

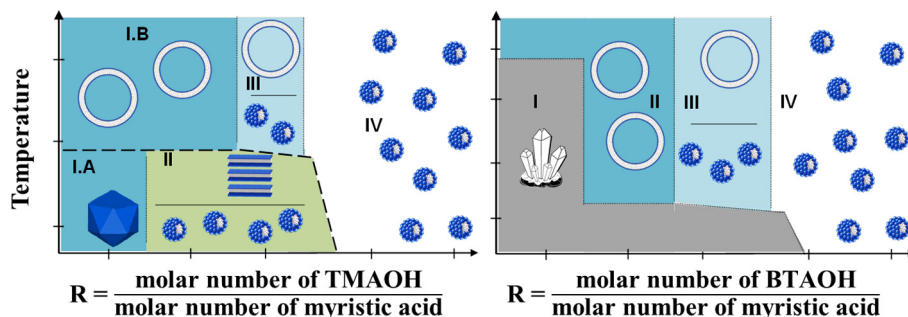


Regular Article

Impact of the molar ratio and the nature of the counter-ion on the self-assembly of myristic acid

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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 June 2017

Revised 13 September 2017

Accepted 14 September 2017

Available online 18 September 2017

Keywords:

Self-assembly

Fatty acid

Counter-ion

Molar ratio

Chain melting

ABSTRACT

Hypothesis: In fatty acid systems, the role of the nature of the counter-ion on their solubility is well described. However, the effect of the molar ratio (R) between the fatty acid and its counter-ion is less explored. We investigated the effect of R as a function of the temperature in aqueous solution between myristic acid and two organic amines under hydroxide form: tetramethylammonium (TMAOH) and benzyltrimethylammonium hydroxide (BTAOH). We compare with the results previously obtained for choline hydroxide as counter-ion (Arnould et al., 2015).

Experiments: We characterized the phase behavior by coupling phase-contrast microscopy, SANS, DSC and WAXS experiments. The myristic acid ionization state was determined by pH, conductivity and infra-red spectroscopy measurements.

Findings: Our results highlight that R tunes the phase behavior. The amount of hydroxide groups in solution fixes the ionization state of the fatty acids, which governs the headgroup interactions. At low R , the counter-ion hydrophobicity plays a role on the phase behavior: TMAOH and choline hydroxide shows a broad polymorphism (faceted and unilamellar vesicles, lamellar phases) due to their hydrophilicity while the more hydrophobic BTAOH gives fatty acid crystals at low temperatures and vesicles at high temperatures. At high R , spherical micelles are observed for all counter-ions.

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1. Introduction

Fatty acids are anionic surfactants used for laundry and personal care since the ancient Egyptian period [1–3]. They are

biomolecules not only interesting for their detergency properties, but also for their antimicrobial properties which could be used in various applications such as agriculture, medicine, and cosmetics [2,4].

Fatty acids are formed by an alkyl chain and a carboxylic headgroup which can be protonated or deprotonated as a function of the pH [5]. The pH controls the morphological behavior of these

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pH-responsive surfactants by carrying the ratios of protonated and deprotonated molecules [6,7]. For example, close to the pKa vesicles are formed, protonated and deprotonated molecules coexist in similar fractions, whereas above the pKa where only the anionic form is present, micelles are present in aqueous solution [8]. However, the pH is not the only parameter to take into account to describe the morphological behavior of the fatty acids. The nature of the counter-ion present in aqueous solution plays also an important role [1]. In the 1970's, it was already known that the nature of the counter-ion modifies the fatty acids solubility [9]. In the 1990's, the use of tetraalkylammonium ions to disperse the dodecanoic acid instead of sodium hydroxide has increased the fatty acid solubility [10]. For example, the stearic acid in the presence of tetrabutylammonium ions is highly soluble with a Krafft point below 0 °C, whereas in the presence of sodium ions the Krafft point is very high around 70 °C [11]. An easy way to decrease the Krafft point of sodium or potassium fatty acids salts is to mix them with organic counter-ions such as guanidium chloride or L-arginine [12–15]. The alkanolamines are also known to decrease efficiently the Krafft temperature of saturated fatty acids [1]. Organic counter-ions of biological origin such as choline or amino-acids are very powerful to disperse fatty acids in aqueous solution [16–22]. For example, the stearic acid mixed with choline hydroxide has a Krafft point below 10 °C, while mixed with sodium hydroxide it is above 60 °C [21].

In many other surfactant systems, the major role of the nature of the counter-ion on the surfactant behavior is well-known [23]. Another way to modify the surfactant's properties is to tune the molar ratio between the surfactant and the counter-ion. It is an efficient way, but less explored in the literature. For fatty acids, the interest of modifying the molar ratio has increased in the last five years in order to improve their dispersion in aqueous solution [1]. Recently, we have shown that the phase behavior of myristic acid in the presence of choline hydroxide as counter-ion is tuned by the molar ratio between these two species [24]. The choline hydroxide is an organic quaternary ammonium counter-ion under hydroxide form (Fig. 1). In the system based on myristic acid in the presence of choline hydroxide as counter-ion, a broad polymorphism was observed in solution ranging from faceted vesicles, nanodisks, multilamellar vesicles, lamellar phases up to spherical micelles as a function of the molar ratio [24]. Such diversity of self-assemblies raises the question of the origin of the link existing between the structure of the choline hydroxide and its role on the phase behavior of the myristic acid when R is modified. In the present study, our objective was to decouple the respective effects of the hydroxide ions and of the structure of the counter-ion on the phase behavior of the myristic acid. To this aim, we chose two

other counter-ions with quaternary ammonium headgroups under hydroxide form as for the choline hydroxide: tetramethylammonium hydroxide (TMAOH) and benzyltrimethylammonium hydroxide (BTAOH) (Fig. 1). These two counter-ions differ from the choline by the presence of a benzyl group for BTAOH and the absence of the hydroxyethyl group present in the choline for TMAOH. Our strategy was to establish the link between the polymorphism at the microscopic scale with the modifications occurring at the molecular level (ionization state and melting transition) as a function of both R and temperature for the two counter-ions. First, we established the phase diagrams for both systems in order to compare with the phase diagram previously obtained for the choline hydroxide by using microscopy techniques and Small Angle Neutron Scattering (SANS). Then, the ionization state of the myristic acid in each phase was determined by coupling conductivity, pH and Fourier Transform Infra-red spectroscopy (FT-IR) measurements. The melting transitions of the alkyl chains have been determined by Differential scanning calorimetry (DSC) and Wide-angle X-ray Scattering (WAXS). In this study, we highlighted the importance of the hydroxide ions which control the pH and the ionization state of the fatty acids directly linked to R, as well as the nature of the counter-ions and more precisely its hydrophobicity which slightly tunes the myristic acid phase behavior.

2. Materials and method

2.1. Sample preparation

Myristic acid (purity >99%), tetramethylammonium hydroxide (10% wt in H₂O) and benzyltrimethylammonium hydroxide (40% wt in H₂O) were purchased from Sigma Aldrich and were used as received. The chemical structures are shown in Fig. 1. Ultrapure water was used in this study for all samples. The concentration of myristic acid was fixed at $4.4 \times 10^{-2} \text{ mol L}^{-1}$ (1% weight in water). The ammonium counter-ion solution was prepared at a fixed concentration of 1 mol L⁻¹. To vary the molar ratio, defined as $R = n_{\text{counter-ion}}/n_{\text{myristic acid}}$ with n the molar concentration in mol L⁻¹, we incorporated the desired volume of counter-ion solution. The concentration of myristic acid was fixed and only the concentration of counter-ion was modified to vary R. Each sample was heated at 75 °C during 5 min. Then, in order to fully dispersed the fatty acid powder, several frozen cycles were used. This freeze-thawing procedure is the best way described in the literature to disperse lipids in an homogeneous way in water [25]. The samples were stored at -18 °C. Before analysis, they were heated again at 75 °C during 5 min and cooled to room temperature.

2.2. Phase behavior

To establish the binary phase diagrams, we kept all the samples three days at a given temperature to ensure to be close to equilibrium. To vary and control the temperature from 10 °C to 50 °C, we used a water bath or an oven. The phase diagram was built by using visual inspection with or without the help of crossed polarizers.

2.3. pH and conductivity measurements

A TIM900 Titration Manager and a CDM230 conductivity meter (Radiometer) were used at 20 °C under stirring to measure the conductivity and the pH, respectively. Three measurements were performed for each sample. The values are the average of these measurements.

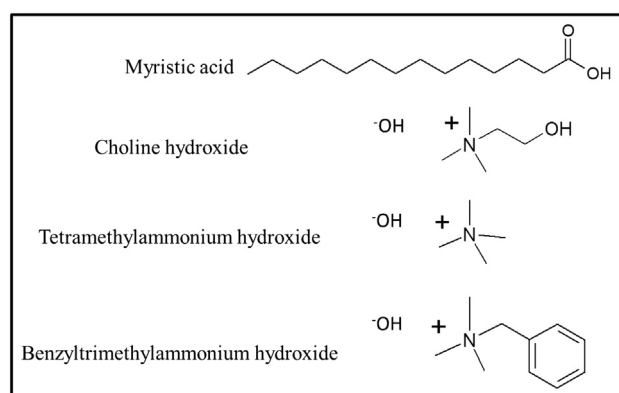


Fig. 1. Molecular structure of the myristic acid, choline hydroxide, tetramethylammonium hydroxide and benzyltrimethylammonium hydroxide used in this study.

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