape for packing in the micelle to compensate additional sterical hindrance. Moreover, head-head interactions (notably through H-bonding) may balance the higher hydrophilicity in some cases when it comes to micelle formation. Theoretical studies (*e.g.* using molecular dynamics) comparing sugar-based surfactants with gradual increase of polar head size (notably in terms of number of sugar residues) could be of interest to elucidate the particular cases in the polar head to CMC trend for sugar-based surfactants.

Secondly, collected data [33, 44, 50, 60, 62, 64, 80, 85, 89] (cf. Supporting Information, Table S1) revealed an increase of γ_{CMC} with the number of sugar residues in the polar head, as shown in Figure 7. This trend is in agreement with general knowledge about surfactants [8, 30] and sugar-based surfactants in particular [19]. Besides, QSPR models for γ_{CMC} of sugar-based surfactants [24] also evidenced a dominant impact of polar head size on this property. Indeed, the most significant descriptor of all developed models was related to the polar head size (e.g. the number of H atoms in the polar head). Moreover, it always appeared with a positive coefficient.

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As proposed by Rosen [30], this trend can be related to sterical hindrance issues. If polar head size is increased, sugar residues should occupy a larger area at the surface. Thus, the proportion of the surface covered with alkyl chains is lower because it is limited by the occupied area of the polar head.

Like γ_{CMC}, pC_{20} of sugar-based surfactants increased with polar head degree of polymerization (DP) (cf. Supporting Information, Table S1). Adding a sugar residue in the polar head usually results in an efficiency loss of about 0.2-0.3 log units. This is also confirmed by QSPR analyses [25]. Indeed, this polar head size effect was included in the final model through the number of rings in the polar head, with a negative coefficient of 0.2 log unit per ring. Again, this may be due to steric hindrance, which unfavors the adsorption at air/water interface. Larger polar heads will be hindered by other polar heads in the adsorption process, resulting in a lower free energy gain ΔG_{ads}, and thus a lower pC_{20}.

No systematic trend was evidenced between polar head size and T_K and the analysis of the effect of this structural parameter from the available experimental data. The examples presented in Supporting Information (Table S1) and Figure 8 illustrate the complexity of the relationship between polar head size and T_K. For polar heads containing cyclic residues, by adding a galactose residue to octyl-β-D-glucoside, T_K increases from below 0°C to 43°C [87]. But adding a glucose residue to dodecyl-β-D-glucoside leads to a T_K decrease from 38°C [90] to below 25°C [91]. For acyclic polar heads, adding one CHOH unit to decyl-1-amino-1-deoxy-D-xylitol, T_K increases from 37°C to 83°C [71], but in the case of N-decyl-N-(2-hydroxyethyl)gluconamide, T_K decreases from 58°C [72] to 52°C [92] through CHOH addition. So, from such qualitative analysis, no systematic trend can be stated neither on the number of sugar units nor on the number of CHOH fragments in acyclic sugar heads. However, quantitative analysis of 152 sugar-based surfactants in QSPR models suggested that increasing polar head size more probably leads to a T_K decrease than to a T_K increase [26].

This complex relationship emphasizes the crucial role of crystal packing to determine T_K of sugar-based surfactants, and therefore the large impact of molecular shape and specific hydrogen-bonding interactions on it [71].

4.2.2   Sugar stereochemistry

Sugar-based surfactants can be distinguished by their stereochemistry. Indeed, carbohydrates are chiral polyols, *i.e* they are constituted by multiple stereogenic centers bearing alcohol function. The configuration of these asymmetric carbons characterizes the carbohydrate nature (glucose, galactose, etc., cf. Figure 9). Moreover, it drives the orientation of the alcohols functions which influences the global shape of the sugar residues in the sugar-based surfactants and their interaction at interfaces and in micelles. There were some data in literature to investigate this structural parameter (in Table 3, with

all corresponding structures displayed in Figure 9), though mostly through binary comparisons. Among these 11 pairs and single triplet of analogues, CMC and γ_{CMC} appear to be only weakly affected by stereochemistry of polar head. At short alkyl chain lengths, CMC is slightly lower for α-D-mannosides than for α-D-galactosides, whereas substitution of galactose polar head by another sugar head seems to either increase or decrease γ_{CMC}: heptyl α-D-mannoside has a lower γ_{CMC} than heptyl α-D-galactoside and heptyl β-D-glucoside has a lower γ_{CMC} than heptyl β-D-galactoside whereas *N*-octyl-D-glucuronamide presents a γ_{CMC} somewhat larger than *N*-octyl-D-galacturonamide.

FIGURE 9 HERE

TABLE 3 HERE

T_K is impacted by the stereochemistry of the sugar used as polar head [71], though the low number of available data does not allow to reveal robust systematic trends. Nevertheless, a lower solubility is observed for galactose-based surfactants [42] compared to glucose-based ones [49]. The same trend is known for the corresponding sugars [93], galactose being less water soluble than glucose. This could suggest that the solubility of a sugar-based surfactant could be anticipated from the solubility of the sugar used as its polar head, as already proposed by Laughlin et al. [12].

4.2.3 Anomeric configuration of the sugar

The configuration of the anomeric carbon was mentioned as an important parameter for surfactant properties of alkyl glycosides [17, 55]. Indeed, in the collected data, the anomeric configuration of the carbohydrate shows a significant influence on T_K (Table 4). Alkyl glucosides with α anomeric carbon demonstrate higher T_K than β analogues (for dodecyl-α/β-D-maltoside and dodecyltriazole-α/β-D-glucoside, the available data are not detailed enough to analyze this trend). However, alkyl galactosides with α anomeric carbon demonstrate lower T_K than β analogues. Packing may explain such phenomenon. For alkyl glucosides, Dorset et al. [94] proposed that α configuration enables a better packing between alkyl chains and polar heads and therefore seems to favor intermolecular interactions between α-anomers, leading to increased T_K.

TABLE 4 HERE

It seems that CMC is only weakly affected by anomeric carbon configuration in most cases (like for dodecyltriazole α/β-D-glucoside, ethylhexyl α/β-D-glucoside, dodecyl α/β-D-maltoside and octyl α/β-D-galactoside). In the case of octyl-α/β-D-glucoside though, α anomer seems to decrease CMC. Heptyl β-D-galactoside has an unusually low CMC, but it is out of the expected linear trend in log and therefore the difference with heptyl α-D-galactoside may be due to experimental uncertainty. For the only two γ_{CMC} comparisons pairs available (heptyl-α/β-D-galactoside and octyl-α/β-D-galactoside), there is also no significant impact of anomeric carbon configuration. Anomeric carbon configuration may have only low impact in the sterical hindrance in micelle or at the surface, thus generally not

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impacting CMC and γ_{CMC}. To the end, pC_{20} is higher for alkyl-β-D-galactosides than for alkyl-α-D-galactosides, but similar for octyl-α/β-D-glucoside.

4.2.4   Nature of the linker

Another important feature of the polar head is the functional group in contact with the alkyl chain, called "linker". The linker is generally used to bond the alkyl chain to the polar head during surfactant synthesis. Its influence on amphiphilic properties (mainly T_K) was already discussed in previous reviews [12, 13, 19, 55].

The most common linkers identified for sugar-based surfactants are ether –O–, thioether –S–, ester –(C=O)-O–, amide –(C=O)-NH– and N-methylamide –(C=O)-(NCH₃)–. Since the ether linker is the most frequent in the database and is present in the well-studied family of alkyl glycosides, it is used as a reference for comparisons in this review.

During our QSPR analysis on CMC [23], surfactants with a thioether linker were identified to have lower CMC than equivalent surfactants with an ether linker. This trend is confirmed by Table 5 and can be explained by the fact that thioether is more hydrophobic than ether [55]. Table 5 also suggests that replacing ether linker by an ester yields lower CMCs. In particular, since 3-*O*-octanoyl-D-glucose has one CH_2 less than 3-*O*-octyl-D-glucose (cf. Figure 10), one would expect a lower CMC and reported data show opposite trend. Thus, it seems that replacing an ether linker by an ester one leads to a more hydrophobic surfactant in this case.

TABLE 5 HERE

FIGURE 10 HERE

Quantum chemical calculations carried out in previous works [23, 95] support both findings. Indeed, the first CH_2 presented a positive partial charge in the case of an ether linker (cf. Figure 11), and almost no charge in the case of a thioether linker or an ester linker. The charge observed on the CH_2 when attached to an oxygen is in line with the approach of Puvvada & Blankschtein [86] that predicts micellization of surfactants with ether linkers considering the first CH_2 as part of the polar head rather than the alkyl chain. This approach may not be valid for thioether or ester linker.

FIGURE 11 HERE

A comparison between alkyl β-D-glucosides and alkyl β-D-thioglucosides (cf. Table 5) suggests that thioether linker leads to lower γ_{CMC} and pC_{20} for short alkyl chain length but that this difference becomes negligible for both properties starting from 8-9 C atoms in the alkyl chain. In the case of γ_{CMC}, this may be due to a lower overall polarity which leads to a better saturation of the interface at CMC for low alkyl chain lengths.

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Regarding pC_{20}, previous QSPR analysis confirms its increase with thioether linker [25]. Since higher efficiency is related to higher hydrophobicity [65], this effect is consistent with the increased hydrophobicity of thioether linker with respect to ether linker. A correlation between pC_{20} and log CMC was also evidenced in the QSPR study [25]. This indicates that the partial charge analysis results for log CMC (Figure 11), supporting the lower partial charge of the first CH_2 of the alkyl chain as lowering log CMC of thioglycoside compounds, may also explain the higher pC_{20} for these compounds.

T_K seems to be particularly impacted by the nature of the linker. As seen in Figure 4, surfactants with thioether linker present higher T_K than analogous surfactants with ether linker. To confirm this trend, systematic measurements of T_K for series of alkyl-β-D-thioglucosides and alkyl-β-D-glucosides may be of interest. Increased Van der Waals interactions in the solid phase may explain the decreased solubility of thioglycoside surfactants, as the atomic radius is higher for the S atom than for the O atom.

TABLE 6 HERE

Bogdan et al. [13] proposed that *N*-methyl-amide-linked surfactants are particularly water-soluble. The data collected in the database are in agreement with this statement. Surfactants with *N*-methyl-amide linker have lower T_K than surfactants with amide linker. Some authors also argued that the introduction of a methyl on the amide linker constrains the crystal packing of sugar-based surfactants [71], and increases water solubility, in agreement with our observations. The observed effect may also be related to the ability of the amide group to be both H-bond acceptor and H-bond donor, favoring crystallization, whereas *N*-methyl-amide group can only be H-bond acceptor [73].

4.3   *Comparison of structure-property trends of conventional and sugar-based surfactants*

To place the analysis of amphiphilic properties of sugar-based surfactants into a broader context, we compared literature values of CMC, γ_{CMC} and pC_{20} of two common sugar-based surfactant homologous series, alkyl-β-D-glucosides [49, 90] and alkyl-β-D-maltosides [49, 64, 96], with conventional nonionic surfactants having polar heads of similar size, alkyl tetraethoxylates (C_nE_4) [30, 97, 98] and alkyl octaethoxylates (C_nE_8) [99, 100], respectively. Both alkyl-β-D-glucosides and C_nE_4 have 12 non-H atoms in their polar heads, and both alkyl-β-D-maltosides and C_nE_8 have 24 non-H atoms in their polar heads, which lead to polar heads of overall similar size. However, sugar heads are expected to be more polar due to their ability to form hydrogen bonds.

As can be seen from Figure 12, for a given alkyl chain length, sugar-based surfactants have a somewhat higher CMC (equivalent to about 1 C less in the alkyl chain), a similar γ_{CMC}, and a lower pC_{20} (equivalent to about 2 C less in the alkyl chain). γ_{CMC} is ≈7 mN/m higher for alkyl-β-D-maltosides and C_nE_8. So, overall, ethoxylated surfactants tend to be more surface active and form micelles a bit more easily than sugar-based surfactants, probably due to polar heads with a lower

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polarity, but the effectiveness of their surface adsorption is similar. More generally, this comparison indicates that polarity of polar head is more important to influence CMC and pC_{20}, whereas the size of the polar head impacts more γ_{CMC} than its polarity.

FIGURE 12 HERE

But the key difference between sugar-based surfactants pertains to their different abilities to dissolve in water. While ethoxylated surfactants tend to dissociate from water at higher temperatures into one micelle-rich phase and one water-rich phase (the critical temperature being called cloud point) [30], sugar-based surfactants exhibit T_K, which lead to precipitation due to temperature decrease before reaching maximum surface activity, and only seldomly exhibit cloud points [4].

Here again, differences in hydrogen bonding probably explain the qualitative difference between the two surfactant families. Compared to sugar-based surfactants which both accept and donate hydrogen bonds in water, ethoxylated surfactants can only accept hydrogen bonds from water, leading to an easier water-surfactant hydrogen bond breaking at higher temperature, which is the major cause of the phase separation occurring at cloud point [5]. Moreover, the high melting points of sugar-based surfactants (compared to ethoxylated surfactants, which are often liquid at ambient temperature [5]) is probably caused by their ability to both accept and donate hydrogen bonds to each other, thus forming strong crystals, even at ambient temperature. Without such a solid state, thermodynamically, T_K cannot be observed above 0°C, i. e. at temperatures in which water is in the liquid state [71].

Conclusion

This work attempted to extract structure-property trends from a large collection of amphiphilic properties of sugar-based surfactants. Four amphiphilic properties (critical micelle concentration, surface tension at critical micelle concentration, efficiency and Krafft temperature), having both fundamental and practical interest, were considered. The impact of the size, branching and unsaturation of the alkyl chain, as well as the size and stereochemistry of the polar head and the nature of the linker between both moieties on these four properties was examined for conventional sugar-based surfactants (*i.e.* with one polar head and one alkyl chain). If further data would be beneficial to cover more widely the diversity of parameters defining sugar-based surfactants and to analyze deeper identified structural trends, numerous structure-property trends (summarized in Table 7) were already proposed for sugar-based surfactants and open perspectives to guide the finding of renewable surfactant alternatives to petroleum-based ones.

TABLE 7 HERE

Some structure-property trends were found in line with experimental knowledge for other surfactants, especially concerning the alkyl chain. For example, CMC is decreased when increasing alkyl chain

length and increased by unsaturation or branching of alkyl chains, and γ_{CMC} is generally larger for oligosaccharidic polar heads.

Nevertheless, sugar-based surfactants present specific features that imply specific structural trends, in particular on the polar head. For example, CMC does not always increase with polar head degree of polymerization, in contrast to polyoxyethylene surfactants. Moreover, hydrophilicity of sugar-based surfactants was not always linked to their ability to dissolve in water, since sometimes surfactants with larger polar heads (more hydrophilic) had higher T_K than surfactants with smaller polar heads (either measured by number of CHOH or number of sugar residues). Regarding this point, the primary role of molecular packing in solid phase in interpretation of T_K values appeared in several of the analyzed structure-property relationships, showing that anticipating such property is challenging since molecular packing in solid phase is difficult to predict from chemical structure. As a result, it can be impossible to find consistent trends for a given molecular parameter across several structures. For example, glucoside α-anomers revealed less soluble than β-anomers whereas the opposite revealed true for galactoside β-anomers.

The chemical nature of the linker of sugar-based surfactants clearly impacts surfactant properties, though there was limited available comparable data. For example, surfactants with thioether linkers were found to have lower CMC and to be less soluble than their analogues with ether linkers. Surfactants with methyl amide linkers revealed more soluble than comparable surfactants with free amide linkers.

Interestingly, most of the trends identified here were in line with those encountered into the QSPR models recently developed for the amphiphilic properties of sugar-based surfactants, like the impact of polar head size on all studied properties or the impact of the linker on log CMC and pC_{20}.

When compared with ethoxylated surfactants of equal alkyl chain length and similar polar head size, sugar-based surfactants tend to exhibit higher CMC (equivalent to about 1C atom less in alkyl chain), similar γ_{CMC} and lower pC_{20} (equivalent to about 2C atoms less in alkyl chain). Moreover, sugar-based surfactants tend to exhibit dissolution issues at lower temperatures whereas ethoxylated surfactants tend to exhibit phase separation at higher temperatures.

This study provides a complete overview about the main structure-property trends of sugar-based surfactants, and shows that every amphiphilic property significantly depends on several different structural features of sugar-based surfactants. Besides, here again, this statement is in agreement with QSPR models that combine the consideration of different affecting parameters.

It can be noticed that two important amphiphilic properties could not be analyzed in the context of this study, the minimal area at interface (A_{min}) and the cloud point. Uncertainty of the available A_{min} values appeared too high, preventing meaningful structure-property trends to be extracted from the data.

Regarding cloud point, too few data were available despite the property being measurable for some sugar-based surfactants. Moreover, in the future, it would be of interest to build a database of characteristic curvatures and lengths for sugar-based surfactants as in the context of HLD-NAC theory, since these properties are of more direct interest for the relevant field of industrial formulation. A similar analysis as that in the present study would extract trends for these properties as well.

This review also encourages further systematic experimental studies, in particular focused on some specific structural features, such as stereochemistry of sugars used as polar head or directly comparable linkers, or on other amphiphilic properties, such as A_{min} or the cloud point. Of course, this data analysis may be also extended to other types of surfactants, such as gemini surfactants, or to other families such as peptide-based surfactants.

Finally, although this review focused on properties in diluted solution, the behaviour of finite concentrations of sugar-based surfactants are also of interest, particularly since liquid crystals formation can be important in a number of applications. Therefore, it would be relevant, in future works, to make a systematic comparison of the phase diagrams of sugar-based surfactants.

Acknowledgements

References

[1] A. Fahim M, A. Al-Sahhaf T, Elkilani A. Fundamentals of Petroleum Refining. Oxford: Elsevier; 2010.

[2] Ghosh TK, Prelas MA. Fundamental and Non-Renewable Resources. New York City: Springer; 2009.

[3] Demirbas A. Biorefineries, for biomass upgrading facilities. London: Springer; 2010.

[4] Ruiz CC. Sugar-Based Surfactants: Fundamentals and Applications. Boca Raton: CRC Press; 2009.

[5] Myers D. Surfactant Science and Technology. 3rd ed. Hoboken: John Wiley & Sons; 2006.

[6] Rojas OJ, Stubenrauch C, Lucia LA, Habibi Y. Interfacial Properties of Sugar-Based Surfactants. In: Hayes D, Kitamoto D, Solaiman D, Ashby R, (editors). Biobased Surfactants and Detergents: Synthesis, Properties, and Applications. Urbana: AOCS Press; 2009. p. 457.

[7] Dembitsky V, Lipids, 2004;39:933.

[8] Esumi K, Ueno M. Structure-Performance Relationships in Surfactants. 2nd ed. Boca Raton: CRC Press; 2003.

[9] Gaudin T. Développement de modèles QSPR pour la prédiction et la compréhension des propriétés amphiphiles des tensioactifs dérivés de sucre: Ph. D. thesis, Université de Technologie de Compiègne; 2016.

[10] Hill K, von Rybinski W, Stoll G. Alkyl Polyglycosides: Technology, Properties and Applications. Hoboken: John Wiley & Sons; 1997.

[11] Rybinski WV, Hill K. Alkyl Polyglycosides. In: Holmberg K, (editor). Novel Surfactants. Boca Raton: CRC Press; 2003. p. 35.

[12] Laughlin RG, Scheibel JJ, Fu YC, Wireko FC, Munyon RL. N-Alkanoyl-N-Alkyl-1-Glycamines. In: Holmberg K, (editor). Novel Surfactants. Boca Raton: CRC Press; 2003. p. 1.

[13] Burczyk B. Novel Saccharide-Based Surfactants. In: Holmberg K, (editor). Novel Surfactants. Boca Raton: CRC Press; 2003. p. 129.

[14] Hill K. Surfactants Based on Carbohydrates and Proteins for Consumer Products and Technical Applications. Surfactants from Renewable Resources. Hoboken: John Wiley & Sons; 2010. p. 63.

[15] Develter DWG, Fleurackers SJJ. Sophorolipids and Rhamnolipids. Surfactants from Renewable Resources. Hoboken: John Wiley & Sons; 2010. p. 213.

[16] Infante M, Pinazo A, Seguer J, Colloids Surf, A, 1997;123–124:49.

[17] Stubenrauch C, Curr Opin Colloid Interface Sci, 2001;6:160.

[18] Hato M, Minamikawa H, Tamada K, Baba T, Tanabe Y, Adv Colloid Interface Sci, 1999;80:233.

[19] Marchant RE, Anderson EH, Zhu J. Polysaccharide Surfactants: Structure, Synthesis, and Surface-Active Properties. In: Dimitriu S, (editor). Polysaccharides, Structural Diversity and Functional Versatility. 2nd ed: Marcel Dekker; 2005. Chapter 45. p. 1055.

[20] Nickel D, Förster T, Rybinski WV. Physicochemical Properties of Alkyl Polyglycosides. Alkyl Polyglycosides: Wiley-VCH Verlag GmbH; 2008. p. 39.

[21] Razafindralambo H, Blecker C, Paquot M. 8. Carbohydrate-Based Surfactants: Structure-Activity Relationships. In: Nawaz Z, (editor). Advances in Chemical Engineering 2012.

[22] Acosta E, Szekeres E, Sabatini DA, Harwell JH, Langmuir, 2003;19:186.

[23] Gaudin T, Rotureau P, Pezron I, Fayet G, Ind Eng Chem Res, 2016;55:11716.

[24] Gaudin T, Rotureau P, Pezron I, Fayet G, J Colloid Interface Sci, 2018;516:162.

[25] Gaudin T, Rotureau P, Pezron I, Fayet G, IJQSPR, 2019;4:29.

[26] Gaudin T, Fayet G, Rotureau P, Pezron I, J Surfactants Deterg, 2018;21:835.

[27] Mukerjee P, Mysels KJ. Critical Micelle Concentrations of Aqueous Surfactant Systems. Washington: National Standard Reference Data System; 1971.

[28] Rangel-Yagui CO, Pessoa-Jr A, Tavares LC, J Pharm Pharm Sci, 2005;8:147.

[29] Arachea BT, Sun Z, Potente N, Malik R, Isailovic D, Viola RE, Protein Expr Purif, 2012;86:12.

[30] Rosen MJ, Kunjappu JT. Surfactants and Interfacial Phenomena. 4th ed. Hoboken: John Wiley & Sons; 2012.

[31] Egorova KS, Toukach PV, J Chem Inf Model, 2012;52:2812.

[32] Lorber B, Bishop JB, DeLucas LJ, BBA - Biomembranes, 1990;1023:254.

[33] Matsumura S, Imai K, Yoshikawa S, Kawada K, Uchibor T, J Am Oil Chem Soc, 1990;67:996.

[34] Shinoda K, Yamaguchi T, Hori R, Bull Chem Soc Jap, 1961;34:237.

[35] Syper L, Wilk KA, Sokołowski A, Burczyk B. Synthesis and surface properties of N-alkylaldonamides. In: Koper GJM, Bedeaux D, Cavaco C, Sager WFC, (editors). Trends in Colloid and Interface Science XII. Vol. 110: Steinkopff 1998. Chapter 41. p. 199.

[36] Arai T, Takasugi K, Esumi K, Colloids Surf, A, 1996;119:81.

[37] Savelli MP, Van Roekeghem P, Douillet O, Cavé G, Godé P, Ronco G, et al., Int J Pharm, 1999;182:221.

[38] Sani FA, Heidelberg T, Hashim R, Farhanullah, Colloids Surf, B, 2012;97:196.

[39] Boullanger P, Chevalier Y, Langmuir, 1996;12:1771.

[40] Lu H, Drelich A, Omri M, Pezron I, Wadouachi A, Pourceau G, Molecules, 2016;21:1301.

[41] Chen G, Li Z, Chen L, Ji S, Shen W, J Disp Sci Technol, 2017;38:506.

[42] Chen G, Li Z, Chen L, Ji S, Shen W, J Surfactants Deterg, 2016;19:1095.

[43] Ji S, Shen W, Chen L, Zhang Y, Wu X, J Mol Liq, 2017;242:1169.

[44] Ji S, Shen W, Chen L, Zhang Y, Wu X, Fan Y, et al., Colloids Surf, A, 2019;564:59.

[45] Shen W, Ji S, Chen L, Zhang Y, Wu X, J Surfactants Deterg, 2018;21:255.

[46] Sun Y-E, Xia W, Tang X, He Z, Chen J, Front Chem Eng China, 2009;3:407.

[47] Wu X, Chen L, Fu F, Fan Y, Luo Z, J Mol Liq, 2019;276:282.

[48] Zhang Y, Chen L, Wu X, J Mol Liq, 2018;269:947.

[49] Lu H. Etude des relations structure-propriétés de molécules amphiphiles issues des agro-ressources: Université de Technologie de Compiègne; 2016.

[50] Varga I, Mészáros R, Stubenrauch C, Gilányi T, J Colloid Interface Sci, 2012;379:78.

[51] Lu H, Drelich A, Omri M, Pezron I, Wadouachi A, Pourceau G, Molecules, 2016;21:1301.

[52] Tanford C, Proc Natl Acad Sci, 1979;76:4175.

[53] Soultani S, Ognier S, Engasser J-M, Ghoul M, Colloids Surf, A, 2003;227:35.

[54] Castro ML, Cirelli A, Kovensky J, J Surfactants Deterg, 2006;9:279.

[55] A. Molina Bolívar J, Ruiz CC. 3. Self-Assembly and Micellar Structures of Sugar-Based Surfactants: Effect of Temperature and Salt Addition. In: Ruiz CC, (editor). Sugar-Based Surfactants: Fundamentals and Applications. Boca Raton: CRC Press; 2009.

[56] Ueno M, Takasawa Y, Miyashige H, Tabata Y, Meguro K, Colloid Polym Sci, 1981;259:761.

[57] Zhang T, Marchant RE, J Colloid Interface Sci, 1996;177:419.

[58] Hutchinson E, Sheaffer VE, Tokiwa F, J Phys Chem, 1964;68:2818.

[59] Dupuy C, Auvray X, Petipas C, Rico-Lattes I, Lattes A, Langmuir, 1997;13:3965.

[60] Burczyk B, Wilk KA, Sokołowski A, Syper L, J Colloid Interface Sci, 2001;240:552.

[61] Pestman JM. Carbohydrate-derived surfactants containing an N-Acylated amine functionality : fundamental aspects and practical applications: University of Groningen; 1998.

[62] Kegel LL, Szabó LZ, Polt R, Pemberton JE, Green Chem, 2016;18:4446.

[63] Handbook of Chemistry and Physics. Internet Version ed. Boca Raton: CRC Press; 2005.

[64] Drummond CJ, Warr GG, Grieser F, Ninham BW, Evans DF, J Phys Chem, 1985;89:2103.

[65] Rosen MJ, J Am Oil Chem Soc, 1974;51:461.

[66] Ferrer M, Comelles F, Plou FJ, Cruces MA, Fuentes G, Parra JL, et al., Langmuir, 2002;18:667.

[67] Rosen MJ, J Colloid Interface Sci, 1976;56:320.

[68] Holmberg K. Novel Surfactants. Boca Raton: CRC Press; 2003.

[69] McLeish TCB, Adv Phys, 2002;51:1379.

[70] Straathof AJJ, Van Bekkum H, Kieboom APG, Starch - Stärke, 1988;40:438.

[71] Van Doren HA. Tailor-made carbohydrate surfactants? Systematic investigations into structure-property relationships of N-Acyl N-Alkyl 1-Amino-1-Deoxy-D-Glucitols. Carbohydrates as Organic Raw Materials III. Hoboken: John Wiley & Sons; 2007. p. 255.

[72] Zhu Y-P, Rosen MJ, Vinson PK, Morrall SW, J Surfactants Deterg, 1999;2:357.

[73] Anslyn EV, Dougherty DA. Modern Physical Organic Chemistry: University Science Books; 2006.

[74] Moroi Y. Relationship between solubility and micellization of surfactants: The temperature range of micellization. In: Hummel K, Schurz J, (editors). Dispersed Systems. Vol. 77: Steinkopff; 1988. Chapter 6. p. 55.

[75] Tsujii K. Thermodynamic Studies on the Krafft point in Aqueous Surfactant Systems: Osaka University; 1987.

[76] Shinoda K, Tamamishi B-I, Nakagawa T, Isemura T. Colloidal Surfactants - Some physicochemical properties: Academic Press; 1963.
[77] Price SL, Chem Soc Rev, 2014;43:2098.
[78] Matsumura S, Imai K, Yoshikawa S, Kawada K, Uchibori T, J Jpn Oil Chem Soc, 1991;40:709.
[79] Nilsson F, Söderman O, Johansson I, J Colloid Interface Sci, 1998;203:131.
[80] Minamikawa H, Hato M, Chem Phys Lipids, 2005;134:151.
[81] Sierra ML, Svensson M, Langmuir, 1999;15:2301.
[82] Satgé C, Granet R, Verneuil B, Champavier Y, Krausz P, Carbohydr Res, 2004;339:1243.
[83] Nettleton JA. Omega-3 fatty acids and health. New York City: Springer; 1995.
[84] Milkereit G, Garamus VM, Veermans K, Willumeit R, Vill V, J Colloid Interface Sci, 2005;284:704.
[85] Söderberg I, Drummond CJ, Neil Furlong D, Godkin S, Matthews B, Colloids Surf, A, 1995;102:91.
[86] Puvvada S, Blankschtein D, J Chem Phys, 1990;92:3710.
[87] Vanaken T, Foxall-Vanaken S, Castleman S, Ferguson-Miller S. Alkyl glycoside detergents: Synthesis and applications to the study of membrane proteins. In: Sidney Fleischer BF, (editor). Methods Enzymol. Vol. 125: Academic Press; 1986. p. 27.
[88] Lu B, Vayssade M, Miao Y, Chagnault V, Grand E, Wadouachi A, et al., Colloids Surf, B, 2016;145:79.
[89] Smułek W, Kaczorek E, Hricovíniová Z, J Surfactants Deterg, 2017;20:1269.
[90] Lu H, Pezron I, Gaudin T, Drelich A, Colloids Surf, A, 2018;540:167.
[91] De Grip WJ, Bovee-Geurts PHM, Chem Phys Lipids, 1979;23:321.
[92] Piasecki A, Pilakowska-Pietras D, J Surfactants Deterg, 2007;10:125.
[93] Linhardt R, Bazin H. Properties of Carbohydrates. In: Fraser-Reid B, Tatsuta K, Thiem J, (editors). Glycoscience: Chemistry and Chemical Biology I–III. New York City: Springer; 2001. Chapter 2. p. 53.
[94] Dorset DL, Rosenbusch JP, Chem Phys Lipids, 1981;29:299.
[95] Gaudin T, Rotureau P, Pezron I, Fayet G, Comp Theor Chem, 2017;1101:20.
[96] Niraula BB, Chun TK, Othman H, Misran M, Colloids Surf, A, 2004;248:157.
[97] Matsubara H, Ohta A, Kameda M, Ikeda N, Aratono M, Langmuir, 2000;16:7589.
[98] García Rey N, Weißenborn E, Schulze-Zachau F, Gochev G, Braunschweig B, J Phys Chem C, 2019;123:1279.
[99] Meguro K, Ueno M, Esumi K. Micelle Formation in Aqueous Media. In: Schick MJ, (editor). Nonionic Surfactants: Physical Chemistry. Boca Raton: CRC Press; 1987. Chapter 3. p. 109.
[100] Berthod A, Tomer S, Dorsey JG, Talanta, 2001;55:69.
[101] Salkar RA, Minamikawa H, Hato M, Chem Phys Lipids, 2004;127:65.
[102] Razafindralambo H, Blecker C, Paquot M. 4. Screening of Basic Properties of Amphiphilic Molecular Structures for Colloidal System Formation and Stability. Amphiphiles: Molecular Assembly and Applications. Vol. 1070: American Chemical Society; 2011. Chapter 4. p. 53.
[103] Hato M, Curr Opin Colloid Interface Sci, 2001;6:268.
[104] Persson CM, Kjellin URM, Eriksson JC, Langmuir, 2003;19:8152.
[105] Biochemistry - Detergents and Bio-Tensides. In: Biomol. p. 46.
[106] Izawa S, Sakai-Tomita Y, Kinomura K, Kitazawa S, Tsuda M, Tsuchiya T, J Biochem, 1993;113:573.
[107] Scorzza C, Godé P, Goethals G, Martin P, Miñana-Pérez M, Salager JL, et al., J Surfactants Deterg, 2002;5:337.
[108] Goethals G, Fernández A, Martin P, Miñana-Pérez M, Scorza C, Villa P, et al., Carbohydr Polym, 2001;45:147.

Tables

Table 1. Comparison of T_K for two surfactants containing branched or linear alkyl chains

surfactant	T_K (°C)	reference
decyl-β-D-glucoside (C10 chain)	26	[101]
3,7-dimethyloctyl-β-D-glucoside (branched C10 chain)	<0	[101]
octyl-α-D-glucoside (C8 chain)	38	[79]
2-ethylhexyl-α-D-glucoside (branched C8 chain)	52	[79]

Table 2. Impact of the unsaturation of the alkyl chain on the various considered amphiphilic properties.

surfactant	n_{Unsat}	CMC (mM)	γ_{CMC} (mN/m)	T_K (°C)	reference
undecyl-α-D-galactoside	0	0.45[1][2]	27.4[1][2]	76	[82]
undecenyl-α-D-galactoside	1	1.66[1][2]	26.8[1][2]	64	[82]
undecyl-β-D-galactoside	0	0.80[1]	27.2[1]	46	[82]
undecenyl-β-D-galactoside	1	3.70[1]	29.0[1]	32	[82]
N-octadecyl-N-methyl–D-lactobionamide	0	0.0033	32.3	<20	[60]
N-oleyl-N-methyl-D-lactobionamide	1	0.0538	34	<0	[60]
N-octadecyl-N-methyl-D-gluconamide	0	0.00285[2]	32.3[2]	49	[60]
N-oleyl-N-methyl-D-gluconamide	1	0.0322	34	<20	[60]
octadecyltriazole-β-D-glucoside	0			64	[38]
oleyltriazole-β-D-glucoside	1			<10	[38]
6-O-oleoyltrehalose	1	0.28[3]			[46]
6-O-linoleoyltrehalose	2	0.36[3]			[46]
6-O-linolenoyltrehalose	3	0.58[3]			[46]

(1) data were measured at 45°C; (2) care has to be taken since these data were measured below Krafft temperature of surfactant; (3) data were measured at 40°C.

Table 3. Impact of the stereochemistry of the sugar on critical micelle concentration and surface tension at CMC.

surfactant	CMC (mM)	γ_{CMC} (mN/m)	pC_{20}	T_K (°C)	ref
heptyl-α-D-galactoside	32.5	39.2	1.8		[41]
heptyl-α-D-mannoside	30.6	31.8	2.3		[48]
octyl-α-D-glucoside				39	[49]
octyl-α-D-galactoside	18.9	32.4	2.3	<25	[41]
octyl-α-D-mannoside	11.7	30.7	2.7	<25	[48]
nonyl-α-D-galactoside	5.2	32.0	2.8		[41]
nonyl-α-D-mannoside	4.0	30.7	3.0		[48]
decyl-α-D-galactoside				<25	[41]
decyl-α-D-mannoside				>25	[48]
dodecyl-α-D-galactoside				>25	[41]
dodecyl-α-D-mannoside				>25	[48]
heptyl-β-D-glucoside	72.3	36.4	2.0		[49]
heptyl-β-D-galactoside	17.5	39	2.2		[42]
octyl-β-D-glucoside	21.2	31	2.7		[49]
octyl-β-D-galactoside	16.2	31	2.6		[42]
N-octyl-D-glucuronamide	3.3	24.4			[102]
N-octyl-D-galacturonamide	4.0	20.5			[102]
nonyl-β-D-glucoside			3.2	<25	[49]
nonyl-β-D-galactoside			3.3	>25	[42]
decyl-β-D-glucoside			3.8	<25	[49]
decyl-β-D-galactoside			3.9	>25	[42]
undecyl-β-D-glucoside				≈25	[91]
undecyl-β-D-galactoside				46	[82]
1-amino-N-decyl-1-deoxy-D-xylitol				37	[71]
1-amino-N-decyl-1-deoxy-D-lyxitol				57	[71]
1-amino-N-decyl-1-deoxy-D-ribitol				34	[71]
1-amino-N-decyl-1-deoxy-D-arabinitol				98	[71]

Table 4. Impact of the anomeric configuration of the sugar on the amphiphilic properties of sugar-based surfactants.
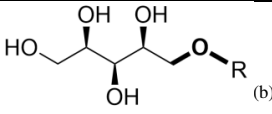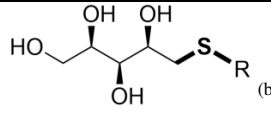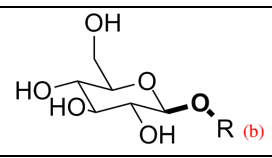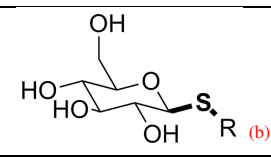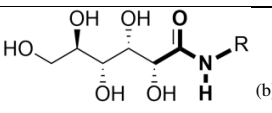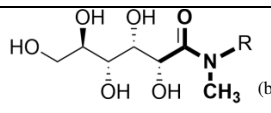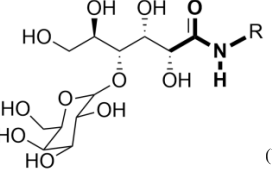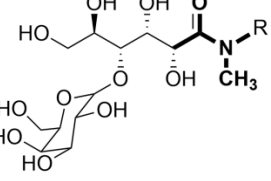
surfactant	CMC (mM)	γ_{CMC} (mN/m)	pC_{20}	T_K (°C)	ref
heptyl-α-D-glucoside	-	-	-	42	[103]
heptyl-β-D-glucoside	-	-	-	<0	[103]
octyl-α-D-glucoside	9.4[(2)]	-	2.8	40	[49, 70]
octyl-β-D-glucoside	21[(2)]	-	2.7	<0	[49, 70, 87]
2-ethylhexyl-α-D-glucoside	44[(1)]	-	-	52	[79]
2-ethylhexyl-β-D-glucoside	48[(1)]	-	-	<10	[79]
nonyl-α-D-glucoside	-	-	-	46	[103]
nonyl-β-D-glucoside	-	-	-	23	[103]
undecyl-α-D-glucoside	-	-	-	55	[103]
undecyl-β-D-glucoside	-	-	-	36	[103]
heptyl-α-D-galactoside	32.5	39.2	1.8	<25	[41]
heptyl-β-D-galactoside	17.5	39.0	2.2	<25	[42]
octyl-α-D-galactoside	18.8	32.4	2.3	<25	[41]
octyl-β-D-galactoside	16.2	32.0	2.6	<25	[42]
nonyl-α-D-galactoside	-	-	2.8	<25	[41]
nonyl-β-D-galactoside	-	-	3.3	>25	[42]
decyl-α-D-galactoside	-	-	3.2	<25	[41]
decyl-β-D-galactoside	-	-	3.9	>25	[42]
dodecyl-α-D-galactoside	-	-	-	>25	[41]
dodecyl-β-D-galactoside	-	-	-	>25	[42]
dodecyl-α-D-maltoside	0.156	-	-	<0	[87]
dodecyl-β-D-maltoside	0.17	-	-	<0	[87, 104]
dodecyltriazole-α-D-glucoside	0.14	-	-	<10	[38]
dodecyltriazole-β-D-glucoside	0.11	-	-	<10	[38]

(1) at 55°C; (2) at 42°C

Table 5. CMC, γ_{CMC} and pC_{20} vs. functional group at linker.

surfactant	linker	CMC (mM)	γ_{CMC} (mN/m)	pC_{20}	ref
hexyl-β-D-glucoside	O	226.7	36.4	1.7	[49]
hexyl-β-D-thioglucoside	S	82.1	32.8	1.9	[47]
heptyl-β-D-glucoside	O	72.3	33.2	2.0	[49]
heptyl-β-D-thioglucoside	S	27.2	31.8	2.4	[47]
octyl-β-D-glucoside	O	21.2	31.0	2.7	[49]
octyl-β-D-thioglucoside	S	10.4	29.6	2.7	[47]
nonyl-β-D-glucoside	O	6.9	29.6	3.2	[49]
nonyl-β-D-thioglucoside	S	2.8	29.6	3.2	[47]
decyl-β-D-glucoside	O	2.19	-	-	[60]
decyl-β-D-thioglucoside	S	0.9	-	-	[105]
octyl-β-D-maltoside	O	23.4	-	-	[87]
octyl-β-D-thiomaltoside	S	8.2	-	-	[106]
decyl-β-D-maltoside	O	1.93	-	-	[104]
decyl-β-D-thiomaltoside	S	0.6	-	-	[106]
1-*O*-octyl-D-xylitol	O	6.7	-	-	[37]
1-*O*-nonanoyl-D-xylitol	O-(C=O)	4.4	-	-	[37]
3-*O*-octyl-D-glucose	O	1.4	-	-	[107]
3-*O*-octanoyl-D-glucose	O-(C=O)	0.61	-	-	[108]

Table 6. Impact of linker on T_K.

n_C[a]	T_K (°C)		ref
4-6	<25	<25	
7-9	<25	>25	[37]
10-18	>25	>25	
6-9	<25	<25	
10	<25	>25	[47, 49]
12	>25	>25	
10	84	<0	
12	95	<0	[60]
14	>100	20	
12	38	<0	[60]
14	46	<0	

(a) number of C atoms in alkyl chain; (b) R is a linear alkyl chain.

Table 7. Summary of structure-property trends identified in this study.

	alkyl chain			sugar			linker
	length	branching	unsaturation	size	configuration	anomeric configuration (w.r.t. α)	type (w.r.t. ether)
CMC	↘	↗(?)	↗	↗→	→(?)	→(?)	thioether, ester ↘
γ_{CMC}	↘	↘(?)	↗(?)	↗	(?)	(?)	thioether →↘(?)
pC_{20}	↗	(?)	(?)	↘	(?)	(?)	thioether →↗(?)
T_K	↗	complex	↘	complex(?)	galactose ↗(?)	complex	thioether, amide ↗, methylamide ↘*

(?) requires further experimental confirmation or investigation with gradual variations of molecular structure; *N-methylamide surfactants exhibit lower T_K than comparable amide surfactants.

Figure captions

Figure 1. Possible systematic modifications of sugar-based surfactants centered on octyl-β-D-glucoside.

Figure 2. Alkyl chain length vs. (a) logarithm of CMC, (b) γ_{CMC}, and (c) pC_{20} for some homologous series of sugar-based surfactants [49-51]
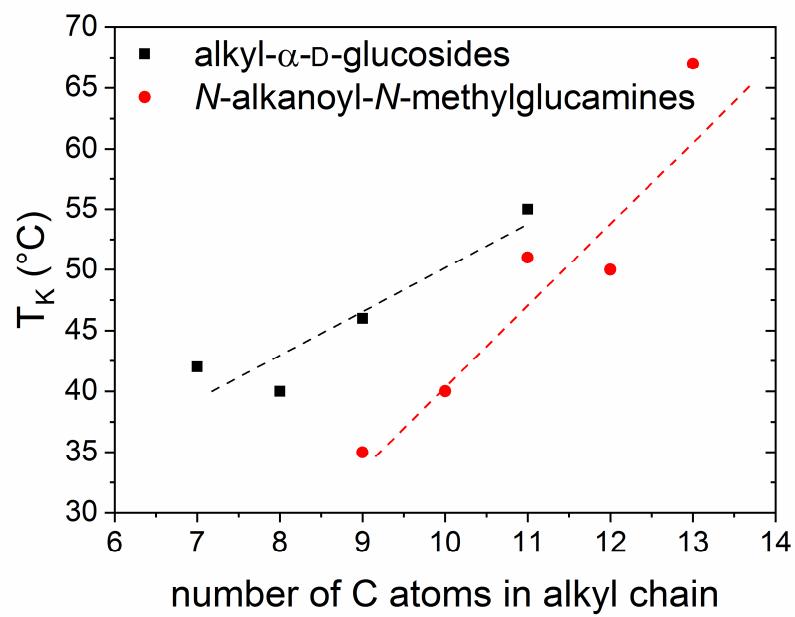
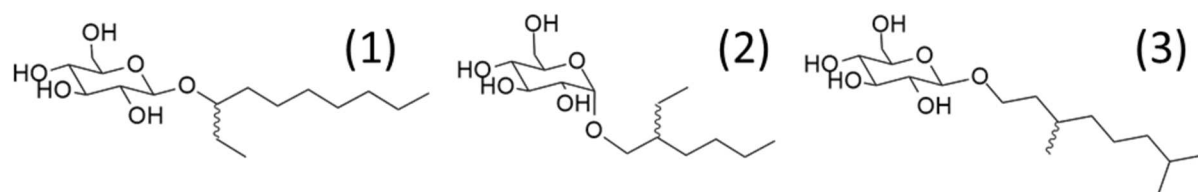Figure 3. T_K vs number of C atoms in alkyl chain [18, 70-72].

Figure 4. Examples of branching schemes identified in literature. (1) at 1st C of the alkyl chain, (2) at 2nd C of the alkyl chain, (3) isoprene-like.
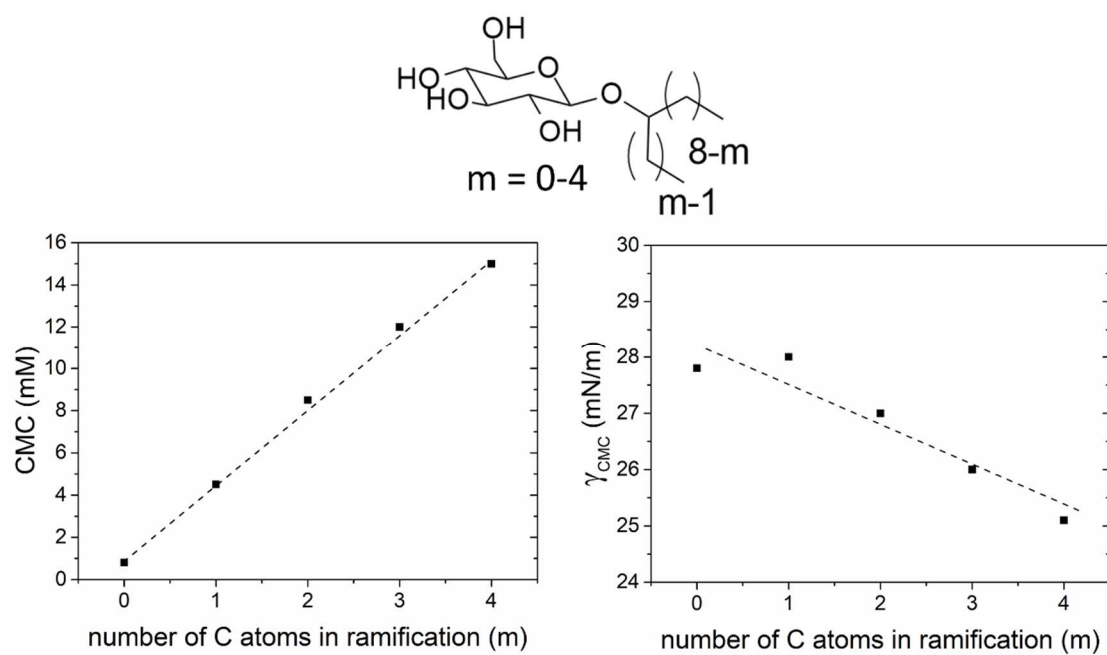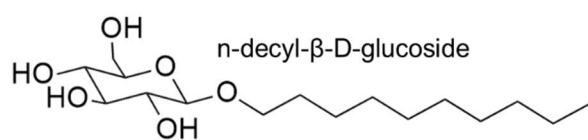
Figure 5. CMC and γ_{CMC} vs the number of C atoms in branched side chain (m) for a series of *sec*-decyl-β-D-glucosides [78].
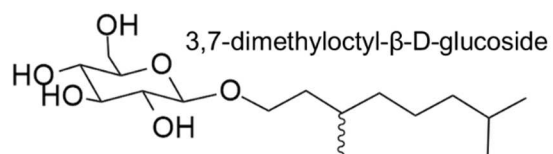
Figure 6. CMC/C_{20} ratios for n-decyl-β-D-glucoside and 3,7-dimethyloctyl-β-D-glucoside [80, 81].

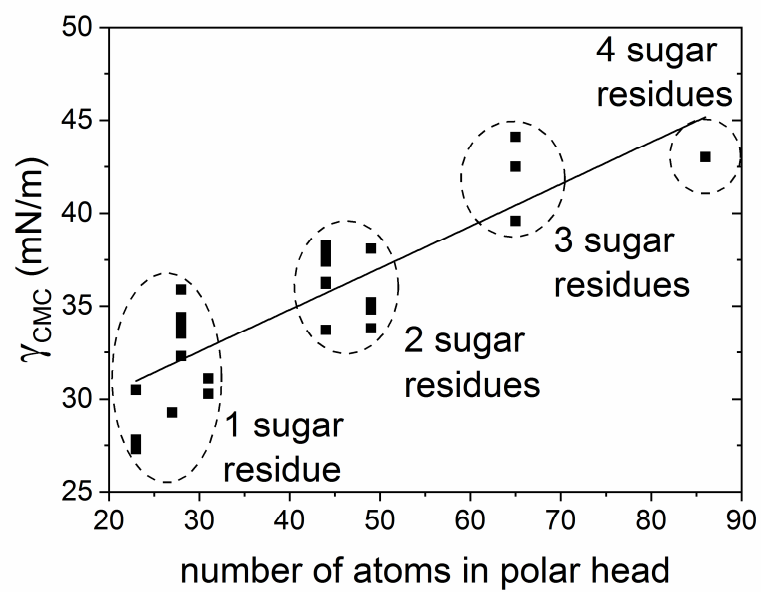Figure 7. γ_{CMC} [33, 44, 45, 50, 60, 62, 64, 80, 85] vs. number of atoms in the polar head.
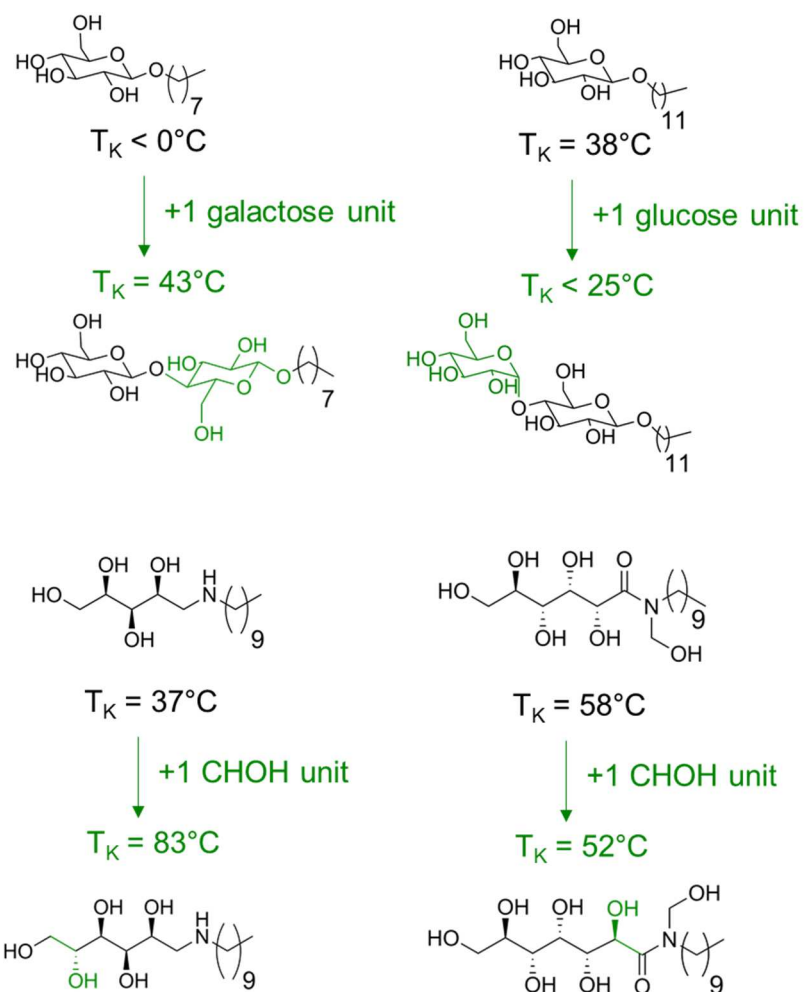
Figure 8. Impact of polar head size on T_K on four examples [71, 72, 87, 90-92]
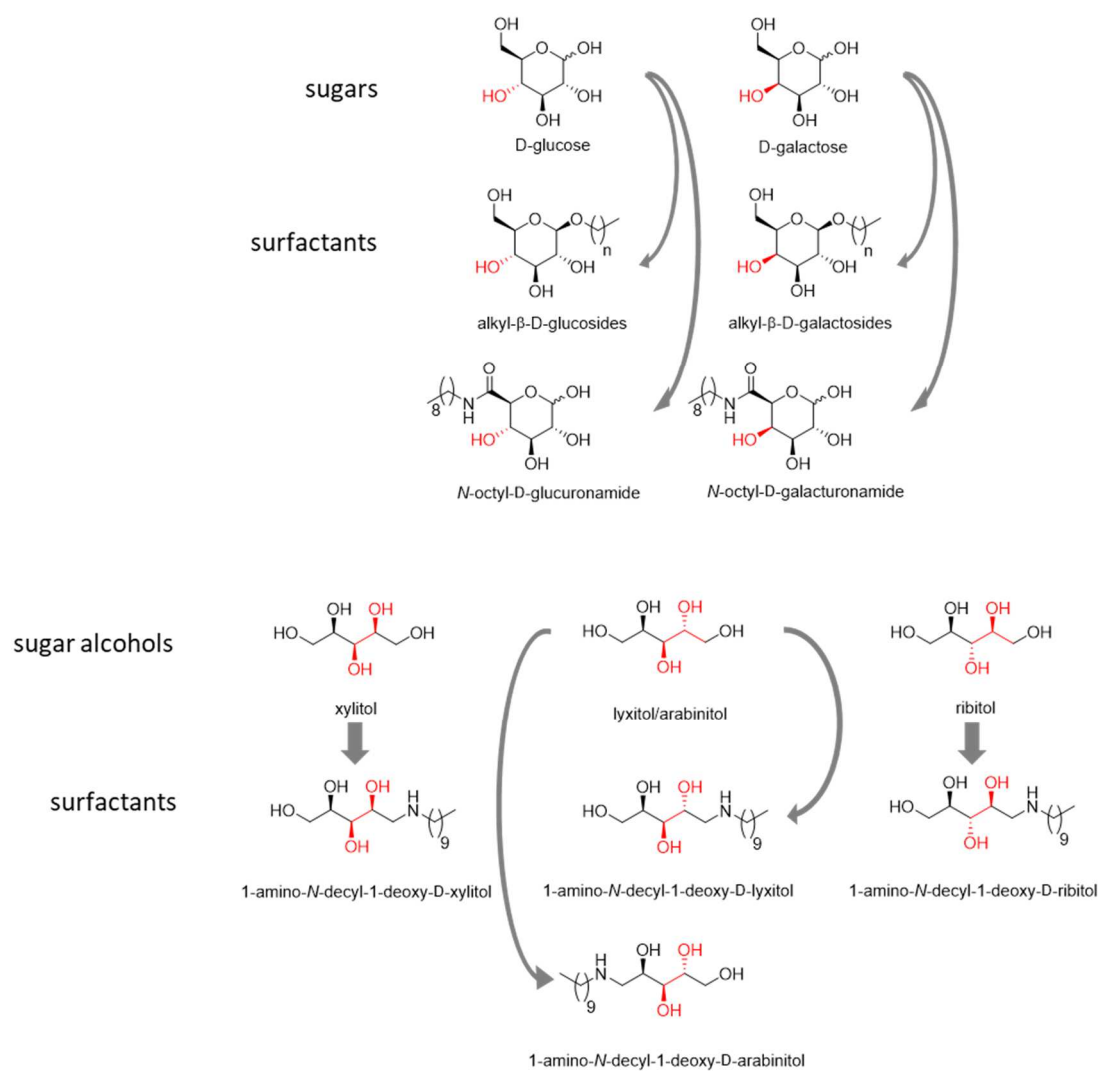
Figure 9. Structures of some sugars, sugar alcohols and corresponding surfactants.

Figure 10. Structures and CMC of 3-*O*-octyl-D-glucose and 3-*O*-octanoyl-D-glucose.

Figure 11. NPA Partial charges calculated at B3LYP/6-31+G(d,p) level for the alkyl chain of octyl-β-D-glucoside and analogues with different linkers [23].

Figure 12. Alkyl chain length vs. (a) logarithm of CMC, (b) γ_{CMC}, and (c) pC_{20} for common alkyl glycosides and alkyl polyethoxylates
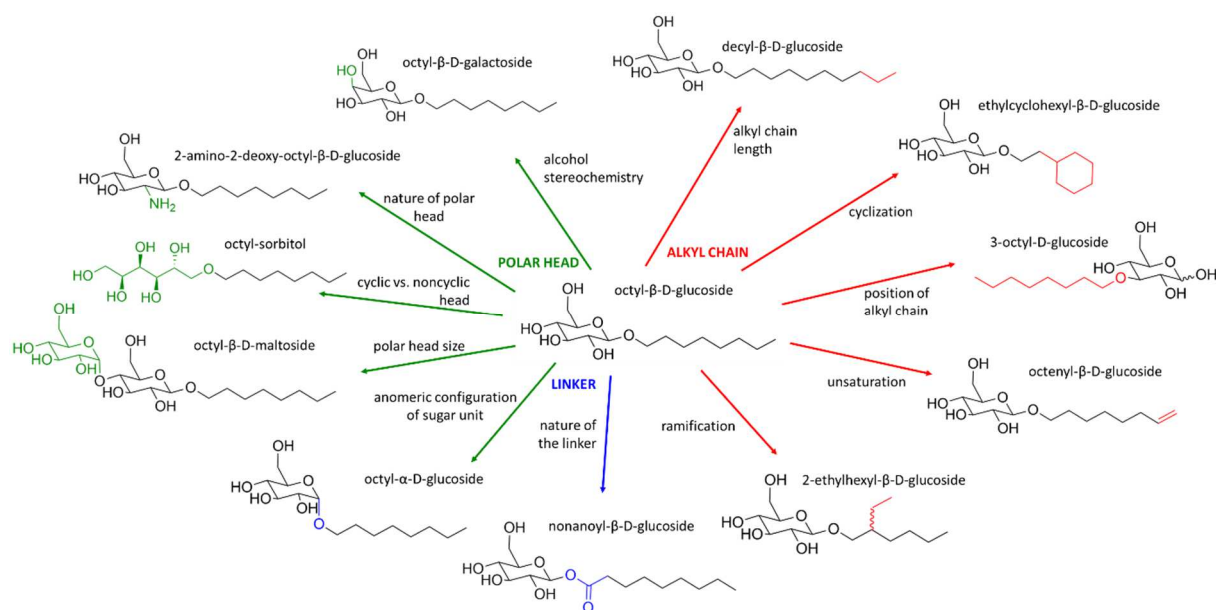
Figure 1. Possible systematic modifications of sugar-based surfactants centered on octyl-β-D-glucoside.
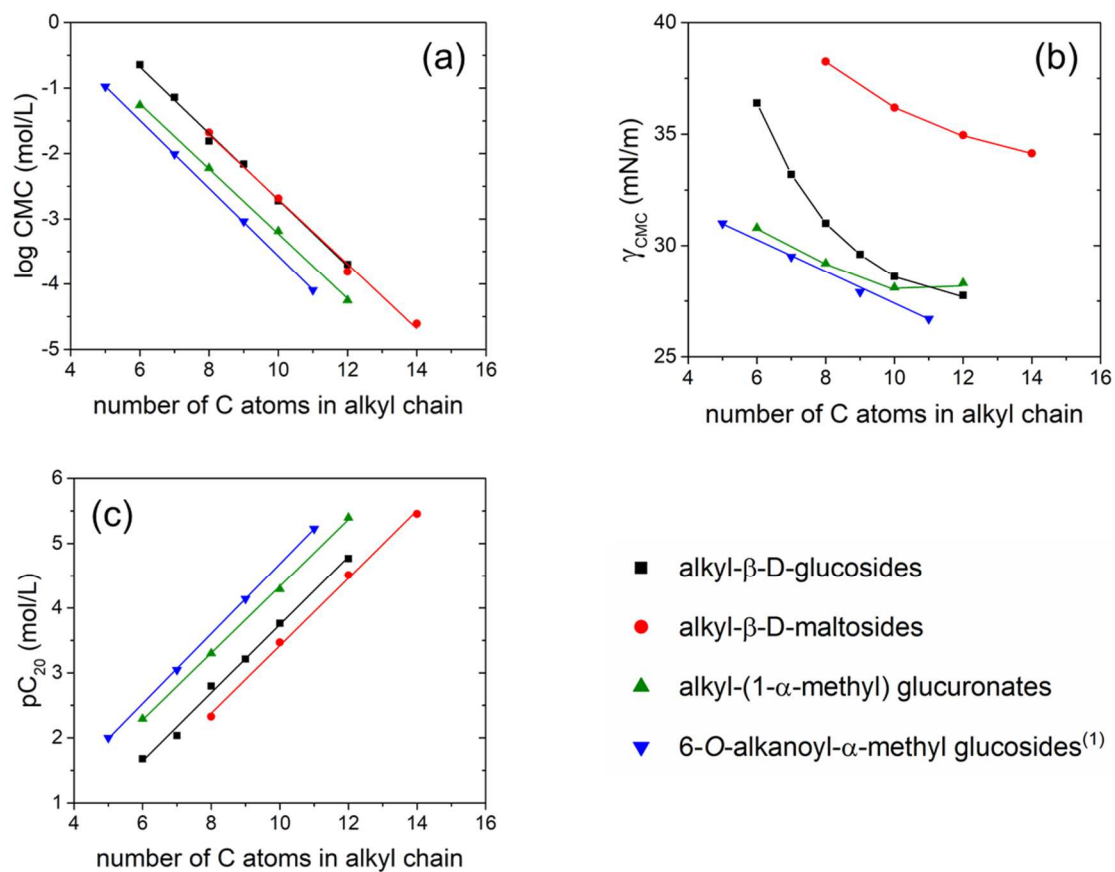
(1) properties measured at 50°C for the decanoyl and dodecanoyl members of the homologous series due to solubility issues

Figure 2. Alkyl chain length vs. (a) logarithm of CMC, (b) γ_{CMC}, and (c) pC_{20} for some homologous series of sugar-based surfactants [49-51]

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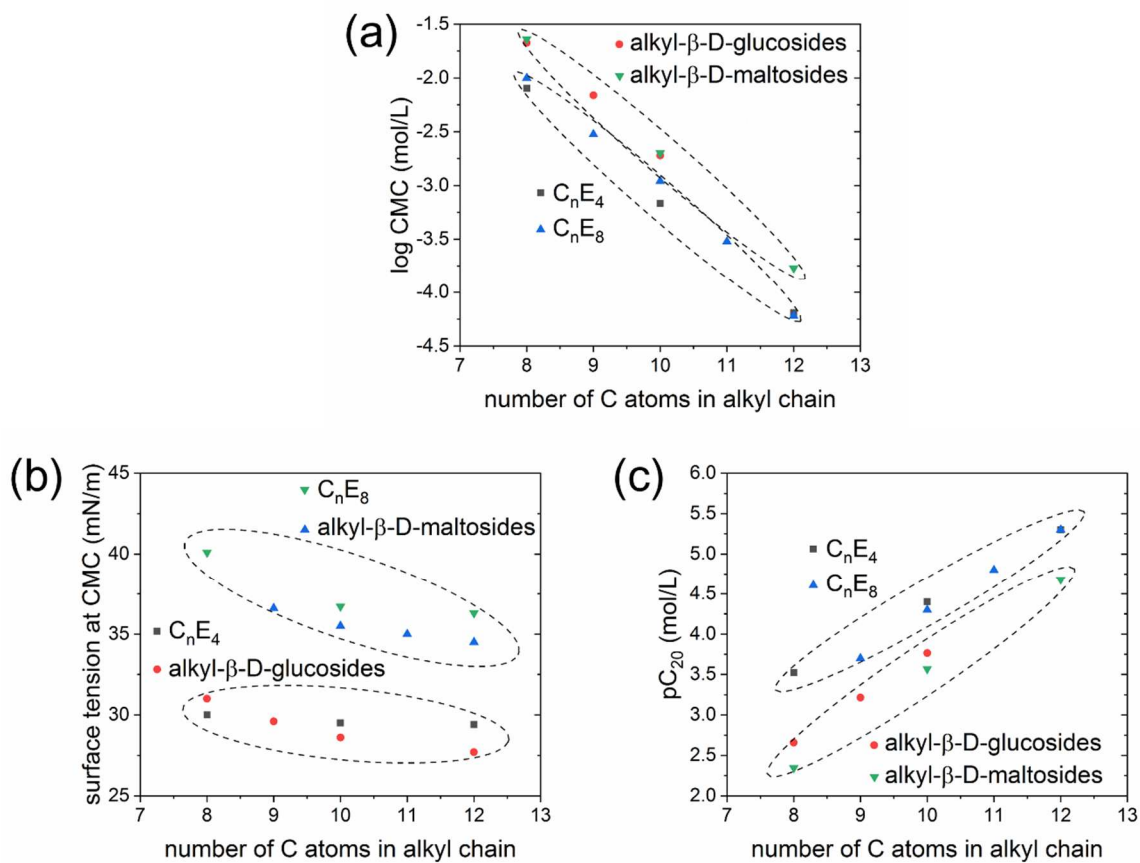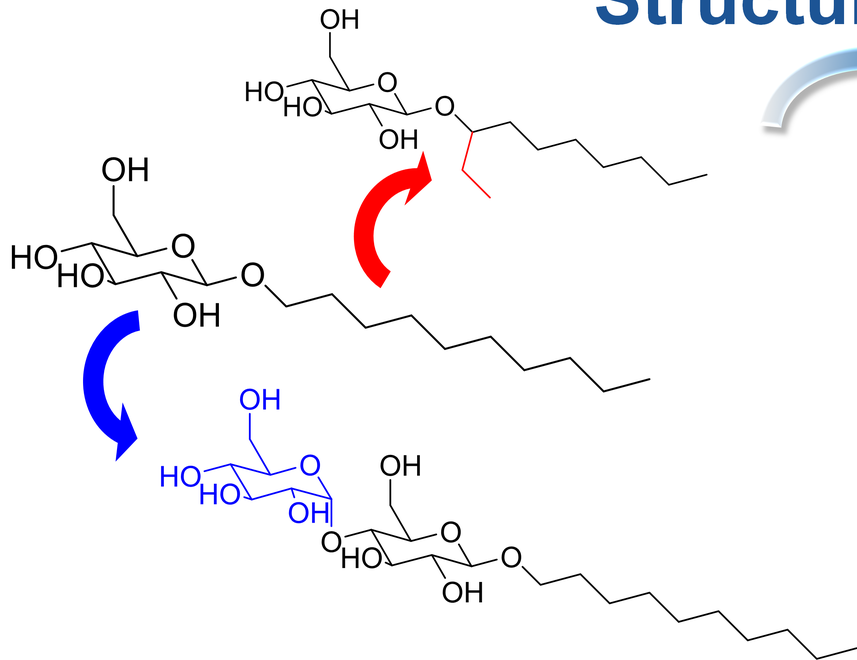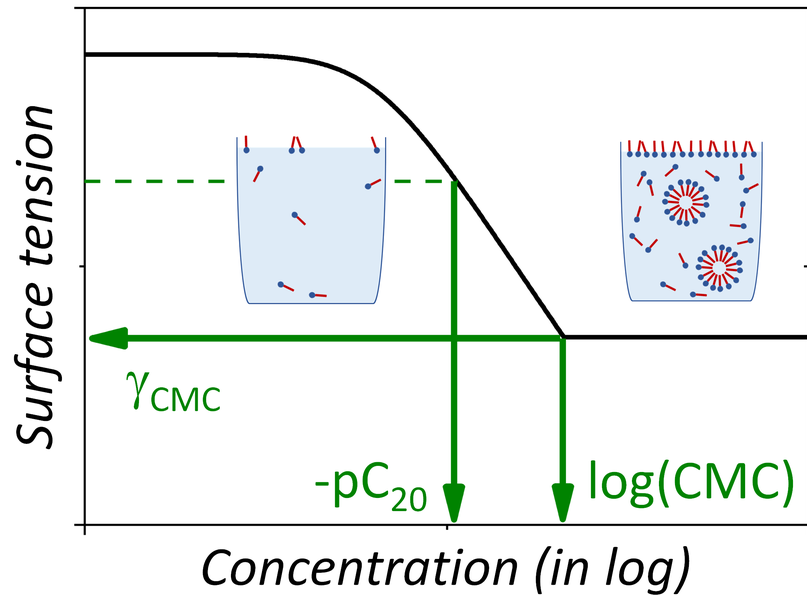Figure 12. Alkyl chain length vs. (a) logarithm of CMC, (b) γ_{CMC}, and (c) pC_{20} for common alkyl glycosides and alkyl polyethoxylates

Structural trends

Sugar-based surfactants

Amphiphilic properties

Surface tension

γ_{CMC}

$-pC_{20}$

$\log(CMC)$

Concentration (in log)