

## Regular Article

## Spontaneous vesicle formation and vesicle-to-micelle transition of sodium 2-ketooctanate in water

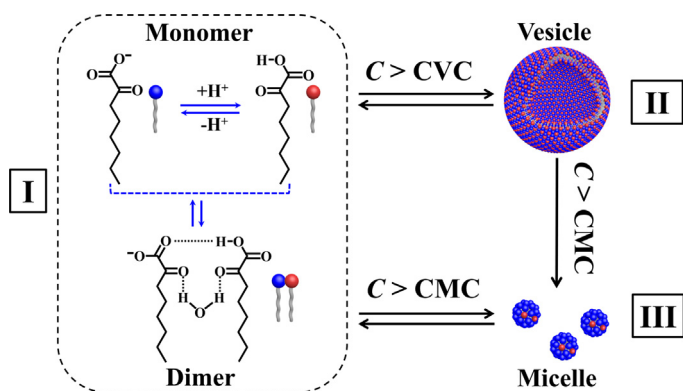


Huifang Xu, Na Du, Yawen Song, Shue Song, Wanguo Hou\*

Key Laboratory of Colloid and Interface Chemistry (Ministry of Education), Shandong University, Jinan 250100, PR China

## GRAPHICAL ABSTRACT

Sodium 2-ketooctanate (KOCOONa) in water can spontaneously form at a low concentration ( $\sim 15$  mM). With an increase in its concentration, a vesicle-to-micelle transition occurs. Based on the chemical equilibrium of various species, the aggregation mechanism of KOCOONa in water was discussed.



## ARTICLE INFO

## Article history:

Received 18 July 2017

Revised 6 September 2017

Accepted 6 September 2017

Available online 7 September 2017

## Keywords:

Sodium 2-ketooctanate

Surfactant

Vesicle

Aggregation

Self-assembly

## ABSTRACT

Single-tailed short-chain alkyl keto-acids/salts, a class of fatty acid/salt derivatives, such as sodium 2-ketooctanate (KOCOONa), are a kind of weakly acid/salt type amphiphiles and plausible prebiotic molecules, and the current understanding of their aggregation behavior in aqueous solutions is still limited. Herein, the aggregation behavior of KOCOONa in aqueous solution was studied by changing its concentration ( $C$ ), using equilibrium surface tension, conductivity, and fluorescence measurements. The aggregates formed were characterized using freeze-fracture and cryogenic transmission electron microscopy, dynamic light scattering, atomic force microscopy, and confocal laser scanning microscopy. A concentration-driven stepwise aggregation was identified in the KOCOONa solution. Vesicles can spontaneously form from the single-component aqueous solution, with a critical vesicle concentration (CVC) of  $\sim 15$  mM, which is obviously lower than that of octanoic acid/salt (120–200 mM). With increasing  $C$ , a vesicle-to-micelle transition can occur, showing a critical micelle concentration (CMC) of  $\sim 80$  mM. In addition, the membrane permeability of the KOCOONa vesicles was examined using small-size Calcein and large-size FITC-BSA as fluorescence probes, showing a size-selective permeability, similar to short-chain (C8–C11) fatty acid vesicles. For the first time, the aggregation behavior of single-tailed keto-acid salt surfactant is reported.

© 2017 Elsevier Inc. All rights reserved.

\* Corresponding author.

E-mail address: [wghou@sdu.edu.cn](mailto:wghou@sdu.edu.cn) (W. Hou).

## 1. Introduction

Amphiphilic molecules in aqueous solutions tend to self-organize into varieties of assemblies such as micelles, vesicles, and lamellar phases [1–4]. The different kinds of assemblies can be translated into each other under environmental stimulation [1,3,5] such as the variation of pH [6–8], temperature [9,10] or salinity [11,12], light irradiation [13], the addition of special ions [14] or organic additives [15], and the mediation of solid surfactants [16,17]. Over the past decades, vesicular structures and structural transition between micelles and vesicles (micelle-vesicle transition) have attracted extensive attention because of their fundamental and practical importance [1–5,18–25]. For instance, vesicles can serve as protocell models [4,13,18,19], drug delivery vehicles [20,21], and material synthesis templates [22,23]. The micelle-to-vesicle transition (MVT) is related to the evolution of primitive cells [19,24], and the vesicle-to-micelle transition (VMT) can be used to the controlled release of drugs that are previously loaded in the vesicles [25].

As is well known, the aggregation behavior of amphiphiles in water is generally determined by the balance between the hydrophobic tails and the hydrophilic head-groups and also by the molecular geometry [2]. Vesicle formation and micelle-vesicle transition are commonly observed in aqueous solutions of multi-tailed surfactants [6,26–28], mixed surfactants [5–7,9–11,15,26], and amphiphilic polymers [8,21,29,30]. A kind of interesting system is single-component aqueous solutions consisting of weakly acid/salt-type single-tailed surfactants (STSs) [3,4,24,31–45], in which not only vesicles can form but also the micelle-vesicle transition can be motivated simply through changing the solution concentration and pH [3,24,32,36,43,44]. And the weakly acid/salt-type STSs that have been studied previously include fatty acids/salts [3,4,18,19,24,31–35,46–49], monoalkyl phosphate (MAP) [36,43], and fatty acid derivatives [37–42,44,45]. The fatty acid derivatives include *N*-acyl amino acid salts [37–41], monoalkyl nicotinate [42,45], and fatty alcohol ether carboxylate [44]. Although the aggregation mechanism of the single-component systems has not been well understood [44], it has been assumed to arise from the hydrogen bonding between polar head-groups [3,4,32,39–45]. For a single-component aqueous solution of one weakly acid/salt type STS, there actually exist two forms of species, i.e., ionized (negatively charged) and acidic (neutral) species. The two forms of species can form so-called ‘acid-soap’ dimers by H-bonding, which are able to motivate the formation of vesicles within a pH range close to its apparent  $pK_a$  ( $K_a$  is the acidic dissociation constant) [3,4,32,39–45]. In addition, fatty acid derivatives in water commonly exhibit a lower critical vesicle concentration (CVC, <3 mM) [38–42,44,45], in comparison with those of fatty acid salts (>50 mM for  $C_8$ – $C_{10}$  fatty acids) [31,33]. More interestingly, they can form some unnormal aggregates in water, such as nanotubes or tubular vesicles, nanorods, thread-like micelles, and cylindrical micelles [38,40,42,45]. The substituent groups in fatty acid derivatives are thought to play an important role for their aggregation [38–42,44,45]. Research on the aggregation behavior of weakly acid/salt type STSs in water is of fundamental and practical importance, which can provide insights into the self-assembly chemistry of surfactants and expand the application of self-assemblies [3,4,24,36,49].

2-Ketooctanoic acid (or 2-oxooctanoic acid, KOCO<sub>2</sub>H), a monoalkyl keto-acid amphiphile, is a derivative of fatty acids. Substitution of the hydrophilic and electron-withdrawing ketone group for the  $\alpha$ -methylene group of fatty acid molecules is expected to affect their aggregation behavior significantly. Furthermore, KOCO<sub>2</sub>H may be considered as a plausible prebiotic molecule [50]. This is because similar substances have been detected in carbonaceous meteorites [51]. In addition, short chain organic com-

pounds are also easily synthesized in Fischer-Tropsch-type reaction [52]. Research on their aggregation behavior may provide valuable information on the formation of primitive membrane structures. Lately, Griffith et al. [50] reported that chemical reaction between KOCO<sub>2</sub>H molecules can occur under simulated sunlight irradiation, resulting in the formation of double-tailed chemically bonded dimer molecules that subsequently self-assemble into vesicles. More recently, we found that single-tailed KOCO<sub>2</sub>H itself can also spontaneously form vesicles in water [53,54]. It is interesting to understand the aggregation behavior of 2-ketooctanoic acid salts such as sodium 2-ketooctanoate (KOCOONa), since fatty acid salts may exhibit aggregation behavior different from that of fatty acids [32,46–48]. So far, there have been no reports on the aggregation behavior of single-tailed alkyl keto-acid salts in water.

Herein, aggregation behavior of KOCOONa in aqueous solution was investigated with increasing its concentration. We found that vesicles with uni- and multilamellar structures can spontaneously form from KOCOONa solution with a CVC of  $\sim 15$  mM, and that a VMT occurs in the solution with increasing its concentration. Furthermore, like short-chain fatty acid vesicles [31,34,55], the KOCOONa vesicles have size-selective permeability. The KOCOONa vesicles may be potentially applicable such as for protocell model, medicine, and biotechnology.

## 2. Experimental

### 2.1. Chemicals

All chemicals were used as received, including 2-Ketooctanoic acid (KOCO<sub>2</sub>H,  $\geq 99\%$  purity, Sigma-Aldrich, China), fluorescein isothiocyanate conjugated bovine serum albumin (FITC-BSA, Hangzhou Xiaoyong Biotechnology Co., Ltd., China) as well as pyrene, Nile red, and Calcein (Aladdin Industrial Co., China). Ultrapure water (resistivity: 18.2 M $\Omega$  cm) was prepared with a Hitech-Kflow water purifier (Hitech, China).

Sodium 2-ketooctanoate (KOCOONa) was synthesized in our laboratory from KOCO<sub>2</sub>H with reference to the literature [42] (details see the [Supplementary Information, SI](#)). The molecular structure of the synthesized sample was validated by <sup>1</sup>H NMR, <sup>13</sup>C NMR, ESI-MS, and FT-IR ([Fig. S1, SI](#)). The solubility of KOCOONa in water at 25 °C was determined using spectrophotometry to be  $\sim 250$  mM ([Fig. S2, SI](#)).

### 2.2. Preparation of KOCOONa solutions

KOCOONa solutions with desired concentrations (C) were prepared with dissolution of KOCOONa in water. The KOCOONa solutions were equilibrated at  $25 \pm 0.5$  °C for at least one week before use. To avoid possible photoinitiated reactions between KOCOONa molecules [50], aluminum foil was used to cover the test samples, and all tests were performed under indirect lighting.

### 2.3. Measurements

#### 2.3.1. Equilibrium surface tension

Equilibrium surface tension ( $\gamma$ ) was measured at  $25.0 \pm 0.1$  °C, using a JYW-200B tensiometer (Chengde Dahua Instrument Co., Ltd., China) with the ring method. Each test solution was equilibrated for at least 10 min and each measurement had three replications with the average  $\gamma$  value reported (accuracy  $\pm 0.1$  mN m<sup>-1</sup>). A thermostatic bath was used to control the temperature of the measurement cell. For the samples containing precipitates, the precipitates were removed by centrifugation prior to measurements.

Download English Version:

<https://daneshyari.com/en/article/4984295>

Download Persian Version:

<https://daneshyari.com/article/4984295>

[Daneshyari.com](https://daneshyari.com)