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Responsive self-assemblies based on fatty acids

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ABSTRACT

Fatty acids are anionic surfactants under their deprotonated forms. They are surfactants with both biodegrability and low toxicity. Fatty acid molecules can self-assemble under various shapes in an aqueous solution. These self-assembled structures can respond to stimuli such as pH, CO_2 and temperature due to changes occurring at the molecular level. These specificities make them surfactants of special interest to tune the properties at a macroscopic scale. The aim of this article is to review the recent advances in the creation and in the understanding of responsive self-assemblies obtained from fatty acid molecules in an aqueous solution. The links between the microscopic, mesoscopic and macroscopic scales are described. The alkyl chain melting phenomenon triggered by temperature at the molecular level leading to thermoresponsive interfaces and foams at the macroscopic scale is highlighted.

1. Introduction

Soft materials which respond to stimuli are on the leading edge of material research and have recently been a subject of growing interest to many scientists [1]. The macroscopic responsiveness relies on the ability to react at microscopic or mesoscopic scales. Stimuli-responsive surfactants that can change their structure in response to a trigger such as pH, temperature, light or magnetic field have attracted great attention due to their versatile applications in various fields (e.g. pharmaceutical, biomedical, nanotechnological, etc.) [2]. A change in the molecular structure of the surfactant activated by stimuli can affect the self-assembled structure in water and the interfacial activity, which can in turn tune the properties at the macroscopic scale such as viscosity, emulsion and foam stability [2].

In the current context of sustainable development, the surfactant industry has increasingly turned its attention for the search of environmentally safer surfactants from renewable sources to replace petrochemical based products. Fatty acids are anionic surfactants under their deprotonated forms coming from renewable sources and have many advantages due their availability in large amount in nature and their biocompatibility [3]. They could be used for applications in various field from washing, material recovery processes, environmental clean-up to encapsulation and drug delivery. Fatty acid molecules have an aliphatic tail and a polar headgroup. As a function of the medium conditions, the alkyl tail can be in crystalline or liquid state and the headgroup can be in its protonated ($-COOH$) or deprotonated ($-COO^-$) state. Due to these intrinsic properties, fatty acid molecules are responsive surfactants under the action of pH, CO_2 and temperature. The modifications occurring at the molecular level under stimuli lead to modifications of the fatty acid self-assembled structures in an aqueous solution at the mesoscopic scale. Recently, some studies have focused on the use of the structural transformations of self-assemblies based on fatty acids occurring at the mesoscopic level to finely control the physical properties at the macroscopic scale. Original macroscopic properties have been found, such as thermoresponsive foams and interfaces [4–6], which cannot be achieved by conventional low molecular weight synthetic surfactants.

In the present short topical review, we will describe the recent results which highlight the interest of using fatty acids as responsive surfactants to tune the properties at the macroscopic scale under stimuli. At the outset of this review, we will provide a brief overview on the molecular nature of fatty acids, how to disperse them in water and the general factors at the microscopic scale leading to various self-assembled morphologies at the mesoscopic scale in dilute aqueous medium. We will then describe how modifications at the molecular level triggered by pH, CO_2 and temperature can tune the self-assemblies based on fatty acids at mesoscopic scale. In the third part, we will focus on the link between these structural transformations and the macroscopic properties: rheological properties, interfacial properties, foam and emulsion stability. In particular, the role of the chain melting process at the molecular level triggered by temperature will be examined in details and

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demonstrated as a tool to control the responsiveness at the macroscopic scale in a reversible manner.

2. Fatty acid molecules as anionic surfactants: fundamentals

2.1. Fatty acid at molecular state

From a chemical structure viewpoint, fatty acids are amphiphilic molecules with an aliphatic tail, which is either saturated or unsaturated, and with a polar headgroup which can be in its protonated ($-COOH$) or deprotonated ($-COO^-$) state. The aliphatic tail can have some additional groups such as hydroxyl group [7]. Fatty acids are usually obtained by hydrolysis of oils from various oleochemical sources such as animal, marine and vegetable [3]. The source of the oils determines the composition of the fatty acid mixture. Most of the animal sources are characterized by a high concentration of saturated fatty acids, whereas marine sources such as fish oils provide long chain and unsaturated acids. For oils coming from vegetable sources, the fatty acid composition is linked to the plant origin and sort. Usually, fatty acids are classified as a function of the aliphatic chain length [3]. Fatty acids with aliphatic tails fewer than six carbons are called “short-chain” fatty acids. Between 6 and 12 carbons, they are called “medium-chain” fatty acids. From 14 up to 22 carbons, fatty acids are classified as “long-chain” fatty acids. Above 22 carbons in the aliphatic tails, they belong to the “very long chain” fatty acids category. Fatty acids become anionic surfactants under their deprotonated form [3]. It is well recognized that anionic surfactants tend to be biodegradable and less toxic compared to the cationic ones [8]. Fatty carboxylates can be degraded by β-oxidation and completely mineralized or incorporated into biomass [9]. Fatty acids can be qualified as anionic surfactants with both low toxicity and biodegradability. The main drawbacks to use fatty acid molecules as surfactant are linked to their low solubility in the aqueous solution and their high sensitivity to divalent and trivalent ions in solution. For example, alkali ions form strong ion pairs with fatty acids which decrease their solubility in water [10,11].

2.2. Self-assemblies based on fatty acids in aqueous solution

Fatty acid properties (solubility, surface activity, self-assembly, etc.) are directly linked to the molecular structure: types and length of the hydrophobic tails, nature of the hydrophilic groups (ionized or non-ionized), presence of additional groups on the alkyl chain and the binding with counter-ions. For all surfactants, the solubility depends on the Krafft point which corresponds to the temperature at which the concentration of maximal solubility equals the critical micellar concentration (CMC) [12]. For fatty acids, the Krafft point is directly linked to the molecular structure and increases rapidly with the increase of the alkyl chain length. This increase of the Krafft point, corresponding to a decrease in solubility, prevents the use of long chain fatty acids in many applications. Various physical-chemistry approaches have been designed to decrease the Krafft point temperature in order to disperse efficiently long chain fatty acids over a wide range of temperatures in the aqueous solution [13]. Obviously, chemical modifications of fatty acids can yield to an increase of fatty acid solubility but other methods can be applied without any modification of the fatty acid molecule [3]. More than 40 years ago, Gebicki and Hicks reported the dispersion of oleic acid in vesicles in an aqueous solution [14]. The bilayer of these vesicles is formed by both the non-ionized and ionized forms of the fatty acid molecule. These two forms interact by lateral hydrogen bonding [15]. The ionized form corresponds to the negatively charged surfactant. The formation and stability of the vesicles depends on the protonation/ionization ratio of the terminal carboxylic acid which governs the formation of hydrogen bonds [16]. This approach was then extended to disperse various saturated fatty acids under the form of vesicles [16]. Another method consists in mixing fatty acids with cationic surfactants to obtain catanionic systems [17]. The electrostatic interactions between the fatty acid and the oppositely charged cationic surfactant enable to disperse the fatty acid in aqueous solution by giving rise to catanionic surfactant pairs with amphiphilic properties. The use of a large organic counter-ion provides another effective method to enhance the solubility of fatty acids by ion-pairing [18]. An interesting point is that the method used to successfully disperse the fatty acid controls the fatty acid properties such as its limit of solubility and the self-assembly [13]. The self-assembly type can be predicted by using the concept based on molecular shape and called the packing parameter defined as $p = \frac{V}{a*lc}$, where a is the effective headgroup area and V is the volume of the hydrophobic chain possessing maximum effective length l [12]. In surfactant systems, it is known that for $p < 1/3$, there is a tendency to form spherical micelles. For $1/3 < p < 1/2$, worm-likes micelles (WLMs) can be present. When $1/2 < p < 1$, bilayers or vesicles are obtained. The nature of the fatty acid and the approach used to disperse it leads to various values of p giving a large variety of fatty acid self-assemblies in aqueous dilute medium (>90 wt.% water) from usual self-assembled morphologies (spherical micelles, worm-like micelles, vesicle and bilayer) to unusual morphologies such as tubes [19], nanodiscs [20], icosahedra [21], buckled membranes [22] or cones [23].

An important parameter to take into account with fatty acid molecules is the pKa [24,25]. The pKa value represents the ionic environment of the solution where 50% of hydrogen atoms are removed from the carboxylic group by the existing OH^- ions in solution [26]. Most of the short-chain fatty acids such as acetic acid (C2) or propionic (C3) acid have a pKa value around 4.8 [26]. The pKa value can increase by increasing the carbon chain length of fatty acids [27]. For example, pKa values around 9 have been found for the palmitic acid (C16) [27]. The increase of the chain length of fatty acids leads to an increase of the hydrophobic interactions between the chains of adjacent molecules, which gives rise to an increase of the pKa value [26–28]. In the same way, the pKa value decreases in presence of unsaturation for long chain fatty acids since the intermolecular distance increases and the area per molecule increases [26]. The environmental conditions have a drastic effect on the pKa value. When fatty acid molecules are embedded in the self-assembly, the pKa values are modified. For example, it has been determined for lauric acid (C12) that the pKa value changes from 7.6 to 4.9 when lauric acid is embedded in anionic (SDS) and cationic (DoTAC) micelles, respectively [29]. As a result, all the modifications of the environmental conditions such as pH or temperature have an impact on the pKa of the fatty acid molecules embedded in the self-assembly, which is important to take into account to produce responsive systems [30,31]. The environmental conditions can tune the fatty acid molecules at the microscopic scale such as the effective headgroup area and effective length of the alkyl chain, which in turn modify the packing parameter. As discussed below, fatty acid self-assembled structures can transit from one morphology to another by modifying the medium conditions such as pH, CO_2 and temperature.

3. Effect of stimuli at molecular level on the fatty acid self-assembled structures at the mesoscopic scale

3.1. pH effect

Surfactants responsive to pH changes are a subject of growing interest owing to their wide potential in novel applications, as pH variations can control the molecular self-assembly [2]. Fatty acid headgroup has a carboxylic group and the pH of the aqueous medium tunes the degree of ionization between the protonate ($-COOH$) and deprotonated ($-COO^-$) forms. Fatty acids are a simple class of pH-responsive surfactants. When the pH is varied, the effective area of headgroup is modified at the microscopic scale. The deprotonated form possesses a bigger effective headgroup area than the protonated form. The corresponding p value for the deprotonated form is reduced in comparison to the protonated form approaching values close to 1/2–1/3, which favors the formation of worm-like or spherical micelles. By finely tuning the pH, the