PAPER

Micellization properties of cardanol as a renewable co-surfactant†

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With the aim to improve the features of surfactant solutions in terms of sustainability and renewability we propose the use of hydrogenated natural and sustainable plant-derived cardanol as an additive to commercial surfactants. In the present study we demonstrated that its addition, in amounts as high as 10%, to commercial surfactants of different charge does not significantly affect surfactant properties. Conversely, the presence of hydrogenated cardanol can strongly affect spectrophotometric determination of CMC if preferential interactions with the dyes used take place. This latter evidence may be profitably exploited in surfactant manufacturing by considering that the concurrent presence of a rigid organic molecule such as Orange OT and 10% hydrogenated cardanol decreases the CMC of CTAB up to 65 times.

Introduction

In recent years with the depletion of non-renewable materials much interest has been gradually addressed towards the development of sustainable species derived from renewable resources. In this framework the efficient conversion of organic starting-materials, that can be naturally replenished in a time compatible with the usage into a large variety of end-products, is a particularly important and challenging topic.[1,2] This is further implemented with the concept of biorefinery, a term that describes and integrates the processes of converting biomasses into valuable chemicals,[3] in analogy with petroleum-based refineries. Moreover, this approach perfectly matches the concept of sustainability that is to say of a development that does not compromise the ability of future generations to fulfil their own needs.[4]

Nature provides a great number of different species suitable for integration into useful and valuable materials. Cardanol is considered one of the most interesting examples of sustainable plant-derived raw materials. It is the main constituent of Cashew Nut Shell Liquid (CNSL), a by-product obtained from

cashew nuts (*Anacardium occidentale* L.), whose final precise composition – depending on the extraction method – is mainly based on cardanol, cardol, anacardic acid and methylcardanol. CNSL represents about 25–30% of the total weight of the nut. So, the worldwide production of CNSL in 2008 was estimated to be 310 000 metric tons per year[5] with expectation to rise up to 450 000 metric tons in the near future[6] as a consequence of the mechanical processing for the edible use of the kernel and the economic development of countries in which the *Anacardium* tree grows (or can find the climatic and pedological conditions to grow). These reasons as well as the low cost of cardanol (less than 1 € kg^{-1}) could strongly motivate its industrial applications.

The cardanol components are again a mixture of four *meta*-C_{15} phenols differing in the degree of unsaturation of the carbon chain [3-(pentadecyl)-, 3-(8*Z*-pentadecenyl)-, 3-(8*Z*,11*Z*-pentadecadienyl)- and 3-(8*Z*,11*Z*,14-pentadecatrienyl)phenol]. These species have a particularly interesting chemical structure due to the presence of different valuable features: a phenolic group offering a wide synthetic flexibility, a *meta* unsaturated or saturated alkyl chain which confers amphiphilic and lipophilic characteristics to the extracted molecules, and an aromatic ring able to give π–π stacking and/or to be easily and differently functionalized.[1,7–10]

Several uses and industrial applications of properly derivatized cardanol are reported in the literature such as in the synthesis of fine chemicals, and of functional materials like polymers (paints, varnishes, resins, *etc.*)[1,7,11,12] and, more recently, in the preparation of nanomaterials *via* self-assembly of cardanol-based molecules (nanotubes, nanofibers, gels, liquid crystals and micelles).[1,13–15] On the other hand the underivatized, phenol hydrogenated, cardanol presents promising

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characteristics as a biocompatible brominating reagent[16] and, as far as the medical field is concerned, as an antioxidant, antiobesity and antidiabetic agent.[17–19] Furthermore, presently, great and increasing interest is devoted, both from academia and industry, to the research on "green" surfactants and to the design of surfactants bearing natural structural motifs (amino acids, sugars and fatty acids). These species, very often originating from renewable raw materials, present good biocompatibility and fast biodegradation and therefore relatively low environmental impact and toxicity.[14] This is exactly the case of hydrogenated cardanol (**HC**) that has a chemical structure similar to that of nonyl phenol ethoxylates (NPEs) and linear alkyl benzenes (LABs), but, different from them, is sustainable and renewable. As a matter of fact, NPEs, widely used as hydrotropes[20] and surfactants for detergents, cleaners, paints, varnishes, surface active polymers,[21] and LABs, largely used as synthetic detergent intermediates in the production of linear alkylbenzene sulfonates (LASs), have been extensively dismissed in the European Union because of their persistence in the environment, particularly in water.[22–24] It has to be mentioned that **HC** doesn't show significant surfactant-like properties[21] since the phenolic OH portion is not charged and is too small in order to act as a good polar head and further derivatization and chemical modifications are needed in order to improve its amphiphilicity.[25–30] On the other hand, it is also well known that the addition of alcohols to charged surfactants favours their aggregation by lowering their critical micelle concentration (CMC);[31] the non-ionic alcohols intercalating the charged heads decrease the surface charge density of the micellar palisade layer and favour micelle formation.

In the present study we have investigated the possibility to use **HC** as a co-surfactant to promote sustainability and renewability of commercial amphiphiles. The aim of this work is to evaluate the effects of this alkyl-saturated unit ($C_{21}H_{36}O$) on the self-aggregation properties of charged and uncharged commercial species. Accordingly we have chosen an anionic, a cationic, a zwitterionic and a neutral surfactant, *i.e.* dodecyl sulfate sodium salt (SDS), hexadecyltrimethylammonium bromide (CTAB), tetradecyldimethylamine oxide (C_{14}DMAO) and 4-(1,1,3,3-tetramethylbutyl)phenyl polyethylene glycol (Triton X-100), respectively (see Chart 1). We report here on the properties of the investigated mixtures in terms of critical micelle concentration (CMC), dimensions and surface charge of the final aggregates by combining various techniques, in particular spectrophotometry, spectrofluorimetry, tensiometry, dynamic light scattering and ζ-potential measurements.

To the best of our knowledge, **HC** (non-derivatized or substituted with other groups) had never been used in micelle preparation or doping before the recently published study on CTAB–cardanol mixtures[4] that have shown an increase in viscosity and a modification of the micellar structure from spherical (cardanol percentage <33%) to rod-like on increasing the cardanol percentage in the mixture until 66%. The potentialities of CTAB micelles as carriers to transport and protect the hydrogenated cardanol were investigated, envisaging medical applications, by reaching 66% of cardanol in CTAB/**HC** mix-
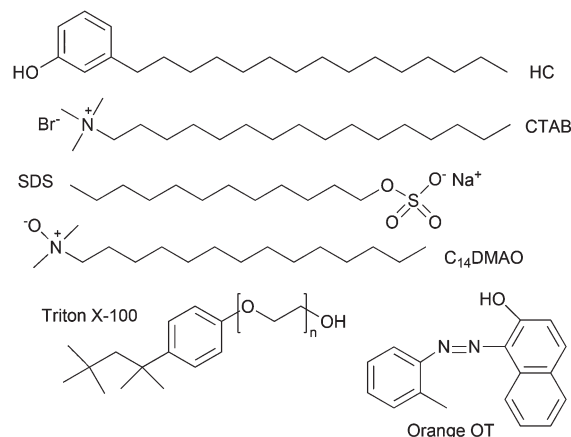

Chart 1   Chemical structure of hydrogenated cardanol (**HC**), the investigated surfactants and Orange OT dye.

tures. Taking these results into account, we have explored different **HC**/S ratios (*i.e.* **HC** = **HC** concentration; S = surfactant concentration) keeping **HC** percentages always equal to or lower than 10% because the goal of the present work is the improvement of commercial surfactants' biocompatibility while preserving their characteristics and properties.

Results and discussion

The most common and typical property of micelles is their CMC value that is generally evaluated monitoring one or more concentration dependent selected physical or chemical properties of the surfactant aqueous solutions, and identifying the concentration corresponding to a discontinuity in the function.

Here we use two different methods for CMC evaluation, providing independent measurements that better validate the final results. In particular we have analysed a series of aqueous mixtures of the commercial surfactants in combination with **HC** at three constant **HC**/S ratios (*i.e.* 0.02, 0.04, and 0.1) but at different concentrations. Two sets of solutions were prepared, the first one in a surfactant concentration range depending on the commercial surfactant (see the Experimental section) was used for surface tensiometry measurements, while the other one, with the same **HC**/S ratios but with surfactant concentrations in the range 1.4×10^{-5}–1.5×10^{-2} M, was added with the azo-dye Orange OT. The latter spectrophotometric method is a widespread and easy method for determining CMC values which exploits the ability of micellar aqueous solutions to dissolve a water-insoluble dye,[32] in our case Orange OT, following its concentration variation in solution *via* absorbance measurements at λ_{max} = 492 nm.

The data obtained for pure commercial surfactants *via* both methods were in agreement with the values reported in the literature although slight variations were obtained as expected when micellar dynamic systems were characterized *via*

different techniques. Unexpectedly, instead, the CMC values obtained by the two techniques were significantly different for **HC** containing mixtures. In particular, the spectroscopic investigation (see the ESI†) evidenced a change of CMC values on varying the **HC**/S molar ratios (Table 1) for all the surfactant mixtures, while the surface tensiometry data evidenced a substantial invariability of the CMC with the investigated **HC**/S ratios for the four surfactant mixtures (Table 2). We have therefore performed some further studies in order to explain this experimental discrepancy by ascertaining whether the presence of Orange OT in the surfactant mixture could promote the formation of pre-micellar aggregates of **HC**.

Several papers have recently reported on the ability of benzene-containing dyes to form ion-pairs, or interact, with conventional surfactants favouring the formation of pre-micellar systems.[33–35] These are aggregates that appear at concentrations below the CMC, a phenomenon already known for some very bulky and structured surfactants such as crown ethers[36] and gemini.[37] Interestingly, pre-micellar aggregates have been observed mainly when monitoring the CMC by using a dye, and it has also been demonstrated that the presence of 1–2% methanol, typically used to remove the insoluble dye in water, may as well favour the stacking.[38] The size of these assemblies is relatively small with aggregation numbers that can be as low as 2–5.[39–41] They have been ascribed to intermolecular interactions favoured by preferable conformations and/or stacking of hydrophilic or hydrophobic

groups.[42] All these findings suggest that in our samples the presence of Orange OT, characterized by a hydrophobic domain containing an aromatic ring and a small polar head group, could favour π-stacking and van der Waals interactions with the similarly structured cardanol thus promoting **HC** aggregation at very low CMC.

To experimentally prove this hypothesis we have prepared six water solutions with different concentrations of **HC** and saturated Orange OT (see the Experimental section). We observed the progressive solubilization of the dye on increasing the **HC** concentration. This evidence was surprising due to the non-micelle forming character of pure **HC**. The absorption spectra of the chromophore are characterized by a significant and monotonic increase of the absorbance values (*ca.* 20-fold) on increasing the **HC** concentration from 1.0×10^{-4} M to 2.0×10^{-3} M (*ca.* 20-fold) (Fig. 1). As a matter of fact, by plotting the absorbance at $\lambda_{max} = 492$ nm (*i.e.* absorption maximum of the azo dye) against **HC** concentration, an almost linear increase is observed (inset in Fig. 1). This could be well explained by the formation of **HC** pre-micellar aggregates, self-association being promoted by the inclusion of the originally water insoluble Orange OT, in agreement with the reported behaviour of other widely used alcohol co-surfactants.[43] It has to be underlined that the spectrophotometric measurements also evidence a red-shift of the λ_{max} of the dye in the more concentrated cardanol solutions (from 492 to 501 nm). This is a further indication of the involvement of the dye in π–π stacking

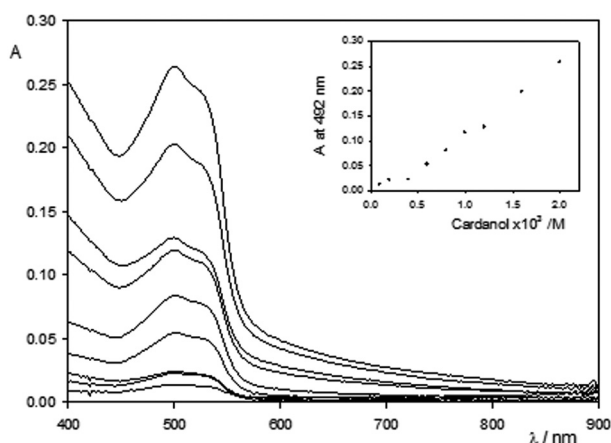**Table 1** CMC values (M) obtained by the spectrophotometric method using Orange OT as the lipophilic dye

Surfactant type	Pure surfactant[a]	HC/S = 0.02	HC/S = 0.04	HC/S = 0.1
SDS	$7.41\ (\pm0.98) \times 10^{-3}$ $n = 11, r = 0.9980$	$4.06\ (\pm0.72) \times 10^{-3}$ $n = 11, r = 0.9991$	$2.75\ (\pm0.54) \times 10^{-3}$ $n = 14, r = 0.9984$	$1.43\ (\pm0.15) \times 10^{-3}$ $n = 10, r = 0.9970$
CTAB	$8.89\ (\pm0.95) \times 10^{-4}$ $n = 11, r = 0.9990$	$5.06\ (\pm0.45) \times 10^{-4}$ $n = 10, r = 0.9990$	$4.66\ (\pm0.35) \times 10^{-4}$ $n = 10, r = 0.9994$	$1.35\ (\pm0.28) \times 10^{-5}$ $n = 9, r = 0.9991$
C_{14}DMAO	$1.80\ (\pm0.34) \times 10^{-4}$ $n = 13, r = 0.9987$	$4.02\ (\pm0.62) \times 10^{-4}$ $n = 11, r = 0.9982$	$4.16\ (\pm0.41) \times 10^{-4}$ $n = 12, r = 0.9995$	$1.27\ (\pm0.22) \times 10^{-4}$ $n = 10, r = 0.9990$
Triton X-100	$2.90\ (\pm0.58) \times 10^{-4}$ $n = 8, r = 0.9984$	$5.05\ (\pm0.56) \times 10^{-5}$ $n = 13, r = 0.9972$	$5.91\ (\pm0.38) \times 10^{-5}$ $n = 11, r = 0.9986$	$1.77\ (\pm0.18) \times 10^{-4}$ $n = 14, r = 0.9990$

[a] n = Number of data used for the fitting; r = correlation coefficient of the linear correlation.

Table 2 CMC (M) and aggregation numbers obtained by the surface tension and fluorescence quenching methods, respectively

Surfactant type	Pure surfactant $[N_{agg}]$	HC/S = 0.02 $[N_{agg}]$	HC/S = 0.04 $[N_{agg}]$	HC/S = 0.1 $[N_{agg}]$
SDS	$8.95\ (\pm0.98) \times 10^{-3}$ $[95 \pm 1]$	$9.57\ (\pm0.13) \times 10^{-3}$ $[83 \pm 1]$	$1.00\ (\pm0.03) \times 10^{-2}$ $[75 \pm 3]$	$1.03\ (\pm0.02) \times 10^{-2}$ $[85 \pm 5]$
CTAB	$1.57\ (\pm0.19) \times 10^{-3}$ $[65 \pm 2]$	$1.44\ (\pm0.02) \times 10^{-3}$ $[58 \pm 1]$	$1.75\ (\pm0.38) \times 10^{-3}$ $[57 \pm 1]$	$1.60\ (\pm0.29) \times 10^{-3}$ $[61 \pm 1]$
C_{14}DMAO	$5.48\ (\pm0.14) \times 10^{-4}$ $2.69\ (\pm0.28) \times 10^{-3}$ $[53 \pm 2;^{a}\ 139 \pm 2]$	$4.97\ (\pm0.50) \times 10^{-4}$ $2.52\ (\pm0.34) \times 10^{-3}$ $[126 \pm 3]$	$4.63\ (\pm0.11) \times 10^{-4}$ $[79 \pm 4]$	$6.14\ (\pm0.42) \times 10^{-4}$ $[49 \pm 5]$
Triton X-100	$5.55\ (\pm0.79) \times 10^{-4}$ $[106 \pm 2]$	$6.31\ (\pm0.49) \times 10^{-4}$ $[116 \pm 3]$	$6.47\ (\pm0.55) \times 10^{-4}$ $[104 \pm 2]$	$6.24\ (\pm0.76) \times 10^{-4}$ $[99 \pm 1]$

[a] Measured at $[C_{14}DMAO] = 1 \times 10^{-3}$ M.

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Fig. 1 Absorption spectra of Orange OT in water in the presence of increasing amounts of **HC**. The concentration of **HC** varies from 1.0 × 10^{-4} M to 2.0 × 10^{-3} M. Inset: absorbance of Orange OT at λ_{max} 492 nm against **HC** concentration. Due to the low solubility of **HC** in water (log P = 3.15 ± 0.27),[44] methanolic concentrated **HC** solutions have been added to aqueous Orange OT solution so as to keep the alcohol percentage below 6% in order not to affect the properties of the aqueous solution.

interactions that are well known to induce bathochromic shifts of the absorption maxima.

Very interestingly the spectroscopic measurements evidence a change of CMC upon changing the **HC**/S ratio in the different surfactants. The obtained data point out that the different characteristics in terms of polarity and charge of the surfactants highly influence their interactions with **HC**. The highest changes of CMC values with increasing amounts of **HC** are observed for SDS and CTAB mixtures with a 3 times decrease and a 40 times decrease of CMC, respectively, on increasing the concentration of **HC** in the surfactant mixture from 2 to 10%. This evidence could be due to the fact that strong π-stacking and van der Waals interactions between **HC** and Orange OT promote aggregation of the surfactants overall when additional effective interactions between the phenolic derivative and the charged head groups of the surfactants can be established. On the other hand, hydrogen bonding of $C_{14}DMAO$ with **HC** appears to compete with the tendency of **HC** to aggregate with Orange OT. The mixed micelles with 2% cardanol have a CMC 2.5 fold higher than that of pure $C_{14}DMAO$. Nevertheless, the presence of excess **HC** on further increasing its concentration restores the tendency of Orange OT to assemble with cardanol and form pre-aggregates. On the other hand, Triton X-100 demonstrated to be strongly affected by the presence of a small percentage of **HC** as a 6-fold decrease of the CMC of Triton X-100 was measured at 2% **HC** with respect to the pure surfactant. Indeed, the formation of complexes of Orange OT and **HC** strongly promotes the formation of Triton X-100 pre-aggregates at a low percentage of **HC** due to the excellent capacity of Triton X-100 micelles to solubilize Orange OT and its assembly with **HC**.[45] On increasing the percentage of **HC** in the surfactant mixture, in the

absence of additional electrostatic interactions with the surfactant, the above mentioned effect dwindles and the relevant CMC of Triton X-100 increases.

Further evidence of the existence of effective interactions between **HC** and Orange OT comes from ESI-MS measurements. As a matter of fact, this technique involves the transfer of ions formed in solution into the gas phase without breaking non-covalent interactions and is demonstrated[46–49] to be appropriate to investigate supramolecular systems although it should be used cautiously when quantitative determination is required.[50] ESI-MS analyses of two aqueous solutions containing saturated Orange OT and different concentrations of **HC** (*i.e.* 1.0 × 10^{-4} M and 2.0 × 10^{-2} M) evidenced additional peaks in the in the spectrum of the most concentrated **HC** solution, thus confirming UV-vis data. In particular, the peak at 594.1 *m/z* can be attributed to the association of azo dye with **HC**, [OT-**HC** + Na]$^+$ (Fig. 2).

All the experimental evidence obtained so far, therefore, indicates that the presence of the dye can significantly influence these systems and affect the measurements due to pre-micellization events. By considering that surfactants are often used as solubilizing agents, the ability of cardanol at concentrations as low as 10% to promote a facile aggregation of charged surfactants at CMC 65 and 4 times lower than those of pure CTAB and SDS, respectively, in the presence of additives such as Orange OT, may be profitably investigated by surfactant manufacturing.

Surface tensiometry measurements are performed on the aqueous solution of the surfactant mixture and samples do not need to be enriched with additional external compounds.
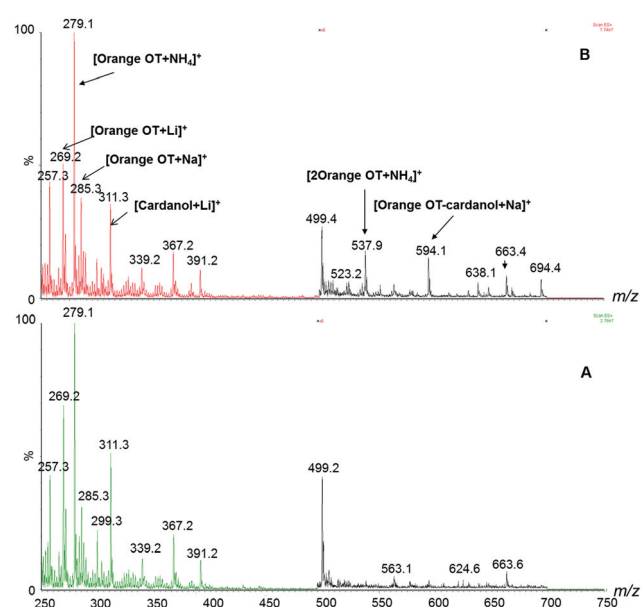
Fig. 2 ESI-MS spectra (*m/z* = 250–750) of aqueous solutions of **HC** and Orange OT (spectrum A: [**HC**] = 1.0 × 10^{-4} M; spectrum B: [**HC**] = 2.0 × 10^{-2} M). The corresponding assignments are reported in spectrum B.

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Moreover **HC** lacks surface activity and therefore the measurements are not affected by the presence of **HC** as in the case of mixtures of surface active agents, as evidenced also in the surface tension *vs.* log surfactant concentration plots reported in the ESI.† For these reasons, tensiometry should be, in the presence of surfactant mixtures containing **HC**, the suitable technique to measure CMC values. In order to properly characterize the obtained micellar solutions we determined as well the corresponding aggregation number (N_{agg}) by using the pyrene fluorescence quenching method. The data obtained by these latter methods are gathered in Table 2. Both CMC values and N_{agg} of pure CTAB, SDS and Triton X-100 surfactants are in agreement with literature values.[43,51,52] In the case of N_{agg} of CTAB and SDS the data are slightly affected by the adopted experimental concentration of the surfactant, as previously reported in the literature.[51,52] As highlighted above, CMC values for cardanol containing mixtures measured by tensiometry do not evidence significant variations and can be considered almost unaffected, within the experimental error, by the presence of different percentages of cardanol for all the investigated surfactants. Accordingly, almost no variation of N_{agg} was detected for SDS, CTAB and Triton X-100 mixtures. The case of $C_{14}DMAO$ appears to be particularly intriguing because the N_{agg} of $C_{14}DMAO$ changes significantly upon varying the **HC** percentage in the mixtures. Indeed, the initial increase of N_{agg} on passing from pure $C_{14}DMAO$ to the 2% cardanol mixture is followed by a strong N_{agg} decrease upon increasing further the **HC** percentage. This could be explained by the well-known tendency of this surfactant to self-assemble into rod-like micelles[53–55] that are described as the only stable shape at concentrations higher than 1×10^{-2} M, the concentration of the surfactant used for fluorescence quenching measurements. Accordingly, at low concentrations of $C_{14}DMAO$ (*i.e.* 1.0×10^{-3} M), a N_{agg} much lower than that determined at 1.0×10^{2} M, and compatible with spherical micelles, was detected (see Table 2). Moreover, a very complex length dependence on temperature, ionic strength and pressure has been reported in the literature.[53,55] Consequently, there is only a very small stability window for the spherical shaped micelles before turning into sphero-cylindrical micelles. Indeed, two CMC values could be measured in the presence of pure and the 2% cardanol mixture, one at a concentration of *ca.* 5×10^{-4} M and one at *ca.* 2×10^{-2} M $C_{14}DMAO$. The first CMC is higher than that reported in the literature for unprotonated $C_{14}DMAO$ (*i.e.* 1.6×10^{-4}–2.7×10^{-4} M)[55,56] and lower than that reported in the literature for protonated $C_{14}DMAO$ (7.0×10^{-4} M).[57] This should be an indication of the fact that in the present case $C_{14}DMAO$ is partially protonated,[55] although the degree of protonation is not very high as confirmed by ζ-potential measurements and in agreement with the pK_a = 5.76 reported for $C_{14}DMAOH^+$ at salt concentrations as low as 0.01 M.[57] The protonation of a few tenths of a per cent of $C_{14}DMAO$ in the absence of salt should not affect the tendency to form globular micelles at a low surfactant concentration. Upon increasing the $C_{14}DMAO$ concentration and due to the formation of hydrogen bonds between protonated

and unprotonated species,[58] elongation of globular micelles can take place as confirmed by the N_{agg} of 139 measured at 1.0×10^{-2} M, significantly higher than that of classical spherical micelles of analogous zwitterionic surfactants.[54,56,59] The observed low ζ-potential is also in agreement with not very stable colloidal solution[60] and subsequent aggregation of micelles with the formation of elongated micelles upon increasing $C_{14}DMAO$ above the first CMC value can be suggested. At the lowest investigated concentration of cardanol, the presence of **HC** does not modify the behavior of $C_{14}DMAO$ despite the decrease of the ζ-potential towards more negative values. *Vice versa*, at the highest concentrations of cardanol, only one CMC has been determined. N_{agg} values for $C_{14}DMAO$ in the presence of 4% and 10% of **HC** are in agreement with values typical of spherical micelles[54,56,59] pointing out that **HC**, promoting the formation of hydrogen bonds with non-protonated $C_{14}DMAO$, disfavors protonation of $C_{14}DMAO$, hydrogen bond formation between protonated and unprotonated species and micelle elongation. The decrease of $C_{14}DMAO$ protonation in the relevant mixtures is also highlighted by the more negative ζ-potential as compared to the pure surfactant. It is important to stress that the steady-state fluorescence quenching method is not particularly effective for the determination of the aggregation number of big spherical micelles and rod-like micelles. As a matter of fact in such aggregates the probe and the quencher, although embedded in the same micelle, can be far enough from each other inhibiting the quenching efficiency[61] and yielding not entirely reliable results. Nevertheless, in our case, the low concentration of the surfactant used is in perfect agreement with spherical or slightly elongated micelles and the determined N_{agg} can be considered reliable.

Although it is well known that tensiometry is not appropriate for measuring CMC in the presence of impurities, in order to support the evidenced Orange OT promotion of micellization of a classical surfactant in **HC**/S mixtures, we measured, as an example, the CMC of **HC**/SDS = 0.1 in the presence of Orange OT by using tensiometry (see the ESI†). This surfactant was chosen by considering the considerable effect observed for this **HC**/S ratio by using spectrophotometry (Table 1). The measured 7.99×10^{-4} M CMC is one order of magnitude lower than the CMC measured by tensiometry in the absence of Orange OT (Table 2) but almost comparable (~60%) to the datum obtained by spectrophotometry.

With the goal to try to find further experimental evidence to support our data and to help us to interpret and correlate the results obtained with different techniques, we performed some dynamic light scattering (DLS) analyses to obtain an estimation of CMC intervals and a measurement of micellar dimensions. DLS, in fact, follows the fluctuations with time of the intensity of the light scattered by particles in random motion in solution to determine their size, typically for objects in the sub-micrometric range. We have therefore measured with DLS five different concentrations for each surfactant and for each ratio (each result was averaged on three repeated experiments). In this way we could clearly evidence whether micelles were formed or not from the size of the particles in

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Table 3 CMC data in terms of concentration range (M), dimensions (nm) and ζ-potential (mV) obtained by dynamic laser light scattering analyses

	Pure surfactant Concentration range [diameter; ζ-potential]	HC/S = 0.02 Concentration range [diameter; ζ-potential]	HC/S = 0.04 Concentration range [diameter; ζ-potential]	HC/S = 0.1 Concentration range [diameter; ζ-potential]
SDS	5×10^{-3}–1×10^{-2} [2.7 ± 0.2; −19][a]	1×10^{-2}–2×10^{-2} [2.7 ± 0.1; −26][a]	1×10^{-2}–2×10^{-2} [3.1 ± 1.2; −30][a]	1×10^{-2}–2×10^{-2} [4.0 ± 2; −31]
CTAB	5×10^{-4}–2×10^{-3} [4.6 ± 0.2; +15]	1×10^{-3}–2×10^{-3} [4 ± 0.1; +27]	1×10^{-3}–2×10^{-3} [5.5 ± 1; +38]	1×10^{-3}–2×10^{-3} [40 ± 7; +54]
$C_{14}DMAO$	1×10^{-4}–5×10^{-4} [6.8 ± 0.4; −0.1]	2.5×10^{-4}–5×10^{-4} [7.0 ± 0.1; −7]	2.5×10^{-4}–5×10^{-4} [8.5 ± 2.5; −3]	5×10^{-4}–1×10^{-3} [10.0 ± 0.4; −10]
Triton X-100	1×10^{-4}–5×10^{-4} [6.7 ± 0.2; −1.1]	1×10^{-4}–5×10^{-4} [8.2 ± 1.0; −5.1]	1×10^{-4}–5×10^{-4} [7.9 ± 1.3; −5]	1×10^{-4}–5×10^{-4} [10 ± 0.1; −3.5]

[a] Measured at $[C_{14}DMAO] = 1 \times 10^{-3}$ M.

solution, thus allowing us to determine two successive concentrations identifying the concentration range that includes the CMC.

Table 3 reports DLS results that demonstrated to be in good agreement with both spectrophotometric and tensiometric data for the pure surfactants, and with tensiometric results when **HC**/surfactant mixtures are considered. On varying the percentage of **HC** in the mixtures, almost no variation of CMC is detected and tensiometric CMC values fall within the ranges for all the surfactants and the mixtures investigated.

As far as sizes are concerned (see the ESI† for DLS traces and correlation functions), the obtained dimensions are in agreement with literature data with SDS forming smaller micelles in comparison with the other surfactants. Moreover, for all the surfactants, the diameter of the particles does not change significantly except for the **HC**/S = 0.1 ratio. In the case of the ionic SDS and CTAB, characterized by a negatively and a positively charged head group, respectively, and a linear hydrocarbon chain, the addition of **HC**, although not influencing significantly their tendency to aggregate, induces a slight change in the shape of the equilibrium particles from spherical to slightly elongated assemblies since, N_{agg} being almost equal (see above), the micellar size slightly increases at high **HC** incorporation. Indeed, **HC** tends to insert parallel to the surfactant molecules with its compact hydroxyl group directed toward the water and the aromatic ring and the n-alkyl chain prevailingly solubilized in the micelle core. Such an arrangement reduces the repulsive interactions between the charged head groups thus promoting their approach and the micellar shape transformation.[43] This effect is strengthened in the case of CTAB. As a matter of fact the reduction of repulsive interactions corresponds to a decrease of the area of the surfactant head group (a) and therefore, the volume of the surfactant (V) and the length of the alkyl chain (l) being almost constant, to an increase of the critical packing parameter [CPP, $i.e.$ CPP = $V/(a \times l)$] that is a well-known index for predicting the favourite packing of the aggregate.[43] It is known that the increase of CPP promotes the transformation of a spherical micelle (CPP = 1/3) into a cylindrical micelle (CPP = 1/2).[43] The elongation of the micelles is confirmed by the ζ-potential increase measured for CTAB micelles on increasing the **HC**

content. As a matter of fact, in rod-like aggregates, positively charged head groups are forced to reside in a space-filling geometry reduced with respect to that of the two distinct charged groups of a spherical micelle inducing a decrease of counter ion binding and conferring to the micelle a higher ζ-potential.[43,62]

Finally, it is important to stress that DLS experiments have been performed by adding 0.1 M KCl, the only exception being SDS samples because the addition of salt caused SDS precipitation. The salting-out determined by the presence of KCl is another factor known to promote elongation of spherical micelles.[43] The slight increase of CTAB micelle diameters on increasing the **HC** percentage is in perfect agreement with the reported presence of rod-like micelles at slightly higher **HC** doping.[4] The fact that this transformation appears in DLS experiments but not in previous measurements ($i.e.$ N_{agg} determination) is ascribed to the fact that DLS experiments are performed in the presence of KCl (as well as data referring to ref. 4 in which the experiments are performed in the presence of different amounts of NaOH). Indeed, it is well known that salt favours, although generally at higher salt concentration, the transition of spherical to rod-like micelles.[63] In this case the synergic effect of the presence of **HC** and the ionic strength affords the transformation that in the absence of salt could not be visualized.

A different situation is monitored for the zwitterionic $C_{14}DMAO$. It is noteworthy that DLS measurements were performed in the presence of 0.1 M KCl and at 0.1 M NaCl the pK_a of $C_{14}DMAO$ slightly increases to 6,[58,64] thus potentially increasing the percentage of protonated $C_{14}DMAO$ in solution. Indeed, at this ionic strength, dimensions of pure cationic $C_{14}DMAOH^+$ and 50% $C_{14}DMAO/C_{14}DMAOH^+$ micelles did not change much in the concentration interval 1.0–30 × 10^{-3} M with the diameter varying in the ranges 2–9 and 20–30 nm,[57] respectively. These values are in perfect agreement with the DLS data in the present study. We did not use DLS for the solution with $C_{14}DMAO$ higher than 1.0×10^{-3} M because DLS is not a suitable technique to discriminate rod-like objects, when the ratio of the two dimensions of an object is quite high, in fact, its motion in solution is no longer totally random, generally preferring to orient the longer dimension parallel to the motion direction. In this case the analysis of the fluctuation of

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the intensity of the scattered light can lead to imprecise results because of being applied to motions that are not totally Brownian. Our data do not evidence any relevant change in the dimension even in the mixture containing 10% of cardanol, in perfect agreement with tensiometric data. The presence of **HC** does not affect the curvature of the micelle due to the fact that hydrogen bonds between **HC** and deprotonated $C_{14}DMAO$ are overwhelmed by hydrogen bonds between protonated and deprotonated $C_{14}DMAO$ in the micelles.

Conclusions

The present study promotes the use of sustainable plant-derived cardanol, once hydrogenated, as a green additive for surfactants. A percentage as high as 10% of hydrogenated cardanol does not affect, in terms of CMC, surface tension, aggregation number, ζ-potential and dimensions, the properties of the surfactant in water as evidenced by tensiometric, spectrofluorimetric and DLS measurements. The addition of 10% hydrogenated cardanol to a zwitterionic surfactant such as $C_{14}DMAO$, known for its multiform self-assembling behaviour depending on the concentration, temperature or pH, demonstrated to strongly promote the formation of small spherical micelles over rod or cylindrical micelles. Besides, our study evidenced that the use of a lipophilic dye can strongly affect CMC determination in surfactant mixtures whenever the dye can establish preferential interactions with one component of the mixture. In the present study we have demonstrated that the concurrent presence of Orange OT and 10% hydrogenated cardanol may decrease the CMC of charged surfactants such as CTAB and SDS up to 65 times.

Experimental

Materials

Hexadecyltrimethylammonium bromide (CTAB), dodecyl sulfate sodium salt (SDS), $C_{14}DMAO$, Triton X-100, pyrene (99%), *N,N*-dibutylaniline (DBA), 1-(*o*-tolylazo)-2-naphthol (Orange OT) and solvents of analytical grade were purchased from Sigma-Aldrich and used without further purification. Hydrogenated cardanol prepared in nearly quantitative yields by catalytic (Pd/C) hydrogenation of cardanol obtained by distillation of CNLS following ref. 65, kindly provided by Prof. Attanasi (University of Urbino), was used as received.

Hydrogenated cardanol (**HC**): white crystals; m.p. 50–52 °C; ^1H NMR (400 MHz, CDCl$_3$), δ = 0.89 (t, *J* = 6.8 Hz, 3H, CH$_3$), 1.27–1.31 (m, 24H, 12 CH$_2$), 1.55–1.63 (m, 2H, CH$_2$), 2.56 (t, *J* = 8.0 Hz, 2H, CH$_2$), 4.75 (brs, 1H, OH), 6.64–6.67 (m, 2HAr), 6.76 (d, *J* = 7.6 Hz, 1HAr), 7.14 (t, *J* = 8.0 Hz, 1HAr); ^{13}C NMR (100 MHz, CDCl$_3$), δ = 14.4 (q), 22.9 (t), 29.5 (t), 29.6 (t), 29.7 (t), 29.8 (t), 29.9 (t), 31.5 (t), 32.2 (t), 36.1 (t), 112.7 (d), 115.5 (d), 121.2 (d), 129.6 (d), 145.2 (s), 155.6 (s); IR (nujol): ν_{max} = 3351, 2968, 2911, 1583 cm^{-1}; MS *m/z* (%): 304 (M$^+$) (53), 149 (18), 121 (28), 108 (100), 77 (16).

ESI-MS measurements

ESI-MS spectra were collected with a ZMD micromass single quadrupole mass spectrometer operating at 4000 *m/z*. The sample was injected directly into the instrument through a Hamilton syringe. The parameters used were a capillary voltage of 3.14 mV, a cone voltage of 30 V and a desolvation temperature of 423.1 K. The 250–1050 *m/z* spectral range was examined in the presence of saturated Orange OT and different concentrations of **HC** (*i.e.* 1.0×10^{-4} M and 2.0×10^{-2} M); no significant peak could be monitored above 750 *m/z*.

Spectrophotometric analyses

A few crystals of Orange OT were added to ten/fifteen solutions at different concentrations of surfactants or **HC**/surfactant mixtures. After at least a day of gentle shaking, the solutions were filtered through a 0.22 μm Millipore filter. The absorbance values of the dye, at λ_{max} = 492 nm, were plotted against the concentration of the surfactants. Data are reported in the ESI.†

Tensiometric analyses

Surface tension measurements were performed with a Sensa-Dyne tensiometer QC6000 *via* the bubble pressure method. The surfactant concentration was varied by adding the concentrated surfactant solution in small portions and readings were taken after thorough mixing and temperature equilibration. The temperature was maintained at 298 ± 0.1 K by circulating water from a thermostat. The accuracy of measurements was within ±0.1 dyne cm^{-1}. Surface tension values (dyne cm^{-1}) were plotted against the decimal logarithm of the molar concentration of the surfactant in order to evaluate the relevant CMC and a representative plot for each investigated mixture is reported in the ESI,† while the results obtained are reported in Table S1.† The investigated concentrations of surfactants were 9.00×10^{-6}–3.00×10^{-3} M for Triton X-100, 8.00×10^{-4}–3.50×10^{-2} M for SDS, 4.00×10^{-5}–6.00×10^{-3} M for $C_{14}DMAO$ and 1.00×10^{-5}–4.00×10^{-3} M for CTAB. An additional measurement was performed on **HC**/SDS 0.1 solutions, within the SDS concentration interval 9.00×10^{-5}–2.00×10^{-3} M, in the presence of Orange OT, in order to confirm the effect of the dye in promoting the formation of micelles.

Aggregation number

The aggregation number was determined by exploiting the fluorescence quenching method[66] and using pyrene as the fluorescent molecule and *N,N*-dibutylaniline (DBA) as the quencher.[64] An appropriate volume of pyrene stock solution in ethanol was added to a cuvette containing the different surfactant aqueous solutions (2.00×10^{-2} M Triton X-100, 5.00×10^{-2} M SDS, 5.00×10^{-3} M CTAB and 1.00×10^{-2} M $C_{14}DMAO$). After evaporation of the ethanol, DBA, dissolved in dioxane, was added to the cuvette in order to obtain a range of quencher concentrations 5–100 μM while keeping the concentrations of pyrene and the surfactant constant. Pyrene was excited at λ 335 nm and the emission intensity (I_0) was monitored at λ 376 nm and λ 395 nm. If the micelles are assumed

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to be monodisperse, the relative intensity of fluorescence emission I is given by the following eqn (1):

$$\mathrm{Ln}(I/I_0) = N\,[\mathrm{Q}]/(C - \mathrm{CMC}) \tag{1}$$

where [C] is the total surfactant concentration, [Q] is the quencher concentration and N is the surfactant aggregation number.

Dynamic light scattering and ζ-potential analyses

The determination of the micelle size of the samples and ζ-potential measurements were performed *via* dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern) in deionized water and in the presence of potassium chloride 0.1 M (where not specified) to maintain the ionic force constant.

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