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Self-assembled structural transition from vesicle phase to sponge phase and emulsifying properties in mixtures of arginine and fatty acids

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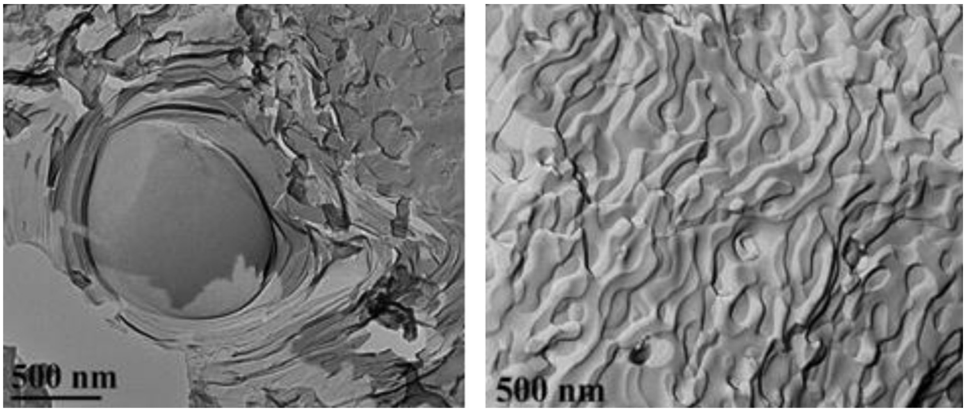
GRAPHICAL ABSTRACT



Phase structural transition from multilamellar vesicles to sponge structures.

HIGHLIGHTS

- Natural biological molecules mixed with fatty acids show richer phase behavior.
- Rheological and emulsifying properties of the mixtures of Arg and fatty acids.
- The formation of the self-assembled structures is mainly driven by the synergistic effect of electrostatic interaction, hydrogen bonding, and hydrophobic interaction.

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ABSTRACT

Two fatty acids, octanoic acid (OA) and decanoic acid (DA) were separately mixed with a natural biological molecule, L-arginine (Arg), in aqueous solutions for comparative investigation. Self-assembled structures including micelles, vesicles, sponge structures, were observed by varying the compositions and chain length of fatty acids. The structures of vesicles and sponge phase were determined by freeze fracture-transmission electron microscope (FF-TEM). The transition of self-assembled structures, especially from vesicles to sponge structure, was significantly reflected in the change of rheological properties. The double hydrogen bonding formed between the guanidyl group of Arg and the carboxyl group of fatty acids is considered to be the crucial force, which drives the self-assembly process combining with other

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Vesicles
Sponge phase
Emulsion

non-covalent interaction, electrostatic interaction and hydrophobic interaction. Depending on the nature of the fatty acid, the systems exhibit good emulsion stability.

1. Introduction

Fatty acids are simple but crucial biomolecules which are industrially important owing to their natural abundance. Free fatty acids and their salts (soaps) have been long used for laundry and personal care since the ancient Egyptian period [1]. Their antimicrobial activity shows potential applications in agriculture, cosmetics, and medicine [2]. In general, fatty acids have been suggested the good models for pH-dependent targeted drug delivery [3]. The extensive applications of fatty acids suggest that a more fundamental understanding of their aggregation behavior is required. A series of salts of fatty acids can self-assemble into a variety of aggregates [4] including micelles [2,5–7], vesicles [8,9], cones [10], nanotubes [11] and ribbons [12], in water. Moreover, dispersions of fatty acids and their hydroxyl derivatives were studied in solution in order to generate a new class of surface active agents in foaming [13] and emulsifying [14,15].

As the basic structural units of proteins, L-α-amino acids having special importance among chemical groups since they are the foundation stones of the living organisms [16]. Arginine is one of the most basic naturally occurring amino acids because of the basic side chain, which is of significant importance for its structures and functions. The side chain almost always has a p$K_a \geq 12$ and the positively charged planar guanidinium group can work as a hydrogen donor in the formation of hydrogen bonds [17]. Amino acid based surfactants in particular have been the focus of great attention because of a fortunate and versatile combination of the diversity of amino acid headgroups, molecular architecture, chirality, and in some cases, temperature and pH sensitive self-assembly [18–21]. These surfactants have been found to possess high levels of biocompatibility and biodegradability [22], which made them the suitable alternatives to conventional surfactants.

In our previous work on the fatty acid/lysine system, we examined the aggregation behavior of lysine with fatty acids with different chain lengths in aqueous solution [23]. As alkaline amino acids, arginine (Arg) and lysine have similar physicochemical characteristics and are often mutually substituted during evolution without affecting protein function [24]. However, the occurrence of Arg and lysine in naturally occurring proteins is highly dependent on their particular biological functions, likely owing to their differing chemical properties which determine their abilities to interact with other amino acids and biomolecules [25]. For example, Arg appears much more frequently in ion channel voltage sensors. In addition, poly-Arg enters cells more efficiently than oligomers of lysine, or histidine. Charged Arg is solvated by more oxygen atoms and can form more H-bonds than lysine. In the present work, fascinating self-assembled aggregates, e.g., micelles, vesicles and sponge structure were observed at different proportions of the fatty acids to Arg. The influence of basicity of amino acid on the phase behavior of OA was discussed. The formation of these aggregates is considered to be driven mainly by the multiple hydrogen bonding, electrostatic interaction and the equilibrium between hydrophobicity and hydrophilicity, which in combination impose preferential molecular orientation and the formation of diverse structures with the variation of composition. Emulsions were successfully produced at room temperature with the tunable stability which could be modulated by the nature and proportion of the fatty acid. The enormous advantage of this approach is the elimination of the need to synthesize the amino acid derived surfactants and the commercial availability of fatty acids and arginine.

2. Materials and methods

2.1. Materials

Decanoic acid (DA) was purchased from Alfa Aesar (>99%, mass fraction). Octanoic acid (OA) and lauric acid (LA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (analytical grade). L-arginine (simplified as Arg) and L-histidine (simplified as His) were purchased from J&K Chemical Company (China, purity > 98%). They were directly used without further purification. Ultrapure water with a resistivity of 18.25 MΩ × cm was obtained using an UPH-IV ultrapure water purifier (China).

2.2. Phase behavior study

The phase behavior of the surfactant mixture was studied by visual inspection of 100 solution samples with the help of crossed polarizers. The samples were obtained by dissolving various amounts of fatty acid to the fixed concentrations of Arg. The concentrations of Arg are 150, 200, 250, 300 mmol L^{-1}, different amounts of fatty acids (from 0 mmol L^{-1} to 1000 mmol L^{-1}) were added to the Arg solution. OA can be easily dissolved in Arg solution at room temperature under stirring. For DA, the samples were heated to about 55 °C under stirring to get homogeneous solutions. The samples were equilibrated at 25.0 ± 0.1 °C for at least 4 weeks until they were unchanged over an extended period of time. The phase boundaries were confirmed based on visual observations and the conductivity measurements.

2.3. Conductivity and pH measurements

Conductivity measurements were performed on a DDSJ-308A (China) conductivity meter with a DJS-1C glass electrode at 25.0 ± 0.1 °C. Two-phase samples were stirred homogeneously during the measurements. The pH value was determined on a PHS-3C pH meter (China) with an E-201-C glass electrode.

2.4. Rheological measurements

The rheological measurements were carried out on a HAAKE RS6000 rheometer with a coaxial cylinder sensor system (Z41Ti) for samples with low viscosity and a cone-plate system (C35/1TiL07116) for samples with high viscosity. In oscillatory measurements for viscoelastic solutions, the stress sweep at a fixed frequency of 1 Hz was carried out prior to the following frequency sweep in order to ensure that the selected stress was in the linear viscoelastic region.

2.5. Freeze fracture (FF)-TEM observations

For FF-TEM observations, a drop of solution was mounted on a specimen holder. The samples were frozen by quickly plunging the specimen holder into liquid ethane cooled by liquid nitrogen. Fracturing and replication were carried out on a freeze-fracture apparatus (EM BAF060, Leica, Germany) at −150 °C. Pt/C was