



## Head group specificity of novel functionalized surfactants: synthesis, self-assembly and calcium tolerance



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### ABSTRACT

The present work describes the synthesis, characterization and application of functionalized surfactants derived through simple organic reaction steps. These surfactants have been particularly tailor made to resist hardness due to calcium ions in water. It is unique of its kind because here the surfactants have an analogous hydrophobic chain but differ structurally in the composition of the head groups in terms of the position of attachment of the chain. The effect of this small variability in the head group on the surfactant property, adsorption, self assembly and calcium tolerance behaviour has been studied in detail. This kind of phenol–keto surfactants has not been reported before. It was also found that one of the surfactants was more tolerant towards Ca<sup>2+</sup> ion than the other. The individual packing behaviour of the surfactants at the air–water interface has been projected to cause this difference which is very interesting.

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There is currently much interest in the properties of bio surfactants as replacements or partial replacements of conventional petrochemical-derived surfactants in a wide range of detergent-based products because of the attractions and potential benefits associated with bio sustainability and biodegradability.<sup>1–6</sup> These serve as an alternative to the common head group of the majority of non-ionic surfactants, that is, polyoxyethylene chains. Also, anionic surfactants, which are major ingredients in many detergent-based products, are notorious for their relative intolerance to water hardness, and a number of strategies have been developed to minimize the impact of hard water conditions.<sup>7–9</sup>

Biosurfactants that act as replacements or partial replacements of conventional petrochemical derived surfactants are promising due to their biodegradability, low toxicity and effectiveness in enhancing biodegradation and solubilization of low solubility compounds. However, greater difficulties in large-scale production and purification have so far hampered their wider application, and as such many applications or potential applications involve their blending with conventional surfactants. Compared to conventional surfactants, biosurfactants have, in general, lower toxicity, more biodegradability, can be synthesized from sustainable sources, and have higher tolerance to pH, temperature and hardness. The higher tolerance of the biosurfactants to hard water conditions is a potentially important feature. The problem of hardness occurs

due to the strong binding of multivalent counter ions and especially calcium, to form eventually insoluble precipitates. Hardness tolerance can be defined as the minimum concentration of multivalent counter ions required to cause precipitation.<sup>5,6</sup> Alargova et al.<sup>10</sup> and Petkov et al.<sup>11</sup> have recently demonstrated and quantified how multivalent counterions (Ca<sup>2+</sup>, Al<sup>3+</sup>) prior to precipitation promote micellar growth for anionic surfactants such as sodium dodecyl diethylene glycol sulfate, sodium lauryl ether sulfate (SLES). In other cases, such as the addition of Ca<sup>2+</sup> to the anionic surfactant, LAS (linear alkylbenzene sulfonate), micellar growth is replaced by a transition from micellar to lamellar structures.<sup>12</sup> These studies<sup>10,11</sup> also highlight one of the frequently used strategies to improve hardness tolerance: the incorporation of a nonionic cosurfactant.<sup>8,9</sup> It has now been demonstrated that, in addition to the insensitivity of the ethoxyolate head group to electrolyte, the larger head group of the nonionic cosurfactant provides a steric hindrance which disrupts and ultimately prevents the formation of the anionic surfactant–ion complexes which drive the micellar growth, structural transitions and ultimately precipitation.<sup>10–12</sup> Furthermore, it has been demonstrated that the ability to disrupt that complex formation is directly associated with the size of the ethylene oxide head group.

Surfactants and phospholipids bearing unsaturated fatty acid chains are particularly useful in the reconstitution of membrane proteins *in vitro*.<sup>12</sup> In this respect, certain glycerophospholipids and surfactants have been synthesized by Bhattacharya et al.<sup>13–16</sup> Furthermore, another important application in the field of novel

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surfactants with aromatic head groups lies in gene delivery.<sup>17–19</sup> Researchers have also shown that multivalent cationic lipids with an aromatic backbone hold a promise for superior gene transfection activities.<sup>20–24</sup>

This Letter describes the synthesis of two functionalized surfactants. It is unique of its kind because here the surfactants have an analogous hydrophobic chain but differ structurally in the composition of the head groups in terms of the position of attachment of the chain. The structures of the two molecules are given in Scheme 1. The molecules were chosen such that there will be the possibility of a chelating complex between the OH group and the Ca<sup>2+</sup> ion at higher (detergent relevant) pH. Thus, these surfactants have been tailored such that they become calcium tolerant in solution. Such phenol–keto surfactants which are environmentally benign and calcium tolerant have not been reported before. The effect of this variability in the head group on the surfactant property, adsorption, self assembly and calcium tolerance behaviour has been studied in detail. For convenience we have named the first compound as FS1 and the second compound as FS2.

Micelles are formed at the critical micelle concentration (CMC), which is detected as an inflection point when physicochemical/microheterogeneous properties such as surface tension or fluorescence intensity ratio are plotted as a function of concentration. In connection with a general investigation of the physicochemical properties of FS1 and FS2 we have determined their CMC in water by two independent methods: fluorescence measurements and surface tension experiments.

Fluorescence spectra were taken with stock solutions of both FS1 and FS2 using a common fluorescent probe coumarin 153 (C153). C153 absorbs at ~440 nm and emits at ~545 nm in pure aqueous solution. Addition of different concentrations of FS1 and FS2 leads to a substantial increase in fluorescence intensity with an appreciable blue shift of ~30 nm in case of FS1 and ~50 nm

in case of FS2 (Fig. 1). Increase in fluorescence intensity as well as extent of blue shift was found to be significantly higher in case of interaction of C153 with FS2 as compared to FS1 (Fig. 2). This shows that the probe partitions better inside the micellar environment of FS2 and experiences a more non-polar environment. It can therefore be assumed that FS2 is a more non-polar surfactant as compared to FS1.

A plot of relative fluorescence intensity and concentration leads us to accurately determine the CMC value of the two surfactants from the emission studies as shown in Figure 3. The CMC is found out to be 0.27 mM for FS1 and 0.45 mM for FS2. A slightly lower value of CMC in case of FS1 compared to FS2 indicates that the head group indeed plays a role in the micellization process, in spite of having similar hydrophobic chain length.

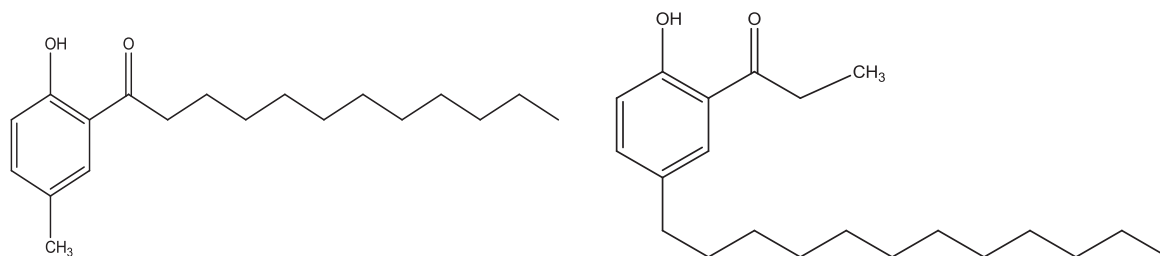
The Gibb's free energy of micellization was also found from the following equation:

$$\Delta G_{\text{mic}}^0 = RT \ln \text{CMC} \quad (1)$$

This was found to be  $-20.36 \text{ kJ mol}^{-1}$  for FS1 and  $-19.09 \text{ kJ mol}^{-1}$  for FS2 indicating that the process of micellization is highly favourable.

A greater lowering of surface tension was found in case of FS2 as compared to FS1. This difference is expected considering the higher CMC of the former species. The relationship between surface tension and the logarithm of the concentration of the surfactants is shown in Figure 4. The breakpoint allows the ready evaluation of the CMC for both the surfactants.

The CMC as calculated from surface tension measurement are found to be 0.33 mM for FS1 and 0.50 mM for FS2. This is in good agreement with those derived from the fluorescence studies. Also it is evident that the micellization occurs at lower concentration for FS1 as compared to FS2.



Scheme 1. Structures of FS1 and FS2, respectively.

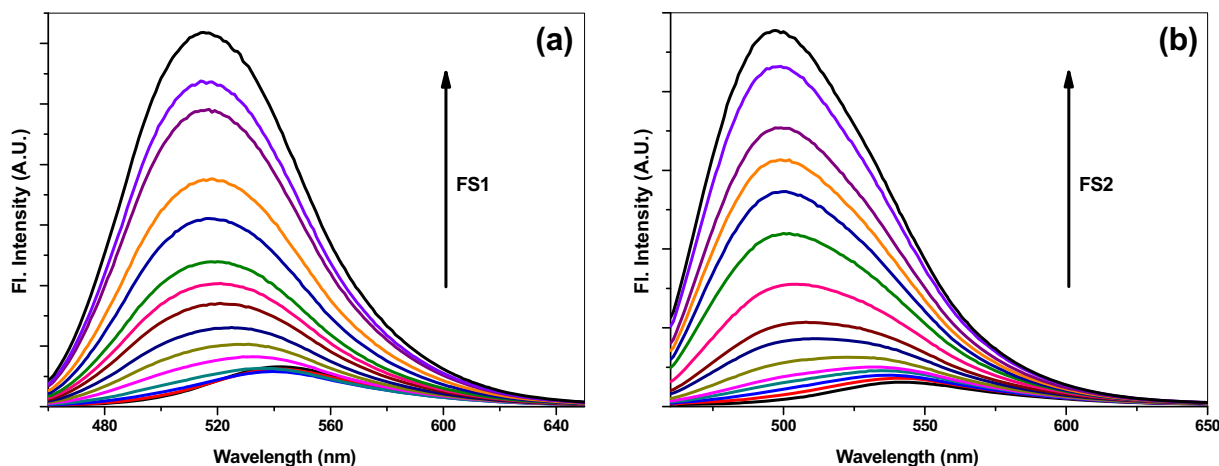


Figure 1. Emission spectra of 5  $\mu\text{M}$  C153 with increasing concentrations of FS1 and FS2. The concentration of both the surfactants varies from 0 mM to 2 mM.

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