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Choline alkylsulfates – New promising green surfactants

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ABSTRACT

In this work we show how a new promising green and highly water-soluble surfactant can be designed based on recent progress in the knowledge of counterion–headgroup binding and crystallization behavior. The result is the combination of a most classical surfactant anion, dodecylsulfate (DS), with choline (Ch), a natural green cation. The advantage of the physiological metabolite choline is its bulky structure that prevents ChDS from easy crystallization and thus leads to a considerable lowering of the Krafft point down to 0 °C. The counterion–headgroup binding is reflected by the aqueous phase behavior of ChDS. Conductivity, surface tension, and cryo-TEM measurements allow the characterization of the dilute micellar region, while the penetration scan technique enables the establishment of a preliminary aqueous phase diagram. In addition, the influence of different mono- and divalent salts on the solubility of ChDS is investigated. The results are compared to the alkali sulfate and alkylcarboxylate homologs, and reveal that ChDS is less sensitive towards addition of salts than, for instance, choline carboxylates due to an increased counterion–headgroup association. Further, cytotoxicity tests on HeLa and SK-Mel 28 cells are presented and compared to other surfactants, showing that ChDS is no more harmful than its sodium counterpart SDS. Taken together, our findings highlight that the harmless green cation choline is of great potential for the design of new surfactants.

1. Introduction

Nowadays, classical soaps (i.e. salts of fatty acids) are still very important for many applications, essentially due to their general availability and low costs. In First World countries, they again receive a growing deal of interest because of their potential as green surfactants. However, their limited water solubility, relatively high pH, and substantial sensitivity to water hardness cause serious problems in the formulation of skin-friendly home- and personal-care products [1–3]. As shown in recent work, choline carboxylates provide a promising alternative to conventional soaps, since they show improved solubility and are as biocompatible as their sodium or potassium homologs [1,4–6]. Nonetheless, they still suffer from the other common drawbacks related to fatty acid surfactants, that is, strong alkalinity and reduced performance in the presence of hard water or simple alkali salts.

The high pH of soaps can be avoided by using a headgroup of higher acidity, such as sulfate. Sodium alkylsulfate surfactants were furthermore shown to be less sensitive to water hardness, while still being readily biodegradable and allowing synthesis from renewable raw materials [7,8]. The most prominent examples of this class of surfactants are certainly sodium dodecylsulfate (SDS) and sodium laurethsulfate, which find broad application as active agents in products like shampoos or shower gels [7]. Pure SDS typically becomes well soluble at temperatures ranging from 12 to 20 °C [9–11]. However, its solubility temperature often exceeds 25 °C when other salts are present (even though this effect is less pronounced than in the case of carboxylate detergents) [12,13]. The use of the more surface-active longer-chain homologs of SDS, such as sodium tetradecylsulfate, is also restricted due to poor solubility [7,10,14].

According to Collins' concept of "matching water affinities" [15,16] and the classification of headgroups in this context [17], sodium is supposed to bind only weakly to the alkylsulfate anion. Further, in contrast to carboxylate soaps, the degree of counterion–headgroup association in alkylsulfate surfactants should increase with the size of the cation ($Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$). This has been confirmed for example by combined small-angle X-ray and neutron scattering (SAXS and SANS) measurements [18–21]. Stronger counterion–headgroup binding usually results in a higher Krafft temperature (T_{Kr}). Correspondingly, it was found that the Krafft points of alkali alkylsulfates increase with growing size of the cations [9], whereas those of alkylcarboxylates decrease [2,4,22].

Interestingly, the water solubility of alkylsulfate surfactants can be extended towards lower temperatures when bulky counterions like tetraalkylammonium (TAA) ions are employed [23–25]. Such behavior is in line with what has been reported for fatty acid soaps,

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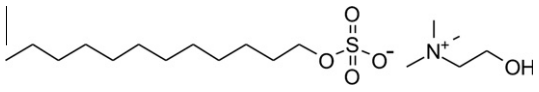

Fig. 1. Molecular structure of choline dodecylsulfate (ChDS).

but conflicts the above-mentioned counterion trend for alkylsulfates [23,26–30]. Nevertheless, an important difference between TAA alkylsulfate and alkylcarboxylate surfactants is obvious in the case of tetrabutylammonium (TBA): with increasing temperature, TBA alkylsulfates show a clouding phenomenon (as it is otherwise only observed for non-ionic surfactants), while such an effect does not occur for TBA alkylcarboxylates [14,28,29,31,32]. Whether TAA ions are more associated to the alkylsulfate anion than for instance sodium has been the object of some debates. Several studies confirmed that the degree of counterion dissociation (α) is less pronounced for TAA ions than for sodium [18,21,24,31,33,34]. In turn, aggregation numbers of TAA alkylsulfate surfactants were found to be lower and micelles smaller than expected on the basis of the critical micellization concentration (*cmc*) and the value of α [24,30,31,35–37]. Zana et al. proposed that, due to sterical hindrance, TAA ions are condensed in two layers over the surface of the micelle, with a first layer being rather compact and a second appearing largely incomplete [30,31]. This hypothesis is supported by a very recent study of Brown et al., who investigated salts of DS and TAA ions amongst others by SANS [24]. Unfortunately, information on the influence of alkali chlorides on the Krafft temperatures of corresponding surfactants is not available to date.

In any case, TAA counterions seem to be suitable for enhancing the solubility of alkylsulfates, probably because their bulkiness prevents efficient lattice packing in the crystals. However, simple TAA ions are toxic and do hence not meet the requirements of most surfactant applications [38–40]. Therefore, we have chosen choline (Ch) – a natural human metabolite – as counterion of dodecylsulfate (DS) in this work and characterized the resulting surfactant (ChDS, shown in Fig. 1) with respect to its Krafft point, *cmc*, and aqueous self-assembly behavior. In addition, cytotoxicity studies were carried out using two different human cell lines, and the influence of various chloride salts on the solubility of ChDS was examined. Results are compared to values obtained for SDS, potassium dodecylsulfate (KDS), and the alkylcarboxylate homologs ChC12, NaC12, and KC12.

2. Experimental section

2.1. Chemicals

SDS (Merck, $\geqslant$99%), sodium laurylcarboxylate (NaC12) (Sigma–Aldrich, 99–100%), lithium chloride (Merck, p.a.), sodium chloride (Merck, p.a.), potassium chloride (Merck, p.a.), choline chloride (Sigma, $\geqslant$99%) and calcium chloride dihydrate (Riedel-de Haën, $\geqslant$99%) were used as received. Titer solutions of potassium hydroxide (0.1 N and 1 N) were purchased from Merck, while choline base (ChOH) was provided by Taminco as a clear (APHA < 300) 46 wt.% aqueous solution. ChC12 was prepared and purified according to a procedure described elsewhere [1]. KC12 was obtained by direct neutralization of dodecanoic acid (Merck, $\geqslant$99%) with 0.1 N KOH. The stock solution of choline hydroxide was stored at −18 °C under nitrogen and protected from light in order to prevent decomposition. The exact concentration of the stock was determined by threefold titration with 0.1 M HCl (Merck).

2.2. Surfactant synthesis

ChDS and KDS were prepared by ion exchange of SDS using a strong cation exchanger (type I, Merck, p.a.). First, the column material was washed successively with 1 M HCl (Merck) and a large amount of Millipore water, such that a near-neutral pH was achieved. Afterwards, the ion exchanger was loaded with the chloride salts, which were available in high purity. For this purpose, 1 M aqueous salt solutions were passed over the resin until the resulting pH value was around 4–5 (corresponding to four times the maximum cation exchange capacity). In order to ensure completeness of the exchange process, the column was subsequently treated with 0.1 M solutions of the respective hydroxides (effluent pH $\approx$ 10). The resin was then rinsed with Millipore water until quantitative removal of any excess base was accomplished (final pH $\approx$ 7). SDS was employed as a 0.1 M solution in an amount lower than 1/3 of the minimum resin capacity. After generously discarding forerunnings, the solid surfactants were obtained by lyophilization of the effluent. The resulting white powders were dried subsequently in a desiccator at a pressure of 10^{-2} mbar for about 2–3 days.

The purity of ChDS and KDS was ascertained by ^{1}H NMR ($CDCl_3$), ^{13}C NMR ($CDCl_3$) and electro-spray mass spectroscopy (ES–MS). NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz with tetramethylsilane (TMS) as internal standard. Mass spectrometry was performed on a ThermoQuest Finnigan TSQ 7000 instrument. Corresponding data are given in the Supporting Information (SI).

2.3. Determination of Krafft temperatures

Precise solubility temperatures were determined by turbidity measurements using an automated home-built apparatus, which was equipped with a computer-controlled thermostat [41]. Turbidity was detected by monitoring the transmission of light emitted by a LED with the aid of a light-dependent resistor (LDR). If necessary, samples were cooled until precipitation occurred, followed by subsequent heating with a rate of 1 °C per hour.

2.4. Density measurements

Densities (required in order to evaluate exact concentrations of the samples) were determined at 25 °C using a vibrating tube densimeter (Anton Paar DMA 60), which was calibrated by measuring purified dry nitrogen and degassed water. The resulting experimental values (see Table S1 in the SI) were found to increase linearly in the studied range of concentrations. Regression of the data gave the following equation for the calculation of density values: ρ/g L^{-1} = 0.51 wt.%$_{ChDS}$ + 997.05/g L^{-1}. The molar volume (V_m) of the surfactant was determined to V_m (ChDS) = 0.3159 L mol^{-1}.

2.5. Surface tension measurements

The surface tension (σ) was measured with a platinum–iridium ring using a Krüss tensiometer (model K100 MK2), which was equipped with a double-dosing system (Metrohm Liquino 711). This setup permits automated data acquisition as a function of the surfactant concentration (reversed *cmc* determination). The temperature was monitored on-line and kept constant at 25 °C ± 0.1 °C. Measured values were corrected according to a procedure introduced by Harkins and Jordan [42]. The resulting progression of the surface tension as a function of the surfactant concentration is shown in the Supporting Information (Fig. S1).

2.6. Conductivity measurements

Conductivities (κ) of aqueous ChDS solutions were measured at 25 °C by means of an autobalance conductivity bridge (Konduktometer 702, Knick), equipped with a Consort SK41T electrode cell. The cell constant was determined by measuring 0.01 m, 0.1 m and