



Enhanced interfacial properties of novel amino acid-derived surfactants: Effects of headgroup chemistry and of alkyl chain length and unsaturation

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ABSTRACT

Amino acid-derived surfactants have increasingly become a viable biofriendly alternative to petrochemically based amphiphiles as speciality surfactants. Herein, the Krafft temperatures and critical micelle concentrations (*cmc*) of three series of novel amino acid-derived surfactants have been determined by differential scanning microcalorimetry and surface tension measurements, respectively. The compounds comprise cationic molecules based on serine and tyrosine headgroups and anionic ones based on 4-hydroxyproline headgroups, with varying chain lengths. A linear dependence of the logarithm of *cmc* on chain length is found for all series, and in comparison to conventional ionic surfactants of equal chain length, the new amphiphiles present lower *cmc* and lower surface tension at the *cmc*. These observations highlight their enhanced interfacial performance. For the 18-carbon serine-derived surfactant the effects of counterion change and of the presence of a *cis*-double bond in the alkyl chain have also been investigated. The overall results are discussed in terms of headgroup and alkyl chain effects on micellization, in the light of available data for conventional surfactants and other types of amino acid-based amphiphiles reported in the literature.

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1. Introduction

The growing need and use of biofriendly surfactants in formulations for *in vivo* application have turned amino acids into excellent molecules for modification and conversion into amphiphiles [1–6]. In addition to these applications, the extensive use of surfactants in both household and industrial products causes their presence in the environment to be of growing concern and thus requires the search for ever “greener” amphiphiles. The synthesis of amino acid-derived surfactants that mimic naturally occurring lipoamino acids has provided molecules with lower toxicity and irritancy towards living organisms [7–11] as well as higher biodegradability in the environment [3,12] when compared to conventional surfactants (e.g. quaternary ammonium surfactants). It has also been observed that in general these new molecules possess antimicrobial and antiviral activity [10,12].

In addition to the enhanced biocompatibility and typically good interfacial performance, amino acid-based surfactants may present *per se* interesting self-assembly and phase behavior in concentrated systems. Such bulk behavior features include the formation of various types of thermotropic liquid crystalline phases in anhydrous

form [13] and the ability to spontaneously form liposomes in aqueous mixtures with other amphiphiles [13–16]. Moreover they can self-assemble into a rich variety of complex supramolecular structures such as helical and twisted ribbons and tubules [6,17,18] (as a consequence *inter alia* of hydrogen bonding and chirality), and they can act as low-molecular-weight gelators [19]. Another relevant feature that has been more recently investigated is their biomedical potential as cationic surfactants in non-viral gene delivery formulations [20,21]. Thus, the basic characterization of the aggregation properties of newly synthesized compounds is of utmost relevance, prior to their application in further aggregation studies at higher concentration or in mixtures with other co-solutes.

With respect to molecular design, the amino acid-based architecture allows the building of multiple structures for the surfactant molecules, since alkyl chains can be incorporated in the amino [5] or in the carboxylic group [22], or even at the end of the amino acid side chain [23]. Moreover, by introducing different numbers of alkyl chains, either single-chained [24], double-chained [23], gemini (dimeric) [25] or bolaform [22] surfactants, among others, can be produced.

In this paper, we report studies on the basic micellization properties of novel single-chained surfactants based on serine (Ser), tyrosine (Tyr) and 4-hydroxyproline (Hyp), with different chain lengths, and discuss their interfacial performance in the light of reported data for other ionic amphiphiles both of conventional or

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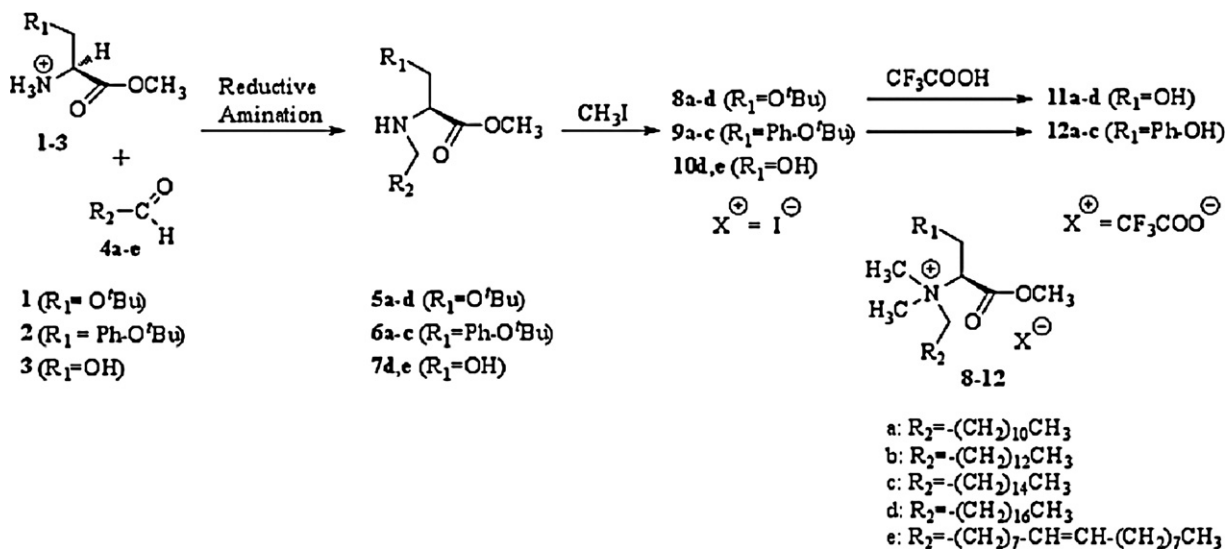


Fig. 1. Synthesis of serine-derived (**10–11**) and tyrosine-derived (**12**) cationic surfactants.

amino acid origin. We further examine the influence of counterion change and of the presence of a double-bond in the alkyl chain, for a Ser-derived surfactant.

2. Experimental

2.1. Materials and synthesis

The surfactants dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulphate (NaDS), used as reference compounds in this work, were both purchased from Sigma (both with purity better than 99%); NaDS was twice recrystallized from a water-ethanol mixture prior to *cmc* determination. The monomeric cationic serine- (**10**, **11**) and tyrosine-based (**12**) and the anionic 4-hydroxyproline-based surfactants (**15**) were prepared on the basis of procedures, and variations thereof, recently developed in our laboratories [26] that will be briefly reviewed here (Figs. 1 and 2). The most efficient methodology for the synthesis of the proposed cationic surfactants consists in the introduction of the alkyl chains into the *O-tert-butyl*-protected amino acid methyl esters (**1**, **2**) by reductive amination of “fatty” aldehydes (**4**), followed by methylation and removal of the *tert-butyl* group using trifluoroacetic acid (TFA). However, with unsaturated fatty aldehydes (**4e**) the use of TFA must be avoided. Therefore, for the obtention of the oleiyl derivative (**10e**), the non-protected amino acid ester (**3**) was used as starting material yielding the corresponding unsaturated cationic

surfactant as iodide (**10e**) instead of trifluoroacetate (Fig. 1). Furthermore, the C18 saturated iodide (**10d**) was also synthesized, in order to probe the effects of alkyl chain unsaturation and counterion change on the *cmc*.

In what concerns the 4-hydroxyproline derivatives (Fig. 2), introduction of the alkyl chains by reductive amination, followed by saponification using KOH/MeOH led to the desired anionic surfactants (**15**) in good overall yields (ca. 60%).

The structure of all the synthesized surfactants was confirmed by ^1H and ^{13}C NMR spectroscopy and by mass spectroscopy (cf. supporting information). Moreover, from the surface tension curves in Figs. 4 and 5, which do not show wells near the *cmc*, it is assumed that surface-active impurities are either absent or present only in vestigial amount.

2.2. Interfacial studies

The Krafft temperatures, θ_{Kr} , of the surfactants were determined by differential scanning calorimetry (DSC) using a Setaram microDSCIII, at a 0.5 K min^{-1} rate.

The surface tension of the aqueous solutions was measured with a Dataphysics DCAT11 tensiometer using the Wilhelmy plate method. Successive aliquots of a surfactant stock solution, freshly prepared in Millipore water, were added to a thermostated vessel with a known volume of dilute solution. The surface tension value in each individual measurement was allowed to vary only

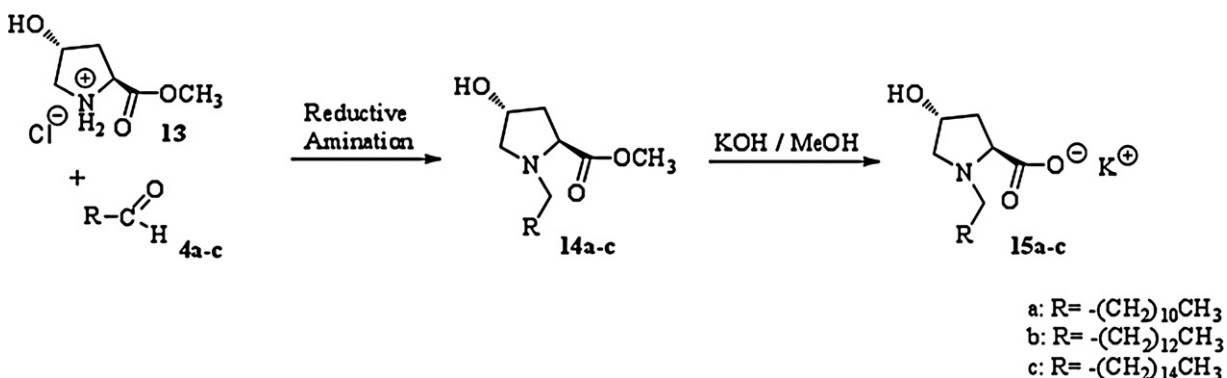


Fig. 2. Synthesis of 4-hydroxyproline-derived anionic surfactants (**15**).

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