Solubilisation of stearic acid by the organic base choline hydroxide

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Abstract

In a previous study we have shown that the substitution of alkali ions in common fatty acid soaps by choline as a counterion of biological origin increases the solubility of the respective soaps without lowering the biocompatibility. Nevertheless, while choline dodecanoate (ChC₁₂), myristate (ChC₁₄), and palmitate (ChC₁₆) have Krafft points below room temperature or even under 0 °C, choline stearate (ChC₁₈) was not soluble below 40 °C. In the present contribution we show that an excess of choline hydroxide is able to solubilise choline stearate at temperatures as low as 14 °C. Furthermore, we compare our results to those obtained for the sodium and potassium salts of fatty acids, with molar ratios of base to acid higher than 1:1. In order to elucidate the solubilisation process regarding the different ion binding to the carboxylic headgroup, we further investigated the effect of different added chloride salts on the solubility of choline stearate. Our findings indicate that the cation affinity to the carboxylate headgroup follows the trend Na⁺ > K⁺ ≫ Ch⁺. The results are discussed in terms of hydrolysis of the fatty acids in combination with Collins’ concept of “matching water affinities”. As a feasible application of choline base, we present the saponification and simultaneous solubilisation of butter as an example of a hardly soluble triglyceride.

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1. Introduction

Surfactants are ubiquitous in every day life. Of these, the anionic sub-class still represent the most frequently used type. Common soaps, such as sodium and potassium carboxylates, are widely used, especially in household and personal cleaning products. Nevertheless, these simple alkali carboxylate surfactants are confined in their applicability due to their poor solubility in water. While the Krafft point is still about 25 °C in the case of sodium laurate (NaC₁₂), it increases rapidly with growing length of the hydrophobic tail and is already about 71 °C for sodium stearate (NaC₁₈) [1,2]. Unfortunately, this undesirable elevation of the Krafft point with increasing hydrophobic chain length, is paralleled by the desirable increases in surface activity and solubilising power [3]. Replacing the alkali counterions by tetraalkylammonium (TAA) ions provides an effective way to enhance the solubility of the respective surfactants [4–6]. For instance, Zana found that a substitution of sodium in NaC₁₈ by tetrabutylammonium (TBA) can lower the Krafft temperature down to 0 °C or lower [7]. However, TAA soaps are toxicologically questionable, since simple TAA ions are known to be toxic [8–11].

Previously, we showed that choline as a quaternary ammonium ion of biological origin provides a biologically compatible alternative to the simple TAA ions [12]. Choline, formerly known as vitamin B₄, has several key functions in the human body [13–15]. Its molecular structure is shown Fig. 1. It serves for instance as a precursor for phospholipids and acetylcholine [14,15]. Generally, choline hydroxide (ChOH) as a strong base provides a technologically interesting alternative to alkali or alkaline-earth metal hydroxides, especially in the field of wafer cleaning in semi-conductor industry [16,17].

Choline carboxylate (ChCm) surfactants were found to be highly soluble in water. Krafft temperatures of ChCm soaps are below room temperature up to m = 16 and partly even below 0 °C [12]. However, the Krafft point of choline stearate (ChC₁₈) is still above room temperature (T_Kr (ChC₁₈) = 40 °C) [12]. McBain and Sierichs have shown that by addition of small amounts of potassium hydroxide to potassium carboxylate solutions, the protonation of the fatty acid ion (“hydrolysis reaction”) is completely suppressed [18]. As a consequence, the solubility temperature of, for example, potassium stearate (KC₁₈) decreases from around 60 °C to 47.5 °C [18]. Furthermore, a similar but less pronounced effect was observed when substituting potassium hydroxide by potassium chloride [18]. On the other hand, if sodium hydroxide is added in minor fractions to sodium carboxylate soaps, the protonation is also suppressed, but the solubility temperature of the respective surfactants is not influenced noticeably [18,19]. Moreover, for instance, Lin et al. showed...
that the addition of sodium chloride to sodium myristate (NaCl14) worsens the solubility of the soap [20].

Considering the different behaviour of sodium and potassium hydroxide with respect to soap solubility, likely two effects are operating. One is the suppression of carboxylate protonation. The other is most probably a “salting-in” or “salting-out” effect of the respective cation.

Based on these observations, we study the solubility of choline stearate as a function of choline hydroxide addition. In order to shed light on the solubilisation process and to distinguish between hydrolysis and specific ion–ion interactions we replace in a second set of experiments the choline base by the different chloride salts of sodium, potassium and choline. Furthermore, we compare our results with those of the corresponding sodium and potassium soaps.

On the basis of our findings, we present, as a potential application of choline base, the saponification and simultaneous solubilisation of butter as an example of a hardly soluble triglyceride.

2. Experimental

2.1. Materials

Dodecanoic acid (Merck, p.a.) and octadecanoic acid (Fluka, puriss, min. 98.5%) were used as received. The chloride salts of sodium and potassium were obtained from Merck (p.a.), choline chloride was purchased from Sigma–Aldrich (min. 98%). Sodium and potassium hydroxide were employed in the form of 1N titre solutions (Merck). Choline hydroxide was obtained as a clear 46 wt% aqueous solution from the company Taminco. The solution was stored under nitrogen at −18 °C and protected against light in order to avoid decomposition. For experiments, small samples were taken and converted immediately. The concentration of the choline base stock was determined precisely to 46.6 wt% by three-fold titration with 0.1 M HCl (Merck). For the butter experiments, a conventional mild acidic butter (“Die streichzarte Butter”, Goldsteig, Bayerwald GmbH) was used, containing typically 82 wt% fat.

2.2. Methods

2.2.1. Sample preparation

Samples for the determination of the influence of excess hydroxide on different soap solutions were prepared as follows. For each investigated molar ratio of base to acid appropriate amounts of the fatty acid were weighed separately. Appropriate amounts of the fatty acid were weighed separately for each investigated molar ratio of base to acid. Then the respective hydroxides were added, yielding solutions containing 1 wt% fatty acid with different molar ratios of base to acid.

For studying the influence of different chloride salts on the solubility behaviour of choline stearate, stock solutions of the soap and the chloride salts were prepared first. For the surfactant stock, two-fold recrystallized ChC18 was used (for details on preparation see Ref. [12]). Afterwards, stock solutions were mixed and diluted correspondingly in order to obtain 1 wt% ChC18 solutions with different molar ratios of the chloride salts to soap.

Regarding the butter experiments, small amounts of the frozen butter (1 wt%) were weighed and treated with different amounts of choline hydroxide.

Each sample was stirred for 12 h and, if necessary, heated in order to obtain homogenous solutions. In all cases, Millipore water was used as solvent.

2.2.2. Determination of the solubility temperature

Solubility (or clearing) temperatures were first determined by direct visual observation, noting the temperature at which the solutions turned completely clear and isotropic. For this purpose, small amounts (−3 mL) of the respective samples were flame-sealed in glass vials and subsequently heated at a rate of about 1 °C/h. Solutions, which were already clear at ambient temperature, were slowly cooled until turbidity was discernible, prior to experiment start.

Precise solubility temperatures were obtained from turbidity measurements using an automated home-built apparatus [21]. Specimen holders were placed in a computer-controlled thermostat. Light emitted by a LED crosses the samples and the transmitted light is detected by a light-dependent resistor (LDR). Samples were cooled if necessary until precipitation occurred and then heated at a rate of 1 °C/h.

2.2.3. Cryogenic-transmission electron microscopy (Cryo-TEM)

Specimens for cryo-TEM were prepared by placing a small drop of the sample on a holey carbon grid. Excess liquid on the grid was removed by a filter paper. The film was then vitrified by plunging the grid into liquid ethane. The grid was examined at temperatures around 90 K using a Zeiss EM922 EF transmission electron microscope (Zeiss NTS GmbH). The acceleration voltage of the TEM was 200 kV. All images were recorded by a CCD camera (Ultrascan 1000, Gatan) and processed with a digital imaging processing system (Digital Micrograph 3.9 for GMS 1.4).

3. Results and discussion

3.1. Influences of different hydroxides on soap solubility

In Fig. 2, the solubility temperatures of stearic and lauric acid are displayed as a function of added choline, sodium and potassium hydroxide. For studying the effect of sodium hydroxide, lauric acid was considered as more suitable than stearic acid, since in the latter case the clearing temperatures reach more than 90 °C upon addition

![Figure 1. Molecular structure of the choline cation.](image1.png)

![Figure 2. Clearing temperature as a function of the molar ratio of NaOH (□), KOH (△) and ChOH (○) to stearic and lauric acid, respectively (fatty acid concentration fixed at 1 wt%).](image2.png)
All of the investigated hydroxides are strong bases. Hence, each base should be capable of a complete deprotonation of the fatty acid, at least at a small excess. Nevertheless, we observed essential divergences among the studied systems. A 5 mol% excess of base enhances the corresponding soap solubility to different extents ($\Delta T = 1^\circ C$ for NaOH/C12, 9.5$^\circ C$ for KOH/C18 and 7$^\circ C$ for ChOH/C18). In the case of the NaOH/C12 system, this excess value correlates with the minimum of the solubility curve, whereas in the other two investigated systems maximum soap solubility can be achieved by addition of still higher amounts of base. 25–50 and 200–300 mol% excess of potassium and choline hydroxide, respectively, are necessary to reach the lowest possible clearing temperatures for the surfactants. Apparently, the amount of hydroxide required to achieve maximum solubility of the corresponding soaps follows the order NaOH < KOH < ChOH. Further addition of alkali hydroxide leads in both cases to a re-increase of the solubility temperature, in the case of NaOH even above the solubility temperature of the 1:1 composition, see Fig. 2. On the other hand, the clearing temperatures of ChOH/C18 remain more or less constant up to high molar ratios of ChOH:C18.

At this point, the most outstanding result of these studies is the fact that it is possible to obtain ChC18 micelles at temperatures as low as 14$^\circ C$ by addition of choline hydroxide, in contrast to the homologous alkali stearates.

Our findings indicate that the solubilisation of fatty acid soaps by hydroxides is also affected by processes other than protonation (hydrolysis), such as “salting-in” and “salting-out” effects. In order to distinguish between the effect due to the degree of protonation and the salt effect, we performed a further series of experiments, in which we added different chloride salts instead of excess choline base to ChClC18 solutions.

### 3.2. Influences of different chloride salts on the solubility of choline stearate

In Fig. 4, clearing temperatures for 1 wt% ChClC18 systems are plotted as a function of the addition of sodium, potassium and choline chloride.

Obviously, the solubility of choline stearate deteriorates upon addition of alkali chlorides in all cases. At a molar ratio of 1:4 of chloride salt to ChClC18, NaCl increases the surfactant’s clearing temperature (46.9$^\circ C$) somewhat less than KCl (48.5$^\circ C$). In turn, at higher chloride salt fractions the solubility temperatures of ChClC18 rise much more steeply when adding NaCl (up to 69$^\circ C$ in the studied concentration regime) than when adding KCl.

$$R \text{–COOH} + H_2O \rightleftharpoons R \text{–COO}^- + H_3O^+ \quad (1)$$
Considering the Krafft temperature of NaC18 ($T_{Kr}$ (NaC18) = 71 °C), it may be concluded that choline as the initial counterion of the soap is progressively substituted by sodium [2,20]. However, one has to be careful to interpret such solubility curves simply based on counterion exchange processes, since it is well known that NaCl exerts a “salting-out” influence on sodium carboxylate solutions, leading to decreased soap solubility [19,20]. Hence, this effect could increase the solubility temperatures of ChC18 in the same manner as the replacement of choline by sodium in the vicinity of the carboxylic would do [20].

Clearing temperatures of choline stearate solutions reach 55 °C and subsequently remain more or less constant at molar ratios of KCl to ChC18 higher than 1:1. Regarding the Krafft temperature of KC18 ($T_{Kr}$ (KC18) = 57 °C), it is again possible to argue that choline is fully replaced by potassium as the counterion of the soap [12]. Furthermore, in contrast to the salting-out effect of NaCl, McBain and Sierichs reported a decrease of the soap solubility temperature by 2 °C when small amounts of KC1 are added to aqueous KC18 solutions [18]. This finding suggests that KC1 can indeed exert a slight salting-in effect on alkali carboxylate soap solutions at low concentrations. However, larger amounts of KC1 were found to induce salting-out of potassium laurate [24]. Whether a counterion exchange of choline by the alkali ions takes place or not will be discussed in the following section.

The addition of choline chloride to ChC18 solutions appears to have no significant influence on the solubility. Initially, a small decrease of the clearing temperature from 40 to 39 °C is observed, followed by a subsequent increase to 40.4 °C. It was shown by other groups that TAA ions exhibit a salting-in effect on alkali carboxylate solutions [20]. Our data do not indicate such an effect of choline chloride on choline carboxylate surfactants.

3.3. Specific ion effects in aqueous alkylcarboxylate surfactant solutions

When discussing solubilities or Krafft points of surfactants, two competing thermodynamic forces have to be considered. These are the free energy of the micellar solution on the one hand, and that of the solid crystalline state on the other. The latter contribution is often considered as the main driving force. However, it is well known that the Krafft points of alkali carboxylate surfactants follow the trend Li+ > Na+ > K+ > Cs+, which is opposite to that observed for alkylsulfates [18,25–29]. This reversed order cannot be explained simply based on different degrees of hindrance in the crystalline packing. Considering this fact and our experiments, we will focus in the following on specific ion interactions.

Previously, the Hofmeister series with regard to the influences of ions on macromolecular properties was interpreted mainly in terms of “making” or “breaking” the bulk water structure. A summary of this discussion is given in Ref. [29]. However, several workgroups have shown that short-range ion–ion interactions are the dominant forces instead of the long-range electrostatic fields generated by simple ions in water, which appeared to be weak relative to the strength of water–water interactions [30–35]. Accordingly, simple monovalent ions do not alter the hydrogen bonding network of the bulk water outside their direct vicinity [30].

Collins’ “law of matching water affinities” provides a straightforward model of specific ion–ion interactions, wherein ion pair formation is controlled by hydration–dehydration processes [33–35]. Essentially, his model divides ions into two classes depending on how they modify the surrounding water molecules. Thereby, ions of high hydration and high surface charge density, such as Li+ and F−, are referred to as “kosmotropes”, while large ions of weak hydrations and low surface charge density, such as Cs+ and I−, are termed “chaotropes” [33–35]. In this context, water is regarded as a medium-size zwitterion. Matching cogenic cations and anions results in a breakdown of the hydration shell and in the spontaneous formation of an inner-sphere ion pair [35]. In turn, when ions are mismatched (kosmotrope–chaotrope or vice versa), they will not dehydrate spontaneously, since their affinities to (the medium-size) water are higher than to each other [35]. Consequently, these ions remain separated by water. The dissolution of salts is accompanied by either the formation of ion pairs or a dissociation of the salt, the latter promoting solubility [25,34].

In the context of this model, sodium is classified as a small and highly hydrated ion (kosmotrope), whereas potassium is more chaotropic. Choline is much bigger and weakly hydrated and hence a very chaotropic ion [35–38]. Furthermore, alkylcarboxylates can be considered as kosmotropes [39]. Applying Collins’ “law of matching water affinities” to the present system thus results in the following affinity trend of the cations to the carboxylate anion: Na+ > K+ ≫ Ch−. While the order of the first two cations has been confirmed by several studies [40–43], there is to our knowledge no work published on the behaviour of choline and alkylcarboxylates in this context. However, it can be supposed that choline approximately behaves like other small quaternary ammonium ions [12]. Sodium, the carboxylate ion, both being kosmotropes, are supposed to form ion pairs in water. In turn, the more chaotropic potassium ion remains separated from the carboxylic headgroup by water. Consequently, the solubilities of sodium carboxylates are expected to be lower than those of the corresponding potassium salts. This prediction is verified by the observed trend of the Krafft points. In this regard, the reversed order reported for alkylsulfates is also easily explained, considering the fact that the alkylsulfate anion is of chaotropic nature [42,44].

The results of our experiments on the influence of different added chloride salts on the solubility of ChC18 agree well with the predictions from Collins’ concept. NaCl was found to decrease drastically the solubility of ChC18 solutions. While there is a similar but less pronounced effect observed for KCI, no noticeable influence could be discerned for KC1. In view of this, it can be assumed that in contrast to choline as counterion, the alkali ions form strong ion pairs with carboxylates and that it requires more energy (higher temperatures) to separate them. At high chloride salt concentrations, however, additional effects may play a significant role as well [45]. Sodium, for instance, as a highly hydrated ion, could remove free bulk water and hence increase the effective surfactant concentration, resulting in a salting-out of the latter [20].

The influence of the different hydroxides on the solubility of the corresponding carboxylate surfactants appears to be more complex. We have found that the amount of hydroxide required to reach maximum soap solubility follows the order NaOH < KOH < ChOH, and ranges up to 200 mol% excess for ChOH. Since all of the investigated hydroxides are strong bases, each should be capable of completely deprotonating the fatty acid. The addition of the choline ion itself is unlikely to decrease the solubility temperature of ChC18 to such a great extent (from 40 °C down to 13.8 °C), as virtually no effect was observed when adding choline chloride.

Taking into account the different cation–anion affinities, we propose two coupled equilibria according to Eq. (2) to explain the experimental results. One is the ionization of the fatty acid and the other is the subsequent formation of ion pairs.

$$R COOH + OH^- \rightarrow H_2O + R COO^- + H^+$$

According to this, the carboxylate anion can be removed from the hydrolysis equilibrium by association with the cation. With regard to Collins’ concept, sodium should be able to shift the equilibrium to the right side, whereas for choline the association step is negligible. Consequently, less NaOH is necessary compared to ChOH to achieve complete ionization of the fatty acid, while KOH adopts an intermediate position in this order. However, further experiments need to be performed to confirm this argumentation.

Nevertheless, for higher amounts of added alkali hydroxides, the solubility of the respective surfactants decreases again, similarly as observed for the chloride salts. At higher salt concentrations, the removal of bulk water by ion hydration apparently becomes more significant, resulting in a more concentrated soap solution. As a consequence, the surfactant “sals out”.

3.4. Saponification and solubilisation of butter by choline base

Butter as a biological product underlies certain fluctuations regarding the contents. As such it is of course not appropriate for detailed chemical studies. Nonetheless, we considered it as suitable for demonstrating the principle of the dissolution of water-insoluble triglycerides in aqueous solutions of choline hydroxide.

Conventional cow butter typically contains around 82 wt% fat, which in turn is composed of triglycerides that are constituted typically by palmitic (~25%), oleic (~25%), stearic (~10%) and myristic (~9%) acid [46,47]. Shorter- and middle-chain saturated fatty acids are further present in a non-negligible amount (~12%) [46,47]. Other appreciable ingredients of the butter are the water-insoluble cholesterol and vitamin E [46,47].

In Fig. 5, a picture of aqueous butter solutions at 25 °C with different mass ratios of choline hydroxide to butter is shown. At small amounts of added ChOH, the butter remains more or less completely insoluble in water. However, continued addition of choline base leads initially to an emulsification and finally to the dissolution of butter. The amount of choline hydroxide required to obtain almost clear and foaming solutions ranges between mass ratios of ChOH to butter of 40–45.

Although quantitative data regarding the composition of the used butter, such as the number of enclosed ester bridges, cannot be given, we suggest the following dissolution process. First, the ester bridges of the water-insoluble triglycerides are split by addition of choline base. Then, by neutralisation, the released fatty acids become surfactants with choline as counterion. These choline soaps in turn are, as shown above, highly soluble in water, particularly when excessive ChOH is present. Subsequently, the generated surfactants can solubilise other water-insoluble compounds, such as cholesterol and vitamin E, resulting in almost clear and foaming aqueous solutions.

4. Conclusion

It was shown that adding excess choline hydroxide to choline stearate solutions is an efficient procedure to reduce the solubility temperature of the soap from 40 °C down to 14 °C. To explain this considerable increase in solubility, the effect of alkali hydroxide addition to aqueous solutions of sodium laurate and potassium stearate was likewise investigated. We observed that the amount of hydroxide required to gain maximum soap solubility follows the order NaOH < KOH < ChOH. Still higher amounts of alkali base induced a re-increase of the respective solubility temperatures, while no further change was found in the case of choline base.

In order to distinguish between the effects of fatty acid hydrolysis and of specific ionic interactions, we additionally studied the influence of sodium, potassium and choline chloride on the solubility of choline stearate. Both alkali chlorides caused an increase of the clearing temperature of the surfactant, the influence of KCl being less pronounced than that of NaCl. By contrast, choline chloride exerted no noticeable effect on the solubility.

Results were discussed in terms of Collins’ “law of matching water affinities” based on different cation–anion affinities and association behaviours. We draw the conclusion that the affinity of the investigated cations to the alkylcarboxylate anion follows the order Na+ > K+ > Ch+.

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