Characterization of micelles formed by sucrose 6-*O*-monoesters

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A B S T R A C T

In the present study we synthesized and purified several 6-*O*-sucrose monoesters by using classical synthetic methods and stereo-regioselective procedures. The compounds have different alkyl chain lengths, with the number of methylene units ranging between 7 and 17. For all the available compounds the physicochemical information concerning the formed micellar aggregates was evaluated by using fluorescent methodologies. Cmc for the series show a clear linear dependence with the length of alkyl chain. Structural properties of the aggregate, like cross-sectional area or aggregation numbers show clear dependence on the number of methylene units. For shorter esters, the cross-sectional area is constant, probably consequence of the size of sucrose head, whereas for the longer ones is dependent on the length of alkyl chain. Aggregation number is dependent of ester concentration for shorter compounds and independent for the longer ones. These results show for 6-*O*-sucrose esters with different length of alkyl chain that its properties depend on the balance of the size of alkyl chain and sucrose head.

1. Introduction

Despite the significant number of publications on sugar fatty acid esters (SFAE) beginning in the mid-1950s, there is a renewed interest in these compounds with a noteworthy increase of studies in the last two decades. These studies have been motivated by their outstanding surface-active properties (surface tension-reducing capacity, penetrability into lipid bilayers, easiness of dispersion, and remarkable emulsifying power, among others) and their environmental advantages, when compared to surfactants derived from petrochemical industry [1,2]. SFAE are nontoxic and non-allergenic surfactants, readily biodegradable in aqueous environments [2,3]. The raw materials involved in their synthesis are low-cost, simple, effortlessly accessible and renewable: fatty acids or their derivatives and sucrose [4–7]. SFAE have a large number of applications in many fields such as cosmetic and health care [8,9]. Like food additives [9], they have a very large variety of functions such as emulsifying, foaming, improving components mixing, improving water holding, preventing denaturation, and avoiding precipitation. Sucrose esters with short hydrocarbon chain are widely employed to solubilize membrane proteins without causing denaturation and to extract specific compounds (i.e. enzymes, receptors, and transport carriers), and can also be removed by simple dialysis [10,11]. These non-ionic carbohydrate-based surfactants contain usually glucose, xylose or sucrose [12] as hydrophilic head. The hydrophobic tail of these compounds corresponds to hydrocarbon chains (of different length with or without insaturations), as a substituent on one specific hydroxylic group of sucrose.

Mixtures of sucrose esters, usually commercial preparations, are used in most of the reported work on physicochemical properties (e.g. characteristic micellar parameters, and surface activity) and functional properties (e.g. emulsification capacity and rheological modifications) [13,14], and a few basic studies have been made with pure sucrose monoesters [15–20] and pure diesters [21]. Commercially available sucrose esters are typically mixtures of mono-, di- and minor quantities of highly polysubstituted isomers, being the proportion of each, responsible for their specific hydrophilic–lipophilic balance (HLB value), among other properties. The recent increase in the number of studies dealing with physicochemical properties of carbohydrate-based surfactants reflects recognition that the knowledge, regarding the influence of the hydrophilic and lipophilic counterparts on application-related properties, needs to be expanded and clarified for this kind of surfactants. The present study, involving fluorescence measurements (steady state and time resolved) and surface tension determinations, intends to obtain and systematize physicochemical information (critical micellar concentration, and properties of the micellar aggregate such as micropolarity, microfluidity, shape and aggregation number) of the micellar aggregates formed by six pure 6-*O*-sucrose esters, with hydrocarbon chains ranging between 7 and 17 methylene units to report a homogeneous set of properties for a complete series of compounds.

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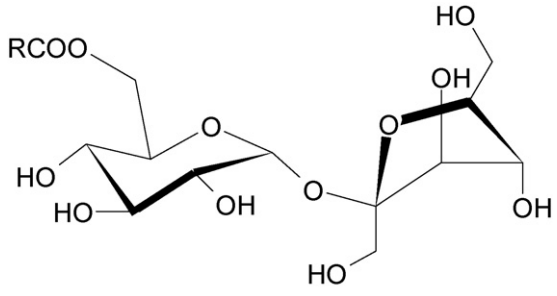
2. Materials and methods

2.1. Chemicals

6-Dodecanoyl-2-dimethylaminonaphthalene, Laurdan, from Molecular Probes and dibutylaniline, DBA, from Sigma were used as received. Pyrene, from Merck, was recrystallized twice from ethanol. Solvents from Merck were HPLC quality. Water was purified with Milli-Q equipment from Waters. Sucrose monoester β-D-fructofuranosyl-6-*O*-capryl-α-D-glucopyranoside (MCS), purchased from Dojindo Molecular Technologies, was used as received. The sucrose monoesters β-D-fructofuranosyl-6-*O*-lauryl-α-D-glucopyranoside (MLS), β-D-fructofuranosyl-6-*O*-miristyl-α-D-glucopyranoside (MMS), β-D-fructofuranosyl-6-*O*-palmityl-α-D-glucopyranoside (MPS) and β-D-fructofuranosyl-6-*O*-stearyl-α-D-glucopyranoside (MSS), were synthesized by a modification of the Osipow–Snell method [22,23], that yields a complex mixture of mono- (mainly 6-*O* and presumably 1-*O*), di- and tri-esters. The sucrose monoester β-D-fructofuranosyl-6-*O*-octyl-α-D-glucopyranoside (MOS) was synthesized by the Lindhart procedure [4]. Both methods yield a relatively complex mixture of mono (mainly 6-*O* and presumably 1-*O*) and polyesters. Chromatography on silica column was employed to isolate pure monoesters of all synthesized compounds, briefly, the reaction mixture was solubilized in chloroform and eluted from a semipreparative silica gel column by using chloroform:methanol:water (20:5:0.7) as mobile phase. Thin layer chromatography (using the same mobile phase and staining with a butanolic solution of urea–orthophosphoric acid) showed mainly one compound in the purified sample. The NMR spectra, obtained in a Bruker ADX 300 spectrometer, with $DMSO_{d\text{-}6}$ containing 5% of CH_3OD to avoid micellization, are in good agreement with previously reported spectra for several monoesters [4,24]. The chemical structures of the studied compounds are summarized in Fig. 1.

2.2. Fluorescence spectroscopy

Steady state fluorescence measurements of Laurdan and pyrene emission were accomplished in a Fluorolog τ-2 spectrofluorometer (SPEX, Jobin Ybon) at controlled temperature. The values of generalized polarization of Laurdan, GP (LAU 3 μM, λ_{ex} = 364 nm, λ_{em} = 440 nm and 490 nm), not corrected against DMSO value, were calculated by using the expression proposed by Parasassi et al., Eq.



R = C_7H_{15}	Octyl acid derivative	(MOS)
R = C_9H_{19}	Capric acid derivative	(MCS)
R = $C_{11}H_{23}$	Lauric acid derivative	(MLS)
R = $C_{13}H_{27}$	Myristic acid derivative	(MMS)
R = $C_{15}H_{31}$	Palmitic acid derivative	(MPS)
R = $C_{17}H_{35}$	Stearic acid derivative	(MSS)

Fig. 1. Chemical structure of studied sucrose monoesters.

Table 1
Critical micellar concentrations (in mM units) of sucrose esters determined by fluorescence measurements and surface tension determinations, at 25 °C

Surfactant	I/III (Py)	GP (Laurdan)	Surface tension
MOS	3.2600	nd	2.3400
MCS	1.4500	1.8000	0.4300
MLS	0.3427	0.3505	0.2726
MMS	0.0484	0.0238	0.0191
MPS	0.0150	0.0080	0.0055
MSS	0.0122	0.0100	–

(1) [25,26]

$$GP = \frac{(I_{440} - I_{490})}{(I_{440} + I_{490})} \quad (1)$$

Pyrene measurements involve the use of the ratio of its first and third emission bands (Py ratio or I_1/I_3, λ_1 = 372 nm, and λ_3 = 384 nm, with excitation at λ_{ex} = 337 nm) [27].

Pyrene time resolved fluorescence measurements were performed by using a Hamamatsu R928 photomultiplier mounted in a homemade housing and fitted to a PTI 01-001 monochromator exit slit port. Photomultiplier signals were monitored with a 500-MHz and 1 GSa/s Hewlett-Packard digital oscilloscope, model 54540A.

All emission measurements were performed at 25.0 ± 0.1 °C, controlling temperature with a Haake thermoregulated bath.

2.3. Measurements of sucrose ester critical micellar concentration

The values of the critical micellar concentration, cmc, were determined with fluorescent techniques by using both, pyrene or Laurdan emission as probes. Surface tension measurements performed with a Du Noüy tensiometer (K8 Krüss, measurement range 5–90 mN/m with Pt–Ir ring of 20 mm) were used also to determine cmc values. From plots of the change in emission intensity or surface tension values against surfactant concentration, cmc was determined from the point of slope change. All described measurements were performed at 25.0 ± 0.1 °C.

2.4. Measurement of sucrose ester aggregation number

Aggregation number, N_{agg}, were determined by employing time resolved fluorescence quenching experiments. Recorded fluorescence decay curves (Fig. 5) in presence of quencher were fitted to the Infelta–Tachiya equation [28,29], Eq. (2), by using GraphPad Prism Version 4.00 for Windows, GraphPad Software, San Diego CA, USA:

$$I = I_0 \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \quad (2)$$

where A_2, A_3 and A_4 are simple fitting parameters. The micelle aggregation number, n_{agg}, may be determined from [30]

$$n_{agg} = A_3 \left\{ \frac{C - \text{cmc}}{[Q]} \right\} [1 + \varepsilon]^2 \quad (3)$$

being ε a correction factor equal to:

$$\varepsilon = \frac{A_2 - \tau^{-1}}{A_3 A_4} \quad (4)$$

3. Results and discussion

3.1. Cmc determination

Cmc values determined by using surface tension measurements and fluorescence procedures are included in Table 1. The values are on the order of those reported for the same compounds enzymatically and non-enzymatically synthesized [1,4,12,13,19]. Cmc values

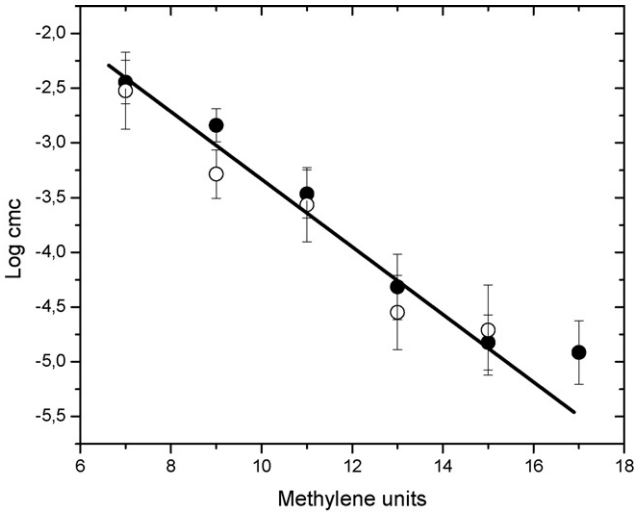


Fig. 2. Log cmc vs. number of methylene units, for surface tension measurements (○) and for fluorescence measurements (●). Values measured at 25 °C.

determined at 25 °C show noticeable differences when photophysical and physical measurements are compared, but the trends observed for the cmc dependence on the number of methylene units are clearly comparable, especially when the cmc values for compounds with longer chains are omitted (Fig. 2). The cmc values determined from both fluorescence and surface tension measurements show an inverse dependence with the number of methylene units (n). Longer alkyl chains, lower water solubility, hence aggregation occurs at lower concentration. If values for MSS are excluded, the dependence of cmc on the hydrocarbon chain length can be fitted according to the empirical equation of Stauff–Klevens (first employed and reported on polyoxyethylenic surfactants series) as can be seen in Fig. 2 [31]. This behavior, as expected, is consequence of the enhancement of chain hydrophobicity with the increase in the number of methylene groups.

For MSS, experimental difficulties (perhaps adsorption on Pt–Ir ring), do not allow the determination of cmc from surface tension measurements. For MOS, the value obtained is in accordance with the value reported by Garofalakis et al. [12], but is several times lower than the one reported by Molinier et al. [19].

3.2. Micelles micropolarity and microviscosity

The Py I_1/I_3 ratio and Laurdan GP are useful dimensionless parameters to determine cmc values, and also contain physical–chemical information of the microaggregate, not reported previously for these compounds. Py scale informs about polarity near the probe localization, meanwhile Laurdan generalized polarization is a measure of microviscosity (fluidity) and/or water accessibility. Both properties were determined when micellization begins and at higher sucrose ester concentrations (when the property reaches a plateau). The values determined for the I/III ratio at concentrations equal to the cmc and at higher concentrations are shown in Table 2. For short esters, the values for I/III ratio indicate a polar surroundings for the probe. For longer chain derivatives, I/III ratio values do not show a clear dependence on alkyl chain length, suggesting that probe senses environments of the same polarity for all cases. These results are indicative of two possible situations: the sensed micro-aggregates have indeed similar polarities independent on the alkyl chain, for $n \geq 12$, indicating a similar but not identical hydrocarbon packing for all systems or the probe migrates towards regions of similar characteristics. According to the Py scale the surroundings sensed by the probe are similar to pure *n*-octanol for higher monoesters and similar to methanol, for shorter ones [27]. For all studied systems there is a slight reduction of I/III ratio when micelle concentration increases, result compatible with an increase in the aggregation number at higher surfactant concentration.

Table 2
Pyrene I/III ratio and Laurdan GP values determined for the studied sucrose monoesters at concentrations equal cmc and in the plateau

Surfactant	I/III			*GP*
	cmc	Plateau	cmc	Plateau
MOS	1.40	1.20	0.097	0.095
MCS	1.25	1.20	−0.019	−0.080
MLS	1.10	0.92	−0.325	−0.341
MMS	1.00	0.98	−0.326	−0.343
MPS	1.08	0.93	−0.371	−0.367
MSS	1.18	0.90	−0.216	−0.215

Experiments performed at 25 °C.

The profiles of Laurdan generalized polarization (GP) values when plotted against sucrose ester concentration show clear breakpoints for shorter chain compounds (MOS to MMS), reaching a plateau. For all the measured compounds GP values are independent of the surfactant concentration, after micellization. The GP value for Laurdan incorporated to micelles, shows a reverse dependence with the increase of the alkyl chain length. This result can be understood in terms of the presence of bulky and highly substituted surfactant heads limiting water accessibility. Then the effect of the alkyl chain length is of secondary relevance over certain chain length. Octyl and lauryl esters, the shorter ones, show higher values of GP, indicating a more closed surface, with reduced water penetration, but higher polarity, according I/III ratio.

3.3. Surface activity

Surface tension measurements allow the determination of several important parameters. Accepting that Gibbs adsorption model describes the behavior of micellization for sucrose esters, from the plot of surface tension values against the natural logarithm of concentration, before micellization, is possible to determine the surface excess and the molecular area, according Eqs. (5) and (6):

$$\Gamma = -\left(\frac{1}{RT}\right)\left(\frac{\partial\gamma}{\partial\ \mathrm{Ln}\,C}\right)_{T,P} \tag{5}$$

$$A = \frac{1}{N_A\Gamma} \tag{6}$$

Fig. 3 shows profiles obtained for surface tension variation upon MMS addition, equivalent plots are obtained for all other SFAEs. None of the compounds studied gave cloudy solutions at work temperatures, as reported for other pure sugar esters [12].

Surface excess values were determined where a linear dependence between surface tension and concentration natural logarithm was observed. The surface excess values depend inversely on the hydrocarbon chain length, the area occupied by each molecule of surfactant increases with the increase of the length of alkyl chain. The values determined for A (cross-sectional area per molecule) are different for each ester, see Table 3. So, A not only depends on the bulky hydrophillic head group dimensions (sucrose plus solvation sphere) but also on packing and stereochemistry of whole structure [12]. Values calculated for A are on the order of the reported ones for pure enzymatically synthesized 6-*O*-monoesters, for 6-*O*-laurylsucrose an 6-*O*-palmitylsucrose Ferrer et al. [1] report values of 44 Å^2 and 91 Å^2, respectively (at 25 °C), and Garofalakis et al. [12] 53 Å^2 and 54 Å^2(at 32 °C). Garo-

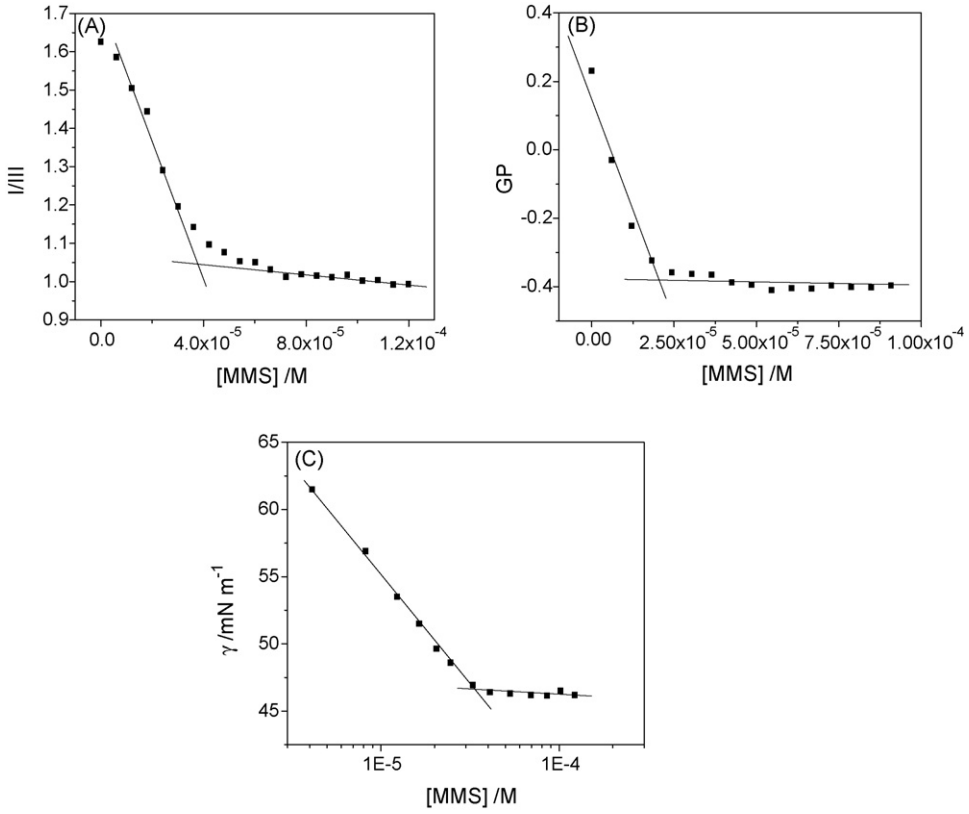


Fig. 3. Cmc determination of MMS employing I/III, GP and surface tension measurements.

falakis also reports values of cross-sectional areas for samples corresponding to mixtures of several monoesters, results that are somehow lower than ours, and always show independence on the alkyl chain length. Our results for cross-sectional areas show a constant value around 40–50 Å^2 for alkyl chains of 7–11 methylene units, but an important increase can be observed for longer alkyl chains, being the lauryl derivative (11 units) the breakpoint of this behavior. These results are shown in Fig. 4. Summarizing, the effect of the hydrophobic chain on the micelle properties, is only observed when the alkyl chain overpasses certain length (in this case the corresponding to a lauryl chain). According to the GP values reported in Table 2, this increase of the cross-sectional area seems not to be accompanied by a higher water penetration into the micelle, being the sucrose head groups an important barrier.

Table 3 also includes the values of surface tension at concentrations higher than cmc, γ_{lim}, which is a measure of the surfactant ability of each compound. The γ_{lim} values determined for the studied compounds are somehow higher than the reported ones [12].

The critical packing parameter, Cpp, defined only from interactions between amphiphilic molecules within the aggregate and geometrical considerations [32], is a useful criterion to predict the aggregate geometry [12,33].

$$\text{Cpp} = \frac{v}{(a_o l_c)} \tag{7}$$

where v corresponds to the hydrocarbon chain volume, assuming an incompressible fluid; a_o is the optimal headgroup area and l_c is the maximum effective length that the hydrophobic chains can assume, which corresponds to a semiempirical parameter known as the critical chain length. According to Tanford [34], for saturated hydrocarbon chain with n carbon atoms these parameters can be

Table 3
Surface excess (Γ), molecular cross-sectional area (A) and limit surface tension (γ_{Lim}) determined at 25 °C for all SFAE's

Surfactant	Γ (10^{-10} mol cm^{-2})	A (Å^2 molecule^{-1})	Cpp	γ_{lim} (mN m^{-1})
MOS	4.08	40.71	0.50	–
MCS	3.31	50.20	0.42	–
MLS	3.64	45.60	0.46	43.14
MMS	2.51	66.20	0.32	48.68
MPS	1.57	105.80	0.20	47.06

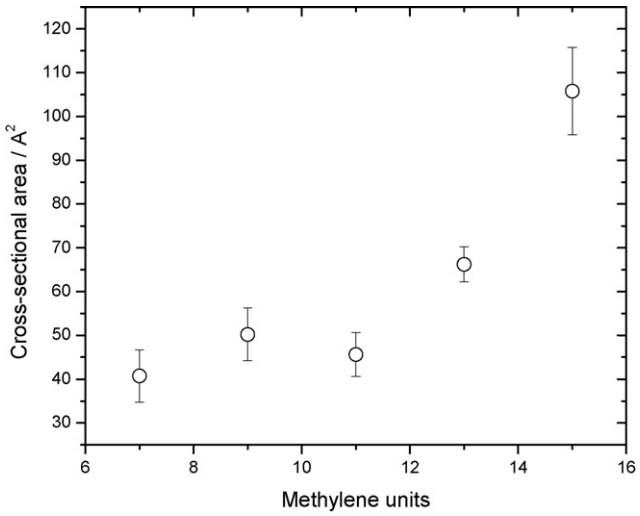


Fig. 4. Dependence of cross-sectional area with alkyl chain length.

calculated using the following equation:

$$l_c \leq l_{max} \approx (0.154 + 0.1265n)\,\text{nm}$$
$$v \approx (27.4 + 26.9n)\ 10^{-3}\,\text{nm}^3 \quad (8)$$

where n, the number of carbon atoms in the sucrose ester hydrophobic chain should only consider the methylene units. The values calculated for the critical packing parameter of the different sucrose esters are included in Table 3. For short alkyl chain sucrose esters (MLS, MCS, and MOS), the determined Cpp values indicate that the most favored structure corresponds to cylindrical micelles ($0.33 < \text{Cpp} < 0.50$) [35]. The value of Cpp for MMS is in the limit between cylindrical and spherical micelles and MPS should form neatly spherical aggregates ($\text{Cpp} < 0.33$) [35]. Previous studies performed on series of sucrose esters did not report this behavior, showing Cpp values almost constant and independent of the alkyl chain length. Our data indicate that alkyl chains can move (inside the micelle) with less restriction in spherical micelles (when sucrose esters have more than 12 methylene units), than in cylindrical ones. In addition, is observed that the random movements (less fluid environment of the probe) correlate with head group cross-sectional areas in these type micro-aggregates.

3.4. Micelle aggregation number determination

The method based on the fluorescence quenching to determine micelle sizes (number of molecules per micelle) relies on the following assumptions: the micelles must be monodisperse; probe and quencher must be hydrophobic and have to be located inside the micelles, with residence times much longer than the unquenched fluorescence life-time of the probe; the observed fluorescence is emitted from probes located in micelles only when there is no quencher, i.e. static quenching occurs; and the random association of probe and quencher with micelles is described by Poisson distribution.

The aggregation numbers determined for micelles of sucrose esters are given in Table 4, and can be fairly compared (are smaller) with the values reported by Kawaguchi et al. [15] The quenching of Pyrene emission by DBA for all studied sucrose ester micelles occurs in the manner predicted by Eqs. (2) and (3) as can be seen in Fig. 5. The aggregation numbers obtained from steady-state measurements, N_S (not reported) despite being incorrect, allow us to explain the behavior of each sucrose ester as a function of surfactant concentration. For the octyl sucrose ester (MOS, shortest hydrophobic alkyl chain studied) the aggregation number shows a positive dependence with concentration or square root of concentration, micelles increase in size systematically, taking values of 50 near to the cmc and reaching a value of 250 monomers at 40 mM. This behavior has been proposed to be a consequence of the transition from micelles to a lamellar phase and has been observed and reported for several Tritons [36]. Furthermore, Cpp values obtained for octyl ester predict micelles of cylindrical shape, so concentration dependence of aggregation number should be expected [35]. The capryl derivative, MCS, in contrast with the response observed

Table 4
Aggregation numbers of the micelles formed with different sucrose esters, measured by time resolved quenching (TQRF) of pyrene fluorescence at 25 °C

Surfactant	DBA	Reported [15]
MOS	CD	
MCS	—	76
MLS	80	96
MMS	90	122
MPS	110	160
MSS	—	

CD: concentration dependent.

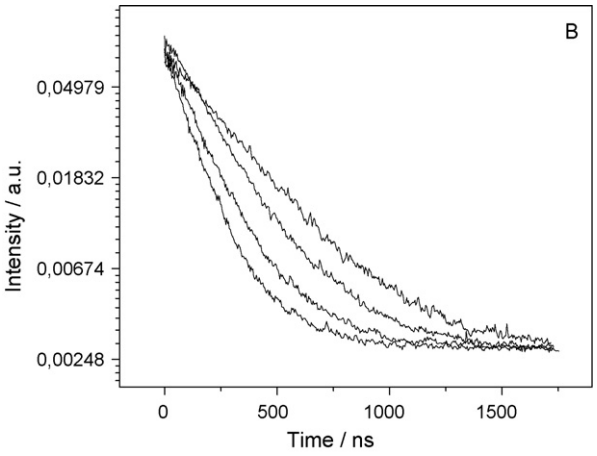


Fig. 5. Time resolved quenching of pyrene emission by DBA.

for other non-ionic surfactants [37,38], shows an initial reduction of the aggregation number reaching a plateau, $N_S = 79$, for concentrations higher than 12.5 mM. The remaining sucrose esters, with longer alkyl chains, show N_S values independent on its concentration. The aggregation numbers determined from TRFQ data, N_D, for longer alkyl chains were found to be concentration independent in the range studied. The values determined for N are smaller than the previously determined using X-ray scattering [15]. Despite the data available for the self-diffusion coefficient of micelles correspond not only to pure regioisomers [19], also a different behavior between short and long chain substituted sucrose esters is reported.

The existence of an important effect of the sucrose head and its solvation core on the micelle properties is postulated, compatible with the work of Molinier et al. [20], related with the regiochemistry of the ester and the formation of intramolecular hydrogen bonds. According to our results, the properties of the formed micelles are ruled by sucrose moiety for esters with shorter alkyl chains, being only balanced for relatively long alkyl chains. Even more, longer alkyl chains directly affect the cross-sectional area of sucrose in the surface of microaggregate.

Summarizing, the physical chemical properties of the micellar aggregates of a whole series of pure 6-*O*-sucrose esters were determined and reported. Cmc values of all studied compounds are comparable with previously reported ones showing the expected linearity against number of methylene units. Aggregation numbers, most of them not previously available, show different dependence on concentration depending on the size of substituents. Cross-sectional areas were calculated from surface activity measurements, allowing us to predict shapes by using the critical packing parameter. These parameters show a breakpoint when are analyzed as function of alkyl chain length. Additionally, properties as micropolarity and microfluidity of micellar aggregates are reported. So, new and systematic information of the micelles formed by pure surfactants with sucrose heads substituted at position 6-*O*, was collected.

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