



Octyl glucoside derivatives: A tool against metal pollutants



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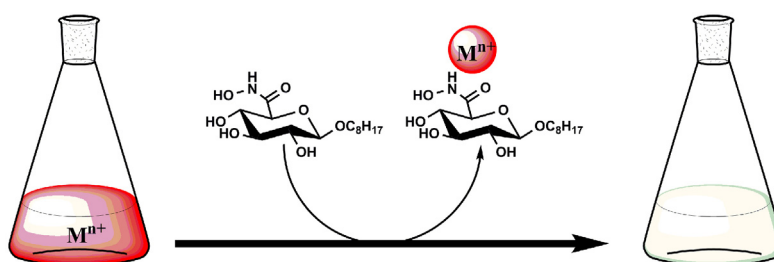
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HIGHLIGHTS

- Sugar based chelating surfactants are used for metal recovery from water phases.
- Relations between surfactant structures and interfacial properties are studied.
- Flotation concerns Fe(III), Cu(II), Cr(III), Cd(II), Zn(II), Ni(II) and As(III) ions.
- Different parameters are modulated for flotation experiments with Fe(III).
- Species distribution diagrams for surfactant-Fe(III) are studied.

GRAPHICAL ABSTRACT



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ABSTRACT

Derivatives of octyl glucoside modified by the introduction of a chemical function (carboxylic acid, hydroxamic acid) able to enhance the complexing properties of the surfactants toward metallic cations have been used as flotation collectors to remove various metallic cations from a water phase. Flotation experiments at the laboratory scale were performed on Fe(III), Cu(II), Cr(III), Cd(II), Zn(II), Ni(II) and As(III) aqueous solutions. The most interesting results were obtained in the extraction of Fe(III) and Cu(II). Interfacial properties were studied, and the effect of the polar head structure and anomeric configuration was analyzed. Structural variations have an influence on the efficiency and the foaming ability of these compounds. The introduction of a chelating functionality preserves the interfacial performances of these surfactants. Complexes equilibrium constants and species distribution diagrams for Fe(III) and the best flotation agents 2a and 2b were determined from multi-wavelength spectrophotometric pH titration. Both compounds showed analogous values for $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$. The bidentate Fe(III)-hydroxamate species (2:1 surfactant-metal ratio) reached a maximum concentration in the pH range of 5.5–6.5. At this pH, the best results in the flotation experiments were obtained for both compounds.

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1. Introduction

Metals and heavy metals are nowadays considered as a problem of public health since they are very toxic and dangerous depending on their concentration [1]. Although they can be of natural

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occurrence (volcano is one of the main natural sources of concentrated metals in the environment), pollution by metals and especially by heavy metals, results mainly from human activities (ore extraction, mine wastes and oxidation of mineral sulphurs, metallurgy [2], domestic wastes, transports [3], agriculture, mud from refining station for water, hunting. . .). Their harmfulness is provided by their accumulation or bioaccumulation in the soils [4] and water [5] and then transferred in plants and animals [6]. Some of them are necessary to the organisms in small amounts (Ni, Cu, Zn) while others are toxic (Hg, Pb) even in small quantities [7]. The World Health Organization considers that Cd, Pb, Hg and As as critical pollutants. Fe is also considered as toxic in some human disorders [8a] or as a nutrient disorder affecting the growth of some rice species [8b].

Remediation of polluted soils and water is a technological problem, and numerous technologies can be employed depending on the pollutant and the polluted material. Among the different treatments of the pollution, biological and chemical methods have been developed. The most used biological treatment is phytoremediation [9] which is the absorption of the metal by a plant organism that needs it. Biosorption of heavy metals by metabolically inactive non-living biomass of microbial or plant origin is an alternative technology [10]. A wide range of chemical treatments is possible. Some technologies to remove soil pollution consist in the transfer from soil to water by solubilisation. This can be done by acidification and/or by the use of a chelating agent like ethylenediaminetetraacetic acid (EDTA). To remove a metal from water, a precipitation can be effected after an oxidation or a pH change. Other technologies are flocculation [11], ion exchange [12], reverse osmosis with a membrane [13], electroremediation [14] and flotation [15,16]. In flotation, metallic pollutants of an aqueous phase are eliminated by addition of surfactants. After complexation of the metal by the surfactant, air is bubbled to make foam rich in metallic particle which is removed from water (Fig. 1).

Ion flotation may be useful, for example, for separating ions of value from a process solution, or for detoxifying waste solutions prior to discharge. Surfactants bearing a complexing functionality like EDTA, amidoxime or hydroxamic acid have been prepared and employed in flotation experiments [17]. Collecting agents must display three properties: being able to chelate the metallic particle, being able to foam and being safe for the environment.

Alkyl glycosides are monomeric non-ionic surfactants. In industrial scale, they are prepared from fatty alcohols and carbohydrates and they are gradually replacing other known non-ionic surfactants derived from petrochemical industry. Due to their excellent biodegradability and the absence of toxic effects, food elaboration, polymer manufacture, and solubilization of biological membranes are some of the wide spectrum of their applications [18]. Different sugar-based surfactants have been described in the literature [19]. The carbohydrate polar head has multiple hydroxyl groups with defined orientation, allowing the formation of strong cooperative hydrogen bonds between the surfactant molecules. This fact, together with the hydrophobic interaction between the long hydrocarbon chains, leads to spontaneous association in water [20]. Sugar based surfactants are compatible with the three properties required, a sugar moiety can chelate cationic species with

hydroxyl groups, they can be good foaming agents and are easily biodegradable. Moreover, alkyl glycosides are easily prepared from renewable raw materials: carbohydrates and fatty alcohols. The synthesis of sugar-based surfactants bearing an additional chelating function would improve the efficiency of the flotation process.

In previous works in our laboratories, the synthesis of a new type of surfactants and the determination of their interfacial and flotation properties with Fe(III) have been described [21]. Carboxylic and hydroxamic acids have been chosen for their known properties as metal collectors. These functionalities were obtained by oxidation of the primary alcohol of the sugar and coupling with hydroxylamine, glycine, aspartic acid and glutamic acid. In this paper, we report on the use of octyl glucoside based surfactants modified with carboxylic or hydroxamic acid group as collecting agents in flotation experiments to extract metallic cations (Fe(III), Cu(II), Cr(III), Cd(II), Zn(II), Ni(II) and As(III)) from aqueous solutions. The influence of structural features on the behaviour of this chelating surfactants is analyzed through changes in interfacial properties: CMC, the critical micellar concentration; Γ_m , the surface excess concentration at surface saturation, a useful measure of the effectiveness of adsorption; a_m^s , the area per molecule at the interface at surface saturation; ΔG°_{mic} , the standard free energy of micellisation; ΔG°_{ads} , the standard free energy of adsorption; pC_{20} , the negative logarithm of the bulk liquid phase concentration of surfactant required to depress the surface tension of the solvent by 20 mN/m, a good measure of the efficiency of the adsorption of the surfactant; and the CMC/ C_{20} ratio, a convenient way of measuring the relative effects of structural factors on the micellisation and the adsorption processes. To better understand the extraction process, we analyzed the complexation for the best extraction experiments i.e. for compounds **2a** and **2b** and Fe(III). Complexes equilibrium constants for compounds **2a** and **2b** and Fe(III) were determined by multi-wavelength spectrophotometric pH titration. The species distribution diagrams allowed identifying the predominant species and the pH conditions for maximum efficiency in metal removal.

2. Materials and methods

2.1. Surfactants and other reagents

The synthesis and the characterization of the surfactants (Fig. 2) have been previously reported [21]. All the reagents used were analytical grade and were purchased from Merck.

2.2. Flotation experiments

Flotation experiments were performed with aqueous solutions containing the studied metal using a device reported previously (Fig. 3) [21a]. A 0.35 mM solution of the corresponding metal (FeCl₃, CuCl₂, CrCl₃, CdCl₂, NiCl₂, AsCl₃) in milli-Q water (solution 1). Separately, a 1.75 mM solution of the surfactant (solution 2) in milli-Q water was prepared. For the flotation experiment, 10 mL of the solution 1 and 10 mL of the solution 2 were mixed, corresponding to a 5.0 ligand/metal ratio. 4 mL of this solution were introduced in the flotation column. Air was bubbled from the bottom of the column

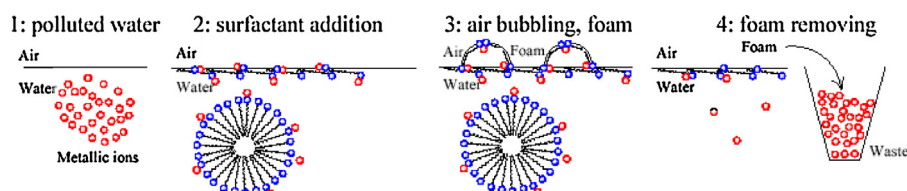


Fig. 1. Schematic representation of the flotation procedure.

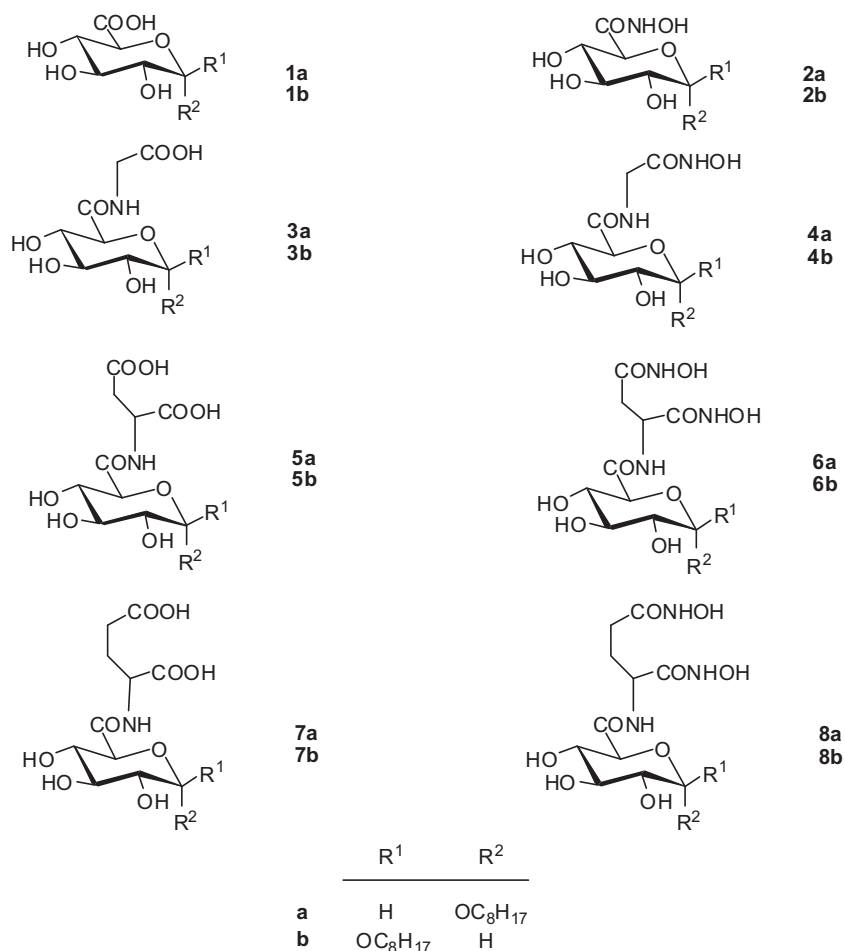


Fig. 2. Chelating surfactants studied.

for 2 min. The foam produced was recovered through the lateral tube. At the end of the experience, the concentration in metal of each phase (foam phase and residual liquid phase) was determined. Flotation experiments were performed in triplicates.

2.3. Analysis of the metallic cation concentrations

The metal concentration in both the extracted foam ($C_{\text{metal}}^{\text{foam}}$) and the residual liquid ($C_{\text{metal}}^{\text{liquid}}$) in the column after flotation was quantified by inductively-coupled plasma-atomic emission spectrometry (ICP) in a Perkin–Elmer Optima 2000 Dual View, using the following conditions: Ar flux plasma 15 L min⁻¹, nebulization 0.5 L min⁻¹, auxiliary 0.7 L min⁻¹, RF 1500 W, wavelengths (Fe) 239.562 and 259.393 nm, (Cd) 228.802 nm, (Cr) 267.176 nm, (Cu) 327.393 nm, (Zn) 213.857 nm, (Ni) 341.476 nm, (As) 189.053 nm and (Y) 371.030 nm. A matrix effect being

observed for the surfactant, the determination was performed using the method of measured additions and/or internal standard (yttrium). Extraction coefficients (EC) of the tested compounds were expressed as the concentration ratio of metal in the foam and in the liquid phase after the flotation experiment, see Eq. (1).

$$EC = \frac{[\text{metal}]_{\text{foam}}}{[\text{metal}]_{\text{liquid}}} \quad (1)$$

2.4. Surfactants interfacial properties

Air–water surface tensions (γ) were measured at 25 °C in a specially adapted tensiometer based on the bubble pressure method [22,23] and plotted vs. log C to get critical micellar concentrations (CMC). CMC measures were performed in milli-Q water. Calibration was performed against a range of standard liquids; excellent agreement with the literature values was found [23]. For some derivatives, their low solubility in water did not allow us to determine the CMC in this solvent, and the measure was done in a 8:2 water–ethyleneglycol mixture, as indicated in Table 1.

$$\Delta G_{ad}^0 = -\frac{RT \ln C_{\pi}}{55.5} - \pi a_m^s \quad (2)$$

$$\Delta G_{mic}^0 = RT \ln \left(\frac{CMC}{55.5} \right) \quad (3)$$

Other interfacial properties were calculated according to known methods [24]. For example, ΔG_{ads}^0 and ΔG_{mic}^0 were calculated using Eqs. (2) and (3):



Fig. 3. Flotation device.

Table 1
n-Octyl α -D-Glucopyranosiduronic acid derivatives.

Compound	γ_{CMC} (mN/m)	CMC/ C_{20}
1a	29.5 \pm 0.7	4.5 \pm 0.6
1b	31.3 \pm 0.7	2.7 \pm 0.3
2a	36.6 \pm 0.7	4.3 \pm 1.4
2b	32.9 \pm 0.7	3.9 \pm 0.5
3a	34.8 \pm 0.7	4.6 \pm 0.8
3b	34.8 \pm 0.7	1.9 \pm 0.1
4a	37.0 \pm 0.7	2.7 \pm 0.3
4b	34.1 \pm 0.7	1.9 \pm 0.2
5a	38.4 \pm 0.7	2.5 \pm 0.3
5b	38.4 \pm 0.7	3.3 \pm 0.2
6a ^a	45.4 \pm 0.7	1.1 \pm 0.2
6b	n.d.	n.d.
7a	32.7 \pm 0.7	2.9 \pm 0.9
7b	39.8 \pm 0.7	2.6 \pm 0.2
8a	40.5 \pm 0.7	3.2 \pm 0.4
8a ^a	46.2 \pm 0.7	1.1 \pm 0.1
8b ^a	44.8 \pm 0.7	1.2 \pm 0.2
Octyl α -D-glucopyranoside	36.4 \pm 0.7	–

^a Determined in 8/2 water–ethyleneglycol. n.d. = not determined due to insolubility.

2.5. Spectrophotometric studies of complexes, constants determination

UV–Vis spectra were recorded with an Agilent 8453 Diode Array Spectrophotometer in a quartz cell in the region 300–800 nm. pH values were recorded with a Hanna pH210 potentiometer (Hanna Instrument). Acid dissociation constants of **2a** and **2b** were determined by potentiometric pH titration. Stability constants of the complexes Fe-**2a** and Fe-**2b** were determined from multi-wavelength spectrophotometric pH titration data using dissociation constants previously calculated. The refinement of thermodynamic constants were performed in PKFIT [25] computer program running in Matlab 7.1 (R14). The experimental setup is shown in Fig. 4.

A 100 mL beaker was filled with 50 mL of a 0.5 mM Fe(III) and 2 mM surfactant solution. An aliquot of HCl 0.1 M was added to reach a suitable pH to start titration (around 2). KNO₃ was added to a final concentration of 0.1 M to maintain the ionic strength

constant during titration. Suitable aliquots of 0.1 M (or 0.01 M) KOH were added to cause a change in pH of about 0.2 units by addition. UV–Vis spectra and pH were recorded after the time needed to assure a stable pH measure (around 2 min). The procedure was repeated to cover all pH range. Using a peristaltic pump Gilson Min-Pulse3 the liquid was continuously delivered to a flow cell placed in a diode array spectrometer and then back to the beaker. A glass pH electrode was placed into the beaker to record the pH. Liquid handling was done using PTFE tubing 0.75 mm ID. The procedure was repeated to cover all pH range. Raw data were smoothed by a Savitzky–Golay filter (11 points) [26].

3. Results and discussion

3.1. Surfactants structure

The chelating surfactants (Fig. 2) possess an octyl chain as lipophilic moiety, whereas the sugar backbone constitutes the polar head. While the hydroxyl groups of the polar head can chelate cationic species, additional complexing functionalities like carboxylic acid or hydroxamic acid would reinforce this property. Monocarboxylic acids or monohydroxamic acids were obtained from octyl glucoside (compounds **1a–b** and **2a–b**) or from further coupling to glycine (compounds **3a–b** and **4a–b**). Dicarboxylic acids and dihydroxamic acids were obtained after coupling to aspartic acid (compound **5a–b** and **6a–b**) or glutamic acid (compounds **7a–b** and **8a–b**).

3.2. Determination of interfacial properties

Interfacial properties are important parameters for flotation applications. The floatability of chelating surfactant–metal complexes depends on both chelating properties and the interfacial behaviour, because stable foam is required for efficient metal removal.

CMC were determined by extrapolation of surface tension vs log(concentration) curves. All compounds showed the typical graphics, with an abrupt change in slope at the zone corresponding to CMC. Plots of γ vs log C for compounds **1–8** are shown (Fig. 5).

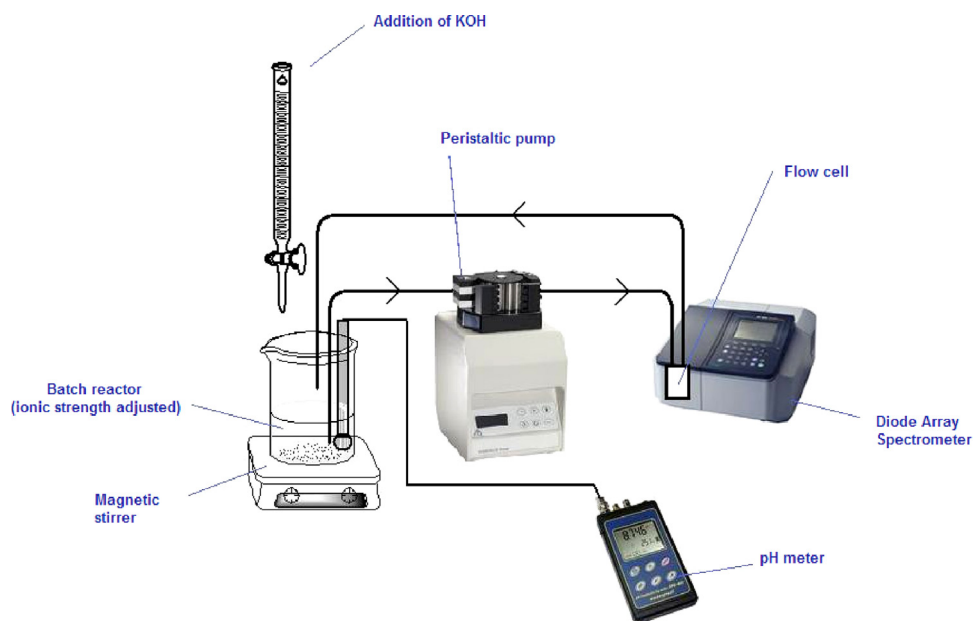


Fig. 4. Potentiometric pH titrator.

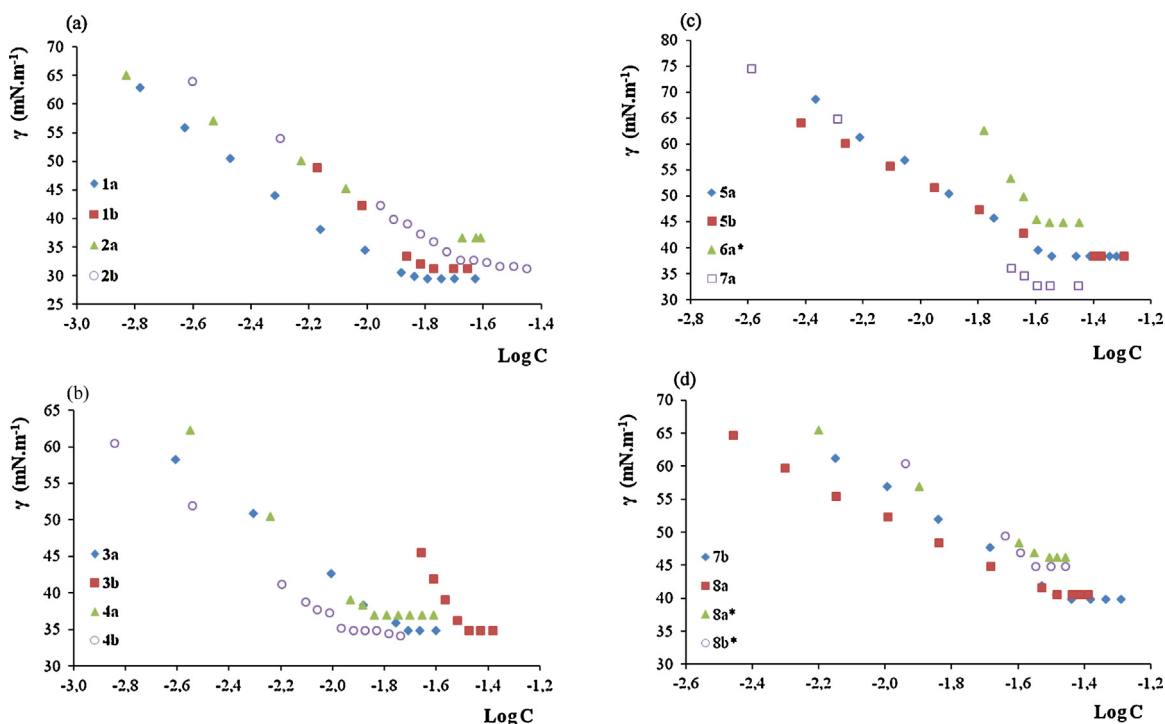


Fig. 5. Surface tension (γ) vs log (concentration) plots for compounds **1–8** in water or (*) in 8:2 water-ethylenglycol. (a) Compounds **1a**, **1b**, **2a** and **2b**. (b) Compounds **3a**, **3b**, **4a** and **4b**. (c) Compounds **5a**, **5b**, **6a*** and **7a**. (d) Compounds **7b**, **8a** and **8b***.

The CMC values and other interfacial properties were calculated from these plots. From the analysis of the CMC and of the surface tension at CMC (γ_{CMC}) values [21b], we concluded on the ability of the surfactants **1–8** to make foam. In the present article we analyze key parameters as γ_{CMC} and CMC/ C_{20} (Table 1). The complete data and their analysis are shown in Table S1 (Supplementary Content).

The surface tension at CMC (γ_{CMC}) is a useful measure of the effectiveness of the surfactants to reduce the surface tension of the solvent and it is the lowest value of surface tension that the surfactant-solvent system can reach. A low surface tension at CMC would favour foaming properties. Values are about the same magnitude than octyl α -D-glucopyranoside. Compound **1a** is the most effective surfactant ($\gamma_{\text{CMC}} = 29.5 \text{ mN m}^{-1}$) and compound **8a** has the highest γ_{CMC} value (40.5 mN m^{-1}) being the least effective one in water (Fig. 6).

It is also interesting to compare the CMC/ C_{20} ratio. A higher CMC/ C_{20} ratio indicates that the hydrophobic groups are less suitable oriented to accommodate themselves in the internal part of the micelles. In general, for all type of surfactants the adsorption on the surface of aqueous solutions is preferred over the formation of micelles [27]. The larger CMC/ C_{20} values indicate a greater preference of the surfactant to be adsorbed at the water-air interface relative to their preference to form micelles. The surfactants

showing the best properties are compounds **1a**, **2a**, **2b** and **3a**. For mono-carboxylate or mono-hydroxamate compounds, CMC/ C_{20} values of α -compounds (**1a–4a**) are higher than those of β -anomers (**1b–4b**). Therefore, the adsorption process is more favoured over the micellisation in compounds bearing axial octyl chains. For di-carboxylate or di-hydroxamate derivatives, however, no correlation can be found, and differences fall into the experimental error.

As the γ_{CMC} values of compounds **1a**, **2a**, **2b** and **3a** are about the same magnitude or lower than the one of octyl α -D-glucopyranoside, we could conclude that the two most efficient and interesting surfactants bearing a carboxylic group are compounds **1a** and **3a**; and the two most efficient and interesting surfactants bearing a hydroxamic group are compounds **2a** and **2b**.

3.3. Extraction of metallic cations from water phases by flotation

Flotation experiments were performed with the device shown in Fig. 3. Briefly, a solution containing the metallic pollutant and 5 equivalents of surfactant was poured in the flotation column and air bubbling was introduced from the bottom during 2 min. The foam formed was recovered by the lateral tube. This duration is sufficient to examine the expected concentration of the metal on the recovered foam. Metal concentration in both the foam and the remaining

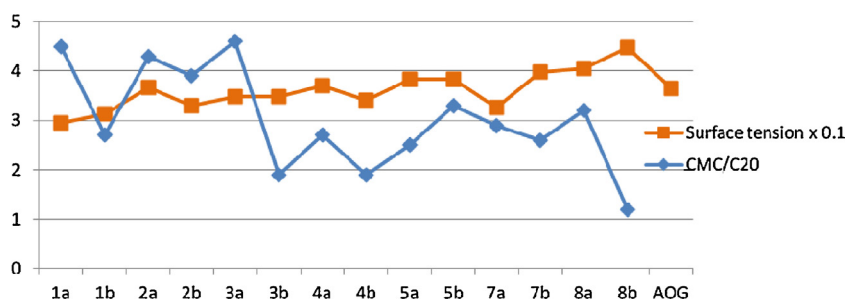


Fig. 6. Surface tension (γ_{CMC} in $\text{mN m}^{-1} 10^{-1}$) and CMC/ C_{20} for compounds **1** glucoside octyl α -D-glucopyranoside (AOG) in water.

Table 2
Extraction coefficient ($[M^{n+}]_{\text{foam}}/[M^{n+}]_{\text{liquid}}$) of metal recovery from water solutions by chelating surfactants in flotation experiments.

Compound	Fe(III)	Cu(II)	Cr(III)	Cd(II)	Zn(II)	Ni(II)	As(III)
1a	1.20 ± 0.05	1.0 ± 0.1	0.8 ± 0.2	1.00 ± 0.08	0.9 ± 0.1	0.82 ± 0.02	n.d.
1b	0.9 ± 0.2	0.70 ± 0.03	0.3 ± 0.2	1.03 ± 0.04	0.92 ± 0.08	0.90 ± 0.03	n.d.
2a	2.3 ± 0.4	2.4 ± 0.3	0.8 ± 0.2	1.01 ± 0.04	1.03 ± 0.05	0.98 ± 0.07	1.01 ± 0.04
2b	3.2 ± 0.3	1.6 ± 0.4	1.1 ± 0.6	1.00 ± 0.05	1.1 ± 0.1	1.0 ± 0.1	1.1 ± 0.1
3a	2.7 ± 0.5	1.00 ± 0.08	1.03 ± 0.07	1.0 ± 0.1	1.09 ± 0.08	1.03 ± 0.05	1.01 ± 0.01
3b	1.7 ± 0.3	1.2 ± 0.4	1.01 ± 0.02	1.05 ± 0.05	1.1 ± 0.1	1.02 ± 0.01	0.98 ± 0.03
4a	1.8 ± 0.6	0.96 ± 0.08	1.05 ± 0.05	0.97 ± 0.03	1.1 ± 0.1	1.05 ± 0.04	1.0 ± 0.1
4b	2.1 ± 0.1	1.1 ± 0.2	0.96 ± 0.05	1.0 ± 0.1	1.22 ± 0.08	1.06 ± 0.07	1.0 ± 0.1
5a	2.2 ± 0.5	1.1 ± 0.3	1.04 ± 0.01	1.02 ± 0.04	0.84 ± 0.08	1.1 ± 0.2	1.0 ± 0.1
6a	1.8 ± 0.6	1.0 ± 0.1	1.08 ± 0.03	1.02 ± 0.06	1.06 ± 0.07	1.3 ± 0.1	1.00 ± 0.05
7a	1.8 ± 0.7	1.0 ± 0.2	1.03 ± 0.02	1.0 ± 0.1	1.0 ± 0.1	1.13 ± 0.08	0.98 ± 0.01
7b	1.0 ± 0.1	1.1 ± 0.2	n.d.	n.d.	1.0 ± 0.1	n.d.	n.d.
8a	2.0 ± 0.5	1.0 ± 0.1	1.1 ± 0.3	1.02 ± 0.07	1.0 ± 0.1	1.14 ± 0.05	1.02 ± 0.03
8b	1.2 ± 0.5	1.0 ± 0.2	1.0 ± 0.1	1.00 ± 0.03	1.01 ± 0.08	1.07 ± 0.04	1.01 ± 0.01

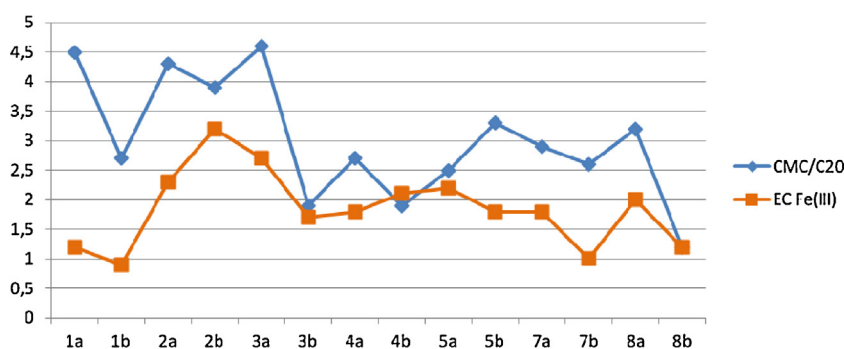


Fig. 7. CMC/C₂₀ (×10) and extraction coefficient of Fe(III) for compounds 1–8.

liquid in the column after flotation were quantified by ICP. The results obtained for our chelating surfactants are summarised in Table 2 for Fe(III), Cu(II), Cr(III), Cd(II), Zn(II), Ni(II) and As(III). They are expressed as the concentration ratio of metal in the foam and in the liquid phase after the flotation experiment.

Some interesting findings can be noted from the results shown in Table 2. Almost all surfactants displayed very good Fe(III) recoveries, the best performances were observed for compounds **2a**, **2b**, **3a**, and **5a** (ratios 2.3, 3.2, 2.7 and 2.2, respectively). It is interesting to note that dicarboxylic and dihydroxamic acids did not present any improvement respect to compounds bearing only one function. Most of the compounds tested were not efficient for Cu(II) recovery, except **2a** and **2b** (ratios 2.4 and 1.6, respectively). Again, no improvement was observed for divalent compounds. All compounds showed poor performance extraction for Cr(III), Cd(II) and As(III) with no improved concentration of the metal in the foam phase. On the other hand, compound **6a** with aspartic dihydroxamate as polar head displayed a slightly improved performance of Ni(II) extraction (ratio 1.3) and compound **4b** with a glycine hydroxamate poorly extract Zn(II) (ratio 1.22). From these results, the simplest hydroxamate **2b** followed by **3a** and **2a** would be the best choice for collecting Fe(III) whereas **2a** followed by **2b** would be the best choice for collecting Cu(II). A trend can be observed between the extraction coefficient of Fe(III) and the CMC/C₂₀ parameter (Fig. 7).

A higher CMC/C₂₀ parameter is favourable to the extraction of Fe(III). The greater preference of the surfactant to be adsorbed at the water–air interface relative to their preference to form micelles should be of importance in the extraction process.

3.3.1. Effect of a mixture of anomers on the extraction coefficient

To envisage a large scale synthesis and industrial applications, it is important to work with the mixture of anomers as their chromatographic separation is difficult. Then we studied the extraction

Table 3
Extraction coefficient of Fe(III) recovery from water solutions by **2a** and **2b**.

Compound	2a	2b	2a + 2b(1:1)
$\frac{[Fe(III)]_{\text{foam}}}{[Fe(III)]_{\text{liquid}}}$	2.3 ± 0.4	3.2 ± 0.3	4.0 ± 0.6

of Fe(III) by compounds **2a** and **2b** (our best flotation results). Surprisingly, a synergistic effect was observed (Table 3) for compounds **2a** and **2b**, as a 1:1 mixture of both compounds allowed to reach a concentration ratio (foam/liquid) of 4.0 for Fe(III).

As the predominant species are FeL_2^+ (see section 3.4), the ternary complex $FeL_\alpha L_\beta^+$ would favour the extraction through a better accommodation of the alkyl chains.

3.3.2. Effect of the foaming properties on the extraction coefficient

Regarding foaming properties, foaming formation and foam stability have been considered qualitatively based on empirical observation during flotation experiments. The influence of foaming performances on metal removal during flotation experiments is more evident for some examples shown in Table 4.

Some surfactants, as compounds **1b** and **7b** are showed poor foaming properties in presence of either Fe(III) or Cu(II), whereas **2b** displayed very good foam formation whatever the metal to be considered. On the other hand, foaming properties of compound **8a** changed from good (for Fe(III)) to poor (for Cu(II)), and this behaviour can be correlated with the differences observed in metal recovery. Most of the time, a good extraction coefficient is correlated to good foaming properties. But formation of foam does not necessarily implicate concentration of the metal in the foam as it is shown for the diad **1a**-Cu(II). It seems that the metal-surfactant complex has to be adsorbed at the water-air interface to be extracted efficiently.

Table 4
Foaming properties of chelating surfactants–metal diades.

Compound	Fe(III)		Cu(II)			
	$\frac{[\text{Fe(III)}]_{\text{foam}}}{[\text{Fe(III)}]_{\text{liquid}}}$	Foaming	Stability	$\frac{[\text{Cu(II)}]_{\text{foam}}}{[\text{Cu(II)}]_{\text{liquid}}}$	Foaming	Stability
1a	1.2	+	+	1.0	++	++
1b	0.9	–	–	0.7	–	–
2b	3.2	++++	++++	1.6	++	+
7b	1.0	+	–	1.1	–	–
8a	2.0	+++	+++	1.0	+	+

3.3.3. Effect of a mixture of metallic cations on the extraction coefficient

Moreover, the foaming/extracting properties of these chelating surfactants for a particular metal seem to be influenced by the presence of other metals. Significant differences were observed on flotation experiments using compound **2a** with a solution containing several metals (Table 5), when compared to the results obtained with the same compound but using a single metal.

Using a solution containing a mixture of Fe(III), Cu(II), Cr(III) and Cd(II) (5 ppm each), a preferential extraction of Cu(II) was observed, with a concomitant diminution of Fe(III). No changes were observed with Cr(III) and Cd(II). This interesting result is important to be taken into account considering that in polluted wastewater metallic cations appear generally as complex mixtures. This result is difficult to analyse, probably due to the complexity of the equilibria and extraction process. Each metal is in competition to form metal-surfactant complexes and each complex can be extracted with the help of the foam generated by other complexes.

3.3.4. Effect of pH on the extraction coefficient

The removal efficiency of metals from wastewater can be influenced by experimental conditions such as operating parameters, physical, chemical and biological factors [28]. pH is a factor which can modify the ionic or neutral state of the ligand and the composition of metallic species. As a first approach, all the flotation experiments have been conducted without pH control to have a general view on the flotation properties. However, depending on the nature and concentration of the ligand or of the metal a pH modification can be induced leading to differences in the flotation results. For instance, in the case of Fe(III), Fe^{3+} is the major specie only at $\text{pH} < 2$. At higher pH, several hydroxyl species can successively be formed as the pH is increased (FeOH^{2+} , FeOH_2^+ , “ $\text{Fe}(\text{OH})_3$ ”, $\text{Fe}(\text{OH})_4^-$ or even polynuclear hydroxyl species). “ $\text{Fe}(\text{OH})_3$ ” denotes the inorganic polymerization giving dimers and oligomers resulting from olation or oxolation condensations [29]. Such olation and oxolation reactions can thus be responsible of the formation of precipitates and lower the concentration of soluble Fe(III) species. The extraction of a metal by flotation, notably the pH thus needs to be optimized for each ligand–metal system. Therefore, pH will influence the complexes formation [30] and their extraction. Extraction coefficients were determined at three pH for the diads **2a**–Fe(III) and **2b**–Fe(III). Acid dissociation constants of **2a** and **2b** were determined by potentiometric pH titration.

$$\text{HL} = \text{L}^- + \text{H}^+ \quad \text{pKa}(\mathbf{2a}) = 9.3 \pm 0.2, \quad \text{pKa}(\mathbf{2b}) = 9.5 \pm 0.2$$

where HL = hydroxamic acid and L^- = hydroxamate anion.

Ion flotation experiments for Fe(III) and compounds **2a** and **2b** were conducted at pH 3.0, 6.0 and 11.0 (Table 6). Maximum

Table 5
Extraction coefficient of one metal solutions vs mixture of metals.

Compound 2a	Fe(III)	Cu(II)	Cr(III)	Cd(II)
Single metal	2.3 ± 0.4	2.4 ± 0.3	0.8 ± 0.2	1.01 ± 0.04
Multiple metals	1.6 ± 0.2	3.0 ± 0.5	1.0 ± 0.1	1.0 ± 0.1

efficiency on metal removal was reached at pH 6.0. No significant extraction was observed at pH 3 or 11.

This can be the result of differences in the composition of Fe(III) complexes and ligand (see Section 3.4). At pH 3, the major Fe(III) complex is FeL^{2+} but most of the ligand stay free in solution. In this case, the flotation is probably due to the free ligand **2a** or **2b**, the major surface active species in solution. FeL^{2+} which is probably not adsorbed at the air–water interface, is then extracted with the water solution. At pH 6, the major Fe(III) complex is FeL_2^+ . It seems that this specie is surface active and responsible of the flotation. At pH 11, the major Fe(III) complex would be $\text{Fe}(\text{OH})_4^-$. The specie responsible of the foam formation is then L^- . At this pH, like at pH 3, the Fe(III) complexes are then extracted with the water solution without adsorption at the air–water interface.

3.4. Stability and dissociation constants determination; speciation modeling of Fe(III)-**2a** and Fe(III)-**2b** systems

Ligand metal complexes may have different stoichiometries depending upon the complex stability constants and the pH of the solution. For a particular metal–ligand system, species distribution diagrams, obtained from spectrophotometric studies show relative abundance of each species as a function of pH. This information is very helpful in clarifying the mechanism and species by which metals are removed from solution. Absorbance matrix obtained for Fe(III)-**2a** and Fe(III)-**2b** are shown in Fig. 8.

Hydroxamic acids are known to form stable complexes with Fe(III). The Fe(III)–hydroxamate system exhibits three complexes at L:Fe mole ratios of 1:1, 2:1, and 3:1. A Principal Component Analysis [31] of data obtained shows three significant factors which explain more than 99% of the spectral variation. These three factors are attributed to FeL^{2+} , FeL_2^+ and FeL_3 species. This may not be concluded by inspection of matrix absorption data. The consistency of the parameters obtained was evaluated by computing the mean square error in the prediction of spectral details (RMSEP), obtaining a RMSEP (**2a**) = 0.008 and RMSEP (**2b**) = 0.002. These values are very close to instrumental noise and indicated an excellent model fit. Stability constants $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ for complex formation of Fe(III) with compounds **2a** and **2b** were simultaneously determined using the previously determined acidity constants pKa as input in the refinement. The results obtained are in accordance with values found in the literature [32] for other Fe(III)–hydroxamate systems.

$$\begin{aligned} \text{Fe(III)} + \text{L}^- &\rightleftharpoons \text{FeL}^{2+} \quad \text{Log}\beta_1(\mathbf{2a}) = 10.15 \pm 0.27, \quad \text{log}\beta_1(\mathbf{2b}) \\ &= 10.15 \pm 0.15 \end{aligned}$$

Table 6
pH effect on extraction coefficient of Fe(III) by **2a** or **2b**.

pH	3	6	11
2a	0.98 ± 0.08	2.2 ± 0.2	1.02 ± 0.09
2b	1.01 ± 0.12	3.1 ± 0.3	1.03 ± 0.09

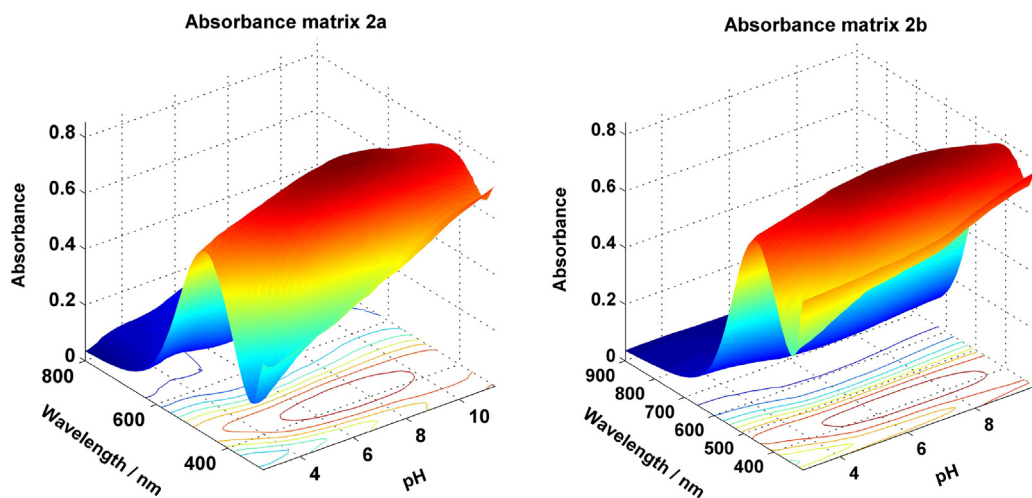
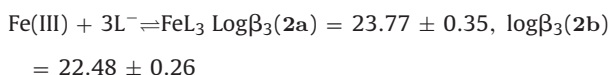
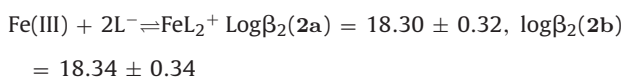


Fig. 8. Absorbance matrix for Fe(III)-**2a** and Fe(III)-**2b** systems.



where L^- = hydroxamate anion.

Both anomers show analogous values for $\log\beta_1$, $\log\beta_2$ and $\log\beta_3$. In order to investigate the coordination chemistry of the compounds **2a** and **2b**, speciation diagrams and spectrophotometric studies were calculated for the Fe(III)-hydroxamate systems at 298 K. The Fe(III)-hydroxamate interaction is characterised in the UV/Vis spectrum by a $\pi(\text{ligand}) \rightarrow d(\text{Fe})$ ligand-to-metal charge-transfer (LMCT) band. We monitored the reaction between Fe(III) and L with an Fe(III)/L ratio from 1:1 to 1:3 by spectrophotometry (Fig. 9).

Upon increasing the Fe(III)/L ratio, a bathochromic shift of the LMCT band was observed together with an increase in the

absorption intensity corresponding to the formation of the mono-, bis- and tris (hydroxamate) complexes of Fe(III). This result is consistent with those previously reported for Fe(III)-hydroxamate systems [33]. The 1:1 complexes give spectra with $\lambda_{\text{max}} \approx 420$ nm (**2a**), 400 nm (**2b**), the 1:2 complexes give spectra with $\lambda_{\text{max}} \approx 425$ nm (**2a**), 420 nm (**2b**), and the 1:3 complexes give spectra with $\lambda_{\text{max}} \approx 465$ nm (**2a**), 460 nm (**2b**). The corresponding speciation diagrams for Fe(III)-**2a** and Fe(III)-**2b** are shown in Fig. 10. Both systems have a 4:1 chelating surfactant/Fe(III) concentration ratio. For compound **2a**, $\text{Fe}(\mathbf{2a})_3$ starts to be present in appreciable concentration around pH 7.0, then the concentration increases from pH 7.0 to 9.0 reaching a plateau at pH 9.3. $\text{Fe}(\mathbf{2a})_2^+$ reaches a maximum concentration around pH 5.5. Meanwhile in the corresponding speciation diagram system for **2b**, $\text{Fe}(\mathbf{2b})_3$ starts to be present around pH 8.0 and its concentration increases from pH 8.0 to 9.5. $\text{Fe}(\mathbf{2b})_2^+$ reaches a maximum concentration around pH 6.5.

According to the results above described, it can be seen that in the pH range 5.5–6.5 the predominant species were FeL_2^+ where the chelating compound-metal ratio was 2:1 for both compounds (**2a** and **2b**). The best results in the flotation experiments were obtained at pH 6.0, supporting that the suggested ratio is the most efficient to remove Fe(III) from the system. These results suggest

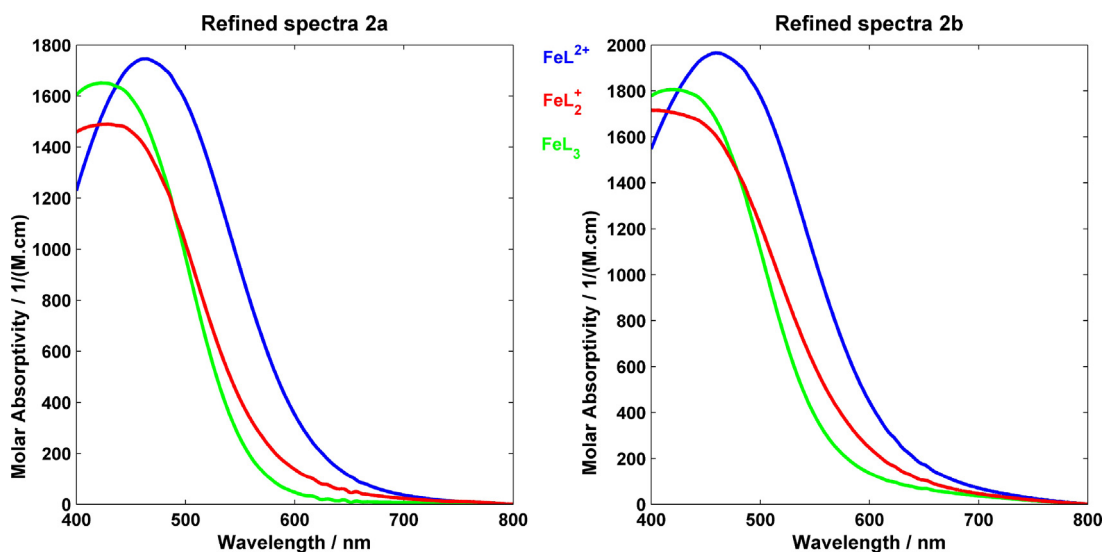


Fig. 9. Molar absorptivities calculated from multi-wavelength pH titration for each species of compound **2a** and **2b**.

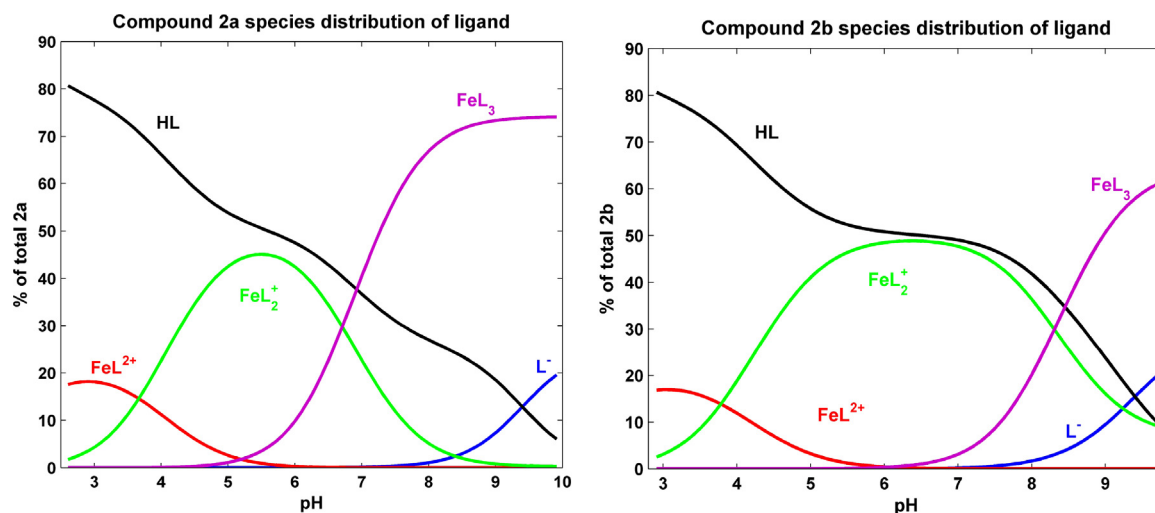


Fig. 10. Speciation diagrams for the Fe-2a and Fe-2b systems.

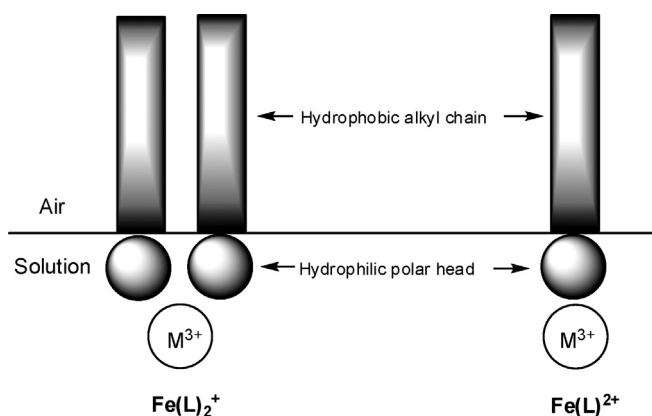


Fig. 11. Schematic configurations of $\text{Fe}(\text{L})_2^+$ and $\text{Fe}(\text{L})_2^+$.

that FeL_2^+ might be more surface active species than either FeL_3 or FeL^{2+} . The predominant species in alkaline and strong acidic media, respectively, would explain the results shown in Table 6.

The sugar $-\text{CONHOH}$ groups in FeL_3 would have to reside in the aqueous phase with all their polar atoms surrounded by water molecules, while the alkyl chain does not need to reside in the solution phase. Rather, it would be energetically favorable for this group to reside in the air phase, thereby allowing the ethylene groups in the alkyl chain to leave the aqueous solution (Fig. 11). Such an arrangement of FeL_2^+ at the solution/air interface would increase the effective hydrocarbon chain length of the FeL_2^+ species, making them more surface-active.

4. Conclusions

The introduction of a chelating functionality hardly affects the interfacial properties of sugar-based surfactants, which display γ_{CMCs} of the same order of magnitude as octyl glucopyranoside. However, subtle structural differences as anomeric configuration have a significant influence on interfacial properties. Changes are also observed between mono- and bidentate compounds. The correlation of interfacial properties or polar head functionalities with metal recovery of chelating surfactants reported here is not straightforward. A trend has been found between CMC/C_{20} of pure surfactants in water and the $\text{Fe}(\text{III})$ extraction coefficient. This indicates the prevalence of the adsorption phenomenon at the interface in the flotation process. The importance of the

adsorption phenomenon can explain the differences obtained for the flotation experiments at different pH. A good extraction coefficient would be dependent of a good adsorption of the complex surfactant-metal at the air-water interface. As a consequence, changes in the surfactant, metal and pH may produce different foaming behaviour and extraction capability. These results suggest that the final metal recovery by flotation is a subtle combination of the surfactant efficiency, the chelating functional group and the metal. Our results showed that in the pH range 5.5–6.5 the predominant species were FeL_2^+ (2:1 chelating compound-metal ratio) for compounds 2a and 2b. Since these compounds present the best results in the flotation experiments, these findings suggest that FeL_2^+ might be the most surface active species.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.09.041>.

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