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# Carbohydrate-Based Surfactants: Structure-Activity Relationships

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#### 1. Introduction

Carbohydrate-based surfactants (CBS) are, today, among the most important classes of amphiphilic compounds (Dembintsky, 2004; Queneau et al, 2008; Ruiz, 2009). Their structure is the result of the saccharide and lipid combination, naturally biosynthesized within living cells, or synthetically prepared by sequential reactions using carbohydrate and fatty materials, through one or several bonds. The growing interests of such compounds arise from many reasons of fundamental, practical, economical, and environmental orders (Razafindralambo et al, 2009, 2011a; Hill, K. & LeHen-Ferrenbach, 2009; Kitamoto et al, 2009). First, they can be easily prepared from the most abundant renewable vegetable raw materials (cellulose, pectin, hemicellulose, starch, etc.) in a wide range of structure and geometry by modular synthesis thanks to the presence of numerous reactive hydroxyl groups. Second, such a structural diversity makes them, on the one hand, as excellent models for getting insight into the surfactant mechanisms in modifying interfacial properties, which control the formation and the stability of colloidal systems such as micelles, vesicles, foams, emulsions, and suspensions (Razafindralambo et al, 2011b). One the other hand, numerous properties and functionalities would be expected from such a quasi-unlimited number of various compounds that can find specific applications in different industrial areas. Third, their compatibility to the environment, for instance, a higher biodegradability and lower toxicity, is an excellent criterion for their uses as alternatives to surfactants from petrochemical sources. Owing to the two former reasons, a systematic investigation of structure-activity relationships, which has rarely been carried out in the past, appears valuable for increasing knowledge on the impact of each CBS structural entity on their activities-functionalities, and ultimately, for achieving successfully a rational design in selecting and combining suitable compounds for further developments and applications. In the present chapter, we report the results of dynamic and equilibrium surface properties of homologous and analogous series of uronic acid derivatives, and evidence, consequently, the impact of different structural entities on their fundamental properties at the air-water interface.

#### 2. Scope of the contribution

The aim of the present contribution is: (1) to review CBS in terms of structural classification based on their molecular size (mono-, oligo-, polymeric surfactants), geometry (standard,

bipolar or bolaform, and gemini surfactants), and the nature of the polar headgroup (charged or not, cyclic or not), the apolar tail (number and length of alkyl chain), and the linker (amide, ester, ...) and/or the spacer; (2) to present systematically results on structure-activity relationships of uronic acid derivatives (UADs), a particular class of carbohydrate-based surfactants. These concern the impact of each structural entity including the polar headgroup (stereochemistry), apolar tail (chain length, number, and unsaturation), and linkage/spacer, on the performance of UADs to change surface properties, and possibly, to form and stabilize colloidal systems.

# 3. Classification of carbohydrate-based surfactants

Carbohydrate-based surfactants, currently known as glycolipids (Chester, 1997; Hato et al., 1999), are constituted by a saccharide unit (mono-, di-, oligo-, or polysaccharide) linked to a hydrophobic part of one, two, or multi-hydrocarbon chains by a single, or several bonds. These may be an ester, thioester, ether, amine, or/and amide group (Stubenrauch, 2001). Generally, glycolipids may be classified according to their amphiphilic structure, which depends on the polar headgroup, the apolar tail, but also the linkage between these main entities. Based on these three structural parameters, glycolipids are grouped in different categories, as presented in Table 1.

Glycolipids	Hydrophilic part	Hydrophobic part	Linkers
, I	Try droprime part		Littleto
Monocatenary		One tail	
Bicatenary	One headgroup	Two tails	
Multicatenary	_	Multi tails	
Glycoglycerolipids		Acylglycerol	Fatan (h.) a atan Edian
Glycosphingolipids		Sphingoides	Ester, thioester, Ether, amine, amide
Bolaforms	Two headgroups	One spacer	_
Geminis		One spacer/two tails	
Alkylpolyglucosides	Multi-headgroups	One or multi-tails	

Table 1. Main classes of glycolipids, based on the amphiphilic structure and geometry

Besides the nature ionic, nonionic, and amphoteric of the polar headgroup, as for all surfactants, glycolipids can also be classified in small, medium, and large compounds, in relation to their molecular mass and size. According to these criteria, three main classes belonging to glycolipid-based monomeric, oligomeric, and polymeric surfactants may be distinguished. In addition to structural criteria, glycolipids may have two origins, those from microbial fermentation, crops, and animals, which are natural products, and those synthetized by chemical, enzymatic, and chemo-enzymatic routes, globally considered as synthetic compounds. In the following section, we try to illustrate by a few representative examples the most important classes of glycolipids with their chemical structure on the basis of their source, molecular mass, and geometry while considering the other classification aspects.

# 3.1 Natural glycolipids

# 3.1.1 Microbial biosurfactants

	Bioglycolipids	Structure	Specificities (headgroup, tail, linkage)
	Intec	Low molecular mass	19en
•	Rhamnolipids	HO OH	nonionic, mono/di, ester, (Dembitsky, 2005)
•	Sophorolipids	SO O SH ON ON ON	nonionic, mono, ester, (Dembitsky, 2005)
•	Trehalolipids	OH OH	nonionic, di, ester, (Dembitsky, 2005)
•	Mannosylerythriol lipid	Hack of the state	nonionic, mono, ester, (Kitamoto et al. 2009)
•	Monogalactosyldiacylglycerol	R-C-O-CH, R-C-O-CH HJC-OH	nonionic, di, ester, (Infante et al. 1997)
		High molecular mass	
•	Cyclo-oligosaccharides	100 100 100 100 100 100 100 100 100 100	nonionic, mono, ester- amide, (Dembitsky, 2005)
•	Emulsan (Polymeric biosurfactant)	CH, CHA, CHA, CHA, CHA, CHA, CHA, CHA, C	nonionic, multi, ester/amide, (Desai et Banat, 1997)

#### 3.1.2 Plant biosurfactants

Bioglycolipids Structure Specificitie		Specificities (headgroup, tail, linkage)	
•	Butanolide glycosides	OR <sub>2</sub> R <sub>1</sub> OOC Me	nonionic, multi, ester, (Dembitsky, 2005)
•	Sucrose ester	R <sub>1</sub> O NO	nonionic, multi, ester, (Dembitsky, 2005)

# 3.1.3 Animal biosurfactants

	Bioglycolipids	Structure	Specificities (headgroup, tail, linkage)
•	Cerebrosides	HO COH OH	nonionic, di, amide, (Dembitsky, 2005)
•	Gangliosides	HO OH OH OH OH OH OH	cationic, di, amine, (Dembitsky, 2005)

# 3.2 Synthetic alycolipids

Glycolipids	Structure	Specificities (headgroup, tail, linkage)	
Monomeric			
Sorbitan monoester	HO, OH	nonionic, mono, ester, (Hill &LeHen- Ferrenbach, 2009)	
Isosorbide derivative	HO	nonionic, mono, ester (Hill &LeHen- Ferrenbach, 2009)	
Uronic acid derivatives: <i>a. Monocatenary</i>	HO OH OH	nonionic, mono, amide (Laurent et al. 2011)	
b. Bicatenary	OH OH	nonionic, di, ester-ether (Richel et al. 2010)	
Alkylglucoside	HO CH <sub>2</sub> OH	nonionic, mono, ether (Vulfson, 1990)	

Glycolipids	Structure	Specificities (headgroup, tail, linkage)
Bolaform		
• α,ω-diamino-(oxa) [Spacer: -(CH <sub>2</sub> ) <sub>n</sub> -]	HO H	nonionic, bi, amide (Wagenaar&Engberts, 2007)
Gemini		
• Glu(n)-2-Glu(n)	C <sub>n</sub> H <sub>2n+1</sub> N N N N C=0 (OH HO OH OH OH OH	nonionic, bi, amides (Sakai, 2008)
	Glu(n)-2-Glu(n) n = 10 and 12	
Oligomeric/polymeric		
Alkylpolyglucoside	HO TON 1 (NO TON )	nonionic, mono, ether (Queneau et al. 2008)
Inulin carbamate	n OHONO OHON	nonionic, mono, ester (Tadros, 2004)

#### 4. Uronic acid derivatives

Uronic Acid-Derivative Surfactants (UADs) are a particular class of monomeric glycolipids (Fig.1). Their polar headgroup represents a considerable part of carbohydrate components, widely distributed in natural plant polysaccharides (Langguth & Benet, 1992). In addition, uronic acids are the result of the primary alcohol oxydation into a carboxylic group within a monosaccharide like glucose and galactose. Thus, they contain, in their structure, both hydroxyl and carboxylic groups that are highly reactive, explaining their potential as a basic unit for generating closely related surfactant compounds. The polar headgroup configurations according to the stereochemistry of OH groups and geometry (cyclic or not, bipolarity), the hydrophobic tail (number and length of alkyl chain), and the type of linker (ester, ether and amide, etc) are among the main variables in their structural entities. Therefore, they represent a set of ideal compounds for investigating structure-surface activity relationships.

L: NH or O  
R1: 
$$(CH_2)_n$$
-CH<sub>3</sub>  
HO

R2:  $(CH_2)_n$ -CH<sub>3</sub>
HO

R3: OH or H  
R4: H or OH

OH

R4: H or OH

Fig. 1. General structure of uronic acid (left) and uronolactone (right) derivatives

Among several activities that CBS are able to develop (Ruiz, 2009), those related to the modification of surface and interface fundamental properties are undeniably the most important to evaluate and understand. Through several research works during last decades, it is established that fundamental properties such as dynamic and equilibrium surface tensions play a key role in the formation and stability of colloidal systems like foams, emulsions, and suspensions (Razafindralambo et al. 2011b). In this chapter, we are only focused on the relationships between chemical structure of UADs and their surface-activities at the air-water interface. UADs are a set of glucuronic and galacturonic acid-based surfactants varying in the polar headgroup configuration, including a cyclic (lactone bond) or non-cyclic structure and a  $\alpha$ - or  $\beta$ - anomeric form, the hydrophobic tail chain length (C8 to C14) and number (mono- and bicatenary), the presence of a double bond, as well as an OH group at the terminal carbon, and in the type of linkage, ester, amide in C6, or ether in C1. These compounds have been synthesized by chemical or enzymatic routes, purified, and their chemical structure has been confirmed by means of various spectroscopic techniques (Nuclear Magnetic Resonance, Infrared, and Mass Spectrometry).

# 5. Surface-active properties

Surface-active properties of any surfactants can be measured through their capacity, either to reduce the surface tension of aqueous solution ( $\gamma_0$ ) to any value ( $\gamma$ ), or to increase the surface pressure ( $\pi = \gamma_0$ - $\gamma$ ) of the air-water interface. Measurements can be performed in both dynamic and static/quasi-static modes. Based on the solubility of the coumpound to characterize, one of the two following approaches must be used. The Gibbs'approach, measuring  $\gamma$  by adsorption, i.e. by migration of surfactant to the surface, is more convenient for short chain derivative surfactants (high solubility in water) whereas the Langmuir approach, determining  $\pi$  after spreading and compressing surfactant molecules at the surface, is rather appropriate for long chain derivative surfactants (low solubility in water). Surface activities of uronic acid derivatives may be evaluated in both dynamic and static/quasi-satic modes using a series of complementary techniques at room temperature comprised between 20-25°C (Razafindralambo et al., 1995; 2009; 2011).

#### 5.1 Dynamic surface properties

In dynamic mode, surface tensions ( $\gamma_{\rm dyn}$ ) are measured using a drop volume tensiometer (TVT1, Lauda, Germany) by determining the critical volume (maximum pending size) of a series of drop created at different growing rates from 3 to 120 s (Razafindralambo et al., 2004).

#### 5.2 Equilibrium surface properties

# 5.2.1 Gibbs approach

In static and quasi-static modes, the equilibrium surface tensions ( $\gamma_e$ ) are measured by means of Wilhelmy plate (Tensimat N3, Prolabo, France), drop volume (TVT1, Lauda, Germany), or pending drop (Tracker, IT-Concept, France)-based tensiometers as detailed in previous papers (Razafindralamboet al., 1995; 2009). These methods consist of measuring continuously  $\gamma_e$  as a function of time, for surfactant solutions at different concentrations. The equilibrium surface tension ( $\gamma_e$ ) can be determined as the fitting value of  $\gamma$  from

representative experimental data, using appropriate mathematical models. All physical parameters such as critical micelle concentration (CMC), surface tension at the CMC ( $\gamma_{cmc}$ ), surface excess ( $\Gamma_{max}$ ), and minimum area per molecule( $A_{min}$ ), can be calculated using Gibbs equations for nonionic surfactants :

$$\Gamma_{\text{max}} = -\frac{1}{RT} \left( \frac{d\gamma}{d \ln C_o} \right)$$

$$A_{cmc} = \left( \frac{1}{\Gamma_{\text{max}} N} \right)$$
(1)

where  $C_0$  is the bulk solution concentration; R = 8.314 J.K<sup>-1</sup>.m<sup>-2</sup>, the gas constant; T, the temperature in Kelvin, and N, the Avogadro's number.

## 5.2.2 Langmuir approach

By Langmuir approach, a small volume of surfactant organic solution is spread drop wise onto the clean milli-Q water surface by means of Hamilton micro-syringe using a reproducibility adapter. After a given laps time, allowing the solvent evaporation, the surface pressure  $(\pi)$  of the monolayer is determined by measuring the horizontal force per unit of length, for a delimited area, during the compression. With an automatic Langmuir film Waage LFW2 3"5 (Lauda, Königshofen, Germany), a total trough area of 927 cm² is available. This is progressively reduced by moving a single barrier made in Teflon, and the force per length unit detected at a float gives the surface pressure of the monolayer at a constant temperature. For characterizing uronic acid derivatives, mainly bicatenary surfactants, the research of optimized experimental conditions is required (Razafindralambo et al. 2011).

# 6. Structure-activity relationships

## 6.1 Polar headgroup effect

#### 6.1.1 Stereochemistry

## **Anomeric forms**

The effect of the octyl glucuronolactone anomeric form is observed for the equilibrium surface properties (Table 2). The anomer  $\alpha$  CMC is about the half of that of the anomer  $\beta$ , all other related parameters being quite similar.  $\gamma_{cmc}$  and  $A_{min}$  are quite similar, indicating that the anomeric form does not affect the molecular arrangement at the air-water interface, but changes that in the bulk water. In other words, the anomer  $\alpha$  self-aggregates readily in water while adopting the same close-packed configuration at the air-water interface than the anomer  $\beta$ . Therefore, the anomer  $\alpha$  appears more hydrophobic than the anomer  $\beta$ , which is attributed to the difference in the steric effect of their polar headgroup. This interacts stronger with water molecules for the anomer  $\beta$ , delaying its self-aggregation process. Concerning their dynamic surface properties, the anomer  $\beta$  appears slightly more efficient than the anomer  $\alpha$  (data not shown), the difference being less important than that observed for equilibrium surface properties.

	$\Upsilon_{ m cmc}$ [mN/m]	CMC [mM]	A <sub>min</sub> [Ų/mol]
$\alpha$ -C <sub>8</sub> - Glucuronolactone	32.8	1.3	43
$\beta$ -C <sub>8</sub> - Glucuronolactone	35.2	2.4	40

Table 2. Physical parameters of octyl glucuronolactone with  $\alpha$  and  $\beta$  anomers

## 4-hydroxyl group (4-OH) axial or equatorial position effect

The second parameter related to the polar headgroup stereochemistry is the axial or equatorial position of the hydroxyl group of the fourth carbon within bicatenary derivatives of galacturonic and glucuronic acids. This stereochemistry effect impacts their configuration and behaviour at the air-water interface, as observed with the ( $\pi$ -A) isotherms (Fig.2). The glucuronic acid derivative (GlcA-C<sub>14/14</sub>) is more expanded when it is spread at the air-water around 20°C, and shows a transition phase under compression, which does not occur for the galacturonic acid derivative (GalA-C<sub>14/14</sub>). This difference is in agreement with film morphologies and thicknesses, and is also supported by molecular models (Razafindralambo et al., 2011). In contrast, the 4-OH axial or equatorial position has no effect when the molecules are vertically oriented, i.e. within a film at a condensed state. Such results have been attributed to the configuration of two alkyl chains, which is in "open" or "close" structure according to the film is in expanded or in condensed state.

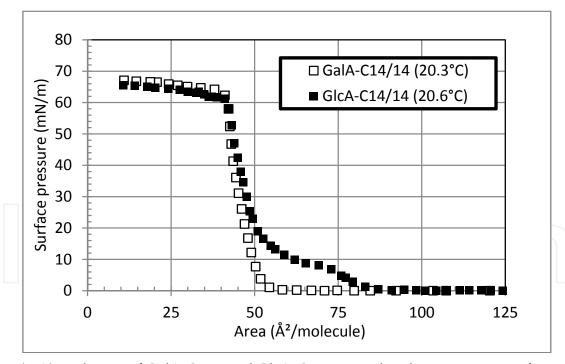


Fig. 2. ( $\pi$ -A) isotherms of GalA-C<sub>14/14</sub> and GlcA-C<sub>14/14</sub> spread at the air-water interface 20°C

# 6.1.2 Impact of the bipolarity: (OH group ending the alkyl chain)

Adding an OH group at the end of the alkyl chain changes the geometry of uronic acid derivatives, which becomes a bipolar asymmetric. Such a modification impacts some dynamic (Fig.3) and equilibrium surface properties (Table 3) of glucuronic acid derivatives.

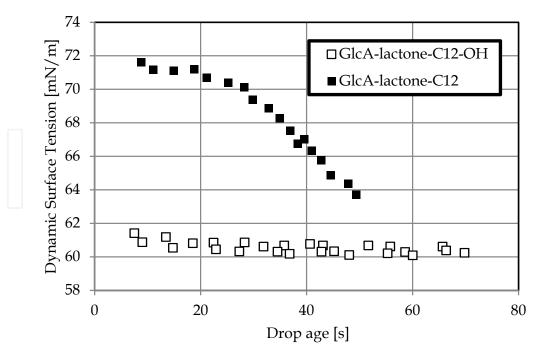


Fig. 3. Dynamic surface tension vs. time of dodecyl glucuronolactones (0.2 g/L), with and without a hydroxyl group at the end, measured by TVT1 at  $20^{\circ}$ C

	$\Upsilon_{cmc}$ [mN/m]	CMC [mM]	$ m A_{min}$ [Å $^2$ /mol]
OH-C <sub>12</sub> -Glucuronolactone	43.9	0.7	65
C <sub>12</sub> -Glucuronolactone	47.2	0.6	34

Table 3. Physical parameters of dodecyl glucuronolactones ending with, and without hydroxyl group

It increases the area occupied per molecule (cross-sectional area), and the performance in the adsorption time by reducing faster the dynamic surface tension. This difference is easy to understand, and may be explained by the fact that the two polar headgroups are directed into the aqueous phase, leaving the hydrophobic spacer in the gaseous phase, and forming, as a consequence, a "convex" configuration. In contrast, it has no significant effect on the equilibrium (long time) surface properties, based on their CMC and  $\gamma_{cmc}$  values.

### 6.2 Hydrophobic effect

#### 6.2.1 Alkyl chain length

The impact of the alkyl chain length on all of interfacial properties can be evaluated with a homologous series of monocatenary and bicatenary uronic acid derivatives. As for all monomeric surfactants, whatever their nature, the general trend is respected with uronic acid derivatives, that is, the longer the alkyl chain length, the lower the CMC of the uronate and uronamide derivatives (Blecker et al., 2002; Laurent et al., 2011). About dynamic surface properties, an optimum chain length of eleven carbon atom gives the best performance, regarding the adsorption time and the maximum reduction of the surface tension. Concerning

bicatenary derivatives, the comparison of GalA- $C_{10/10}$  and GalA- $C_{14/14}$  monolayer properties shows that the shorter the two alkyl chains ( $C_{10/10}$ ), the more expanded and compressible the spread molecules, and the less stable the molecular film (Fig.4). Such behaviour of the shorter chain derivatives is attributed to stronger interactions with the subphase, which is comparable with the case of the dimyristoyl-phosphatidylcholine (DMPC), an ionic phospholipid having the same alkyl chains than that of GalA- $C_{14/14}$  (data not shown).

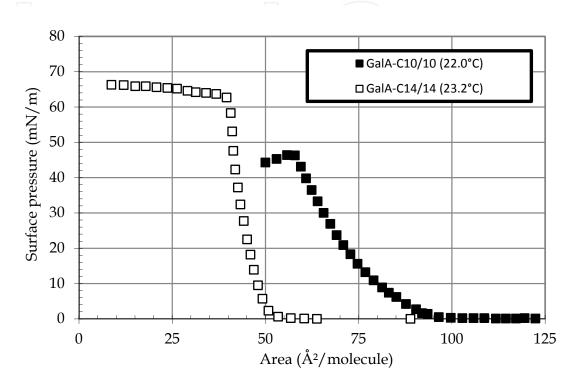


Fig. 4. ( $\pi$ -A) isotherms of GalA-C<sub>10/10</sub> and GlcA-C<sub>14/14</sub> spread at the air-water interface

#### 6.2.2 Alkyl chain number (Monocatenary vs. bicatenary)

The alkyl chain number of uronic acid derivatives also appears crucial on their surface properties characterized by the Langmuir approach. When a second alkyl chain is added to the polar headgroup, that is, the compound becomes bicatenary, the mechanical properties of the film at the air-water interface are improved, regarding its collapse pressure (Fig.5). It is to be noted, from this figure, that the inclusion of a cyclic ester bond into the polar headgroup affects slightly the behaviour of the monolayer.

#### 6.2.3 Unsaturation

By including a double bond at the end of the alkyl chain, no significant effect has been observed on the equilibrium surface properties, the  $\gamma_{cmc}$ , CMC, and  $A_{min}$  values being similar and equal to  $34.2 \pm 1.1$  mN/m,  $0.12 \pm 0.01$  g/L, and  $39.0 \pm 2.0$  Ų/mol., respectively. In contrast, it impacts extensively the dynamic surface properties of the undecanoyl glucuronate (Fig.6). The derivative with an unsaturated chain migrates faster at the airwater interface, and reduces readily the dynamic surface tension, compared to the saturated one. It is attributed to the "shortening effect" of the double bond inclusion (Milkereit et al. 2005), reducing the hydrophobicity of the surfactant, and therefore, its adsorption time.

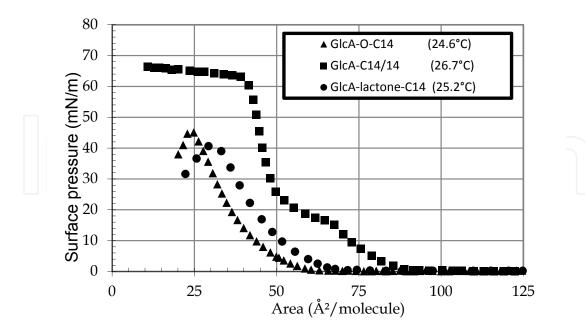


Fig. 5. ( $\pi$ -A) isotherms of GlcA-O-C<sub>14</sub>, GlcA-lactone-C<sub>14</sub>, and GlcA-C<sub>14/14</sub> spread at the airwater interface 25°C.

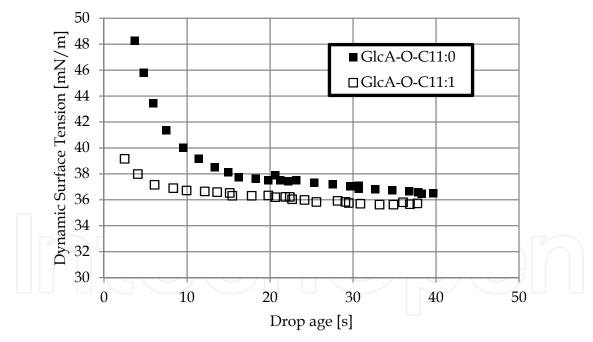


Fig. 6. Dynamic surface tension vs. time of undecanyl (C11:0) and undecenyl (C11:1)-glucuronolactones (0.1~g/L) measured by TVT1 at  $20^{\circ}C$ .

# 6.3 Linkage effect

#### 6.3.1 Ester bond direction

One of the spectacular effects of the linkage between the polar headgroup and the hydrophobic tail is the change of the ester bond orientation within the octyl sugar

derivatives. By comparing the dynamic and equilibrium surface properties of glucose octanoate (C8-CO-O-Glc) and octyl glucuronate (C8-O-CO-GlcA), significant differences are observed (Table 4). When the carbonyl group is closed to the polar headgroup constituted by glucuronic acid (C8-O-CO-GlcA), the surfactant is more hydrophobic, and the polar head group is larger. The consequence is the increase of dynamic properties, and the decrease of the CMC (10.7 mM vs. 19.1 mM). When the carbonyl group is close to the alkyl chain (C8-CO-O-Glc), there is an "interruption" of the hydrophobic tail, which reduces its hydrophobicity (Razafindralambo et al. 2009). The molecular area becomes smaller and the CMC is higher. On the other hand, the adsorption time rate characterized by t\* and  $v_{max}$  are increased, reducing its performance on dynamic surface properties.

Parameters	Glucose octanoate [Glc-O-C <sub>8</sub> ]	Octylglucuronate [GlcA-O-C <sub>8</sub> ]
Dynamics (1):		
t* (10-3 s)	36.1	3.4
n	0.14	0.56
$v_{max}(mN/m/s)$	0.024	0.0081
Equilibrium :		
$\Upsilon_{\rm cmc}$ (mN/m)	25.1	28.0
CMC (mM)	19.1	10.7
$A_{min}$ (Å <sup>2</sup> /mol)	37	44

Table 4. Physical parameters of glucose octanoate and octyl glucuronate; <sup>(1)</sup> Compared at 1.63 mM (25°C).

### 6.3.2 Ester vs. amide bond

By comparing the surface properties of three derivatives with an octyl chain, the impact of the type of the linkage bond can be evidenced, despite the difference in the ratio alpha/beta of anomeric forms (Table 5). It appears that the uronamide is the most effective in terms of equilibrium surface tensions. This result may be attributed to the difference in the molecular area occupied by the two octyl derivatives. The amide bond has a smaller bulk size than the ester ones. In comparison with a unique form of octyl glucoside, the glucuronamide is more effective. Even though the linkage is not at the same position, on the C1 for glucoside, and on the C6 for glucuronamide, the impact may be significant, considering the similarity in the molecular mass, and the number of the OH group available.

	C8-glucuronate	C8-glucuronamide	C8-glucoside (25°C)
Physical parameters	[C6-Ester linkage]	[C6-Amide linkage]	[C1-Ether linkage]
			α;β
	$\alpha/\beta=1.5$	$\alpha/\beta=0.6$	[Boyd et al, 2000]
$\Upsilon_{\rm cmc}$ (mN/m)	28.0	24.0	35.2;31.3
CMC (mM)	10.7	3.3	12.0; 18.2
$A_{min}$ (Å <sup>2</sup> /mol)	$44;45^{(1)}$	25; 35 <sup>(1)</sup>	42;42(2)

Table 5. Physical parameters of glucuronic acid and glucose derivatives containing different linkages at the air-water interface. (1) By modeling; (2) by linear fit

#### 7. Conclusion

In the present chapter, we contribute to a better understanding of the structure-surface activity relationships of uronic acid derivatives, a promising class of carbohydrate-based surfactants. Each structural element impacts either their dynamic performances, measured over a short period range, or their equilibrium activities, evaluated after a longer period. Besides scientific interests of such fundamental information, the approach also leads to the identification of some suitable structures for practical performances in forming and stabilizing colloidal systems like foams, emulsions, and suspensions, which are encountered virtually in all soft manufactured products.

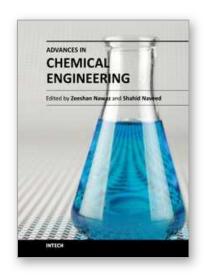
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#### **Advances in Chemical Engineering**

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Chemical engineering applications have been a source of challenging optimization problems in terms of economics and technology. The goal of this book is to enable the reader to get instant information on fundamentals and advancements in chemical engineering. This book addresses ongoing evolutions of chemical engineering and provides overview to the sate of the art advancements. Molecular perspective is increasingly important in the refinement of kinetic and thermodynamic molding. As a result, much of the material was revised on industrial problems and their sophisticated solutions from known scientists around the world. These issues were divided in to two sections, fundamental advances and catalysis and reaction engineering. A distinct feature of this text continues to be the emphasis on molecular chemistry, reaction engineering and modeling to achieve rational and robust industrial design. Our perspective is that this background must be made available to undergraduate, graduate and professionals in an integrated manner.

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