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Colloids and Surfaces A: Physicochemical and Engineering Aspects

Foaming and emulsifying properties of fatty acids neutralized by tetrabutylammonium hydroxide

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ABSTRACT

Our paper aims at determining the interfacial, foaming and emulsifying properties of a series of dispersions made of long chain fatty acids (carboxylic acids) and hydroxyl derivatives neutralized by tetrabutylammonium hydroxide (TBAOH). Those fatty acids were myristic, palmitic and stearic acid as saturated fatty acids and juniperic and 12-hydroxystearic acid as the hydroxyl fatty acids. All these systems are already known to form micelles in water at room temperature. Here, we determined the critical micelle concentration (CMC) for all those systems using electrical conductivity. Foaming and emulsifying properties were then studied below and above the CMC. Relatively stable emulsions can be produced above but not below the CMC. There is a noticeable effect of the alkyl chain length and the presence of a hydroxyl group. The foamability is good but the foam stability is low in all cases above the CMC. Below the CMC, the foamability depends on the fatty acid and foams destabilize very quickly. Thus, the use of TBAOH to disperse fatty acids in water at room temperature allows using long chains fatty acids and hydroxylated derivatives for the production of emulsions and foams, the stability of which can be modulated.

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1. Introduction

Dispersing long chain fatty acids in aqueous solution appears as an interesting challenge in the search for environmentally safer surfactants from renewable sources and a springboard for further applications [1,2]. Our work on dispersions of saturated fatty acids and hydroxylated derivatives forms part of these efforts in that it seeks to demonstrate the potential contribution of these biological compounds of plant origin could make as a new class of green surface active agents. Despite the fact that fatty acids are widely used in household and personal cleaning products, as common soaps, such as sodium and potassium carboxylates, they are confined in their applicability due to their poor solubility in water [3,4]. Besides, it is known that the sodium and potassium salts of fatty acids have the advantage that their surface properties could be varied easily in a relatively wide range by changing the chain length of the surfactant [5–7]. The main problem with these solutions is that long

chain fatty acids crystallize in aqueous solutions at room temperature. Therefore, strong efforts have been made to determine the pertinent parameters allowing their dispersion in water. The solubility of fatty acid salts (Na+ or K+, for instance) depends on the Krafft point which is the minimum temperature at which surfactants form micelles [4,8]. Below that temperature, the fatty acids crystallize. While the Krafft point is still about 25 °C in the case of sodium laurate (NaC12), it increases rapidly with the increase of the alkyl chain length and is about 71 °C for sodium stearate (NaC18) [9]. The nature of the counter-ion strongly influences that Krafft point. For instance, it has been reported recently that choline, an amine of biological interest allows dispersing fatty acids under the form of micelles [1]. In the same way, tertrabutylammonium hydroxide (TBAOH) allows dispersing saturated fatty acids under the form of micelles at room temperature and below [10]. Those micelles from C12 to C20 were shown to be stable at 2–3 °C for periods of weeks. Fatty acids do not crystallize during this period. Thus, those solutions made of long chain fatty acids could now be used at room temperature for many applications such as foams and emulsions production. The TBAOH salt of palmitic acid, omega-hydroxy palmitic acid and 12 hydroxy stearic acid have also been shown to form micelles in solution and exhibit low foaming and emulsifying properties [2]. However, this previous study was only performed at a given concentration and the CMC had not been determined

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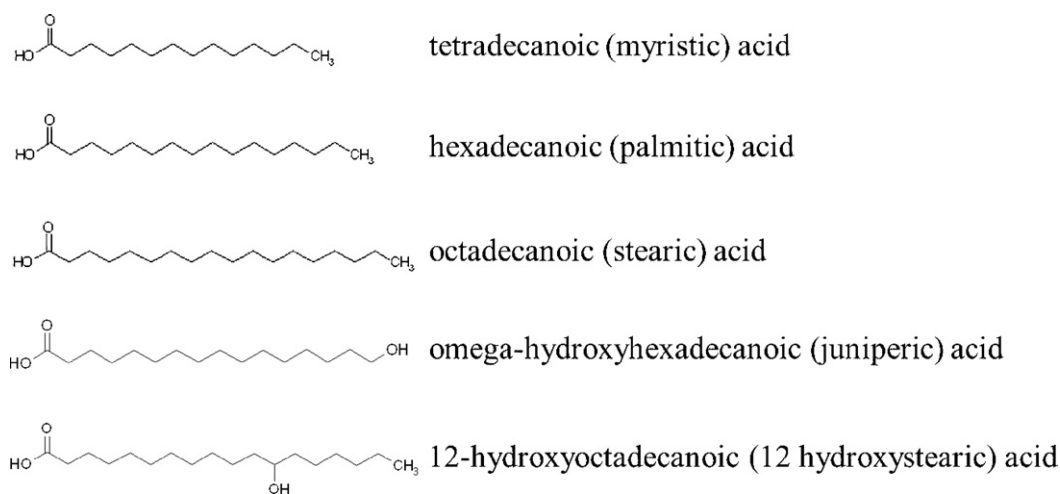
Fig. 1. Fatty acid chemical structures.

[2]. The current study aims at complementing this previous work since many applications of surfactants such as foaming, emulsifying and detergency are based on their abilities to decrease the surface or interfacial tensions, their solubility, the critical micelle concentration and their surface activity [7]. For that purpose a much broader fatty acid concentration range was investigated since it is known that foaming and emulsifying properties strongly depend on the concentration of surfactants and their CMC [11–13] and on the nature of the fatty acids. With this aim, we choose a large panel of fatty acids including myristic (tetradecanoic), palmitic (hexadecanoic) and stearic (octadecanoic) acids as saturated fatty acids and juniperic (omega-hydroxyhexadecanoic) and 12-hydroxystearic (12-hydroxyoctadecanoic) acids as the hydroxyl fatty acids (see chemical structures in Fig. 1). This allows studying the effect of the alkyl chain length and the presence of a hydroxyl group (and its position) along the alkyl chain length. First, the CMCs of the fatty acid/TBAOH systems were measured. Then, emulsions were produced by sonication below and above the CMC and the creaming kinetics of the emulsions were evaluated with the percentage of backscattering of light profiles as a function of time. Foams were obtained from the fatty acid/TBAOH system (below and above the CMC) by bubbling nitrogen through a glass filter, and the results were analyzed in terms of foamability and foam stability. In addition, the interfacial properties of all those systems at the air/water and oil/water interfaces have been studied by drop tensiometry. Thus, the capacity of the fatty acid dispersions to form and stabilize foams and emulsions has been studied in relation with their interfacial properties. It is well known that a quantitative comparison of the common methods used to study foaming and emulsifying properties is impossible as each of these methods has different measuring conditions. However, a qualitative comparison should be possible.

2. Materials and methods

2.1. Sample preparation

Fatty acid and hydroxylated fatty acid were of the best available grade (Sigma Aldrich) and used as received. The commercially available 1 M aqueous solution of tetrabutylammonium hydroxide (TBAOH, 99% *purissimum*) was used. The TBAOH salts of the fatty acids were directly obtained as aqueous solutions of known concentration as follows. A given mass of fatty acid was mixed in a glass flask with a known volume of water and the desired volume of a 1 M solution of TBAOH to reach the stoichiometric equivalence (molar ratio fatty acid/base: 1/1). Samples were heated and vortexed at 70 °C for a least 20 min until and frozen at −20 °C. This procedure was repeated until all the fatty acid material (powder) was perfectly dispersed. We believe that during such a procedure, freezing of water facilitates breaking of relatively big lipid aggregates whereas heating and shaking allows dispersing small remaining lipid lumps in water. In any case, this freeze-thawing procedure is commonly used for dispersing lipids in water to ensure homogeneity [14]. Then, samples were stored at 8 °C and prior to be used, each sample was re-heated at 70 °C for 15 min and cooled back at room temperature.

2.2. CMC determination

The CMC were determined using the electrical conductivity method. The conductivities of fatty acid/TBAOH solutions were measured using the CDM230 Conductivity Meter (MeterLAb, Radiometer Copenhagen) using a Metrohm electrode calibrated with a NaCl solution (84 μS/cm, Hanna Instruments, Italy). The conductivity measurements in aqueous solution were carried out by continuous addition of water into a concentrated fatty acid salt solution. The conductivity was measured after each addition of water and after a lap of time which allowed the stabilization of the conductivity (variation less than 1%).

We determined the CMC by plotting the specific conductivity versus its concentration (see Fig. 2). A break is observed on each curve indicating the concentration at which the micellization occurs. Thus, the value for the critical micelle concentration (CMC) is taken at the intersection of the tangent lines drawn before and after the break. The conductivity below the CMC is due to the sum of contributions of the free surfactants. Above the CMC, micelles are forming and those aggregates have a lower mobility than the free surfactants owing to their size and potential dissociation. Thus, the increase of conductivity is less important.

2.3. Preparation of emulsions

Emulsions were prepared with 25 vol.% n-hexadecane (Sigma Chemicals) as the oil phase and 75 vol.% of the fatty acid dispersion at 44 mM or at 0.5 mM. Both these fatty acid concentrations stand for concentrations above and below the CMC (respectively) for all systems presently studied (see Section 3). The fatty acid dispersion (4.5 mL) is first poured in the glass tubes and then hexadecane (1.5 mL) is added and solutions are further sonicated. In all cases, a fixed volume (6 mL) of emulsion was prepared with an ultrasound