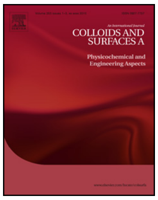
Colloids and Surfaces A: Physicochem. Eng. Aspects 509 (2016) 48–55

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Effect of organic salts on the aggregation behavior of tri-(trimethylsiloxy)silylpropylpyridinium chloride in aqueous solution

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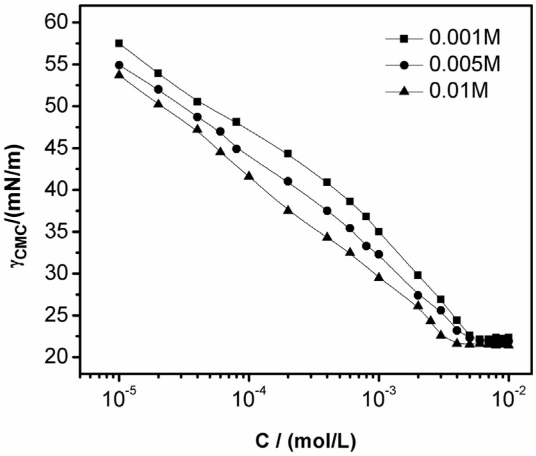
HIGHLIGHTS

- The organic salts affect the aggregation and surface activity of cationic silicone surfactant.
- Spherical-like structured aggregates were obtained in all mixed solutions may have potential applications in many fields.
- The adsorption of Si_4pyrCl at the interface is stronger than the aggregation in solution.

GRAPHICAL ABSTRACT

The Figure shows the surface tension curves of Si_4pyrCl with sodium acetate at different concentrations. The CMC values of Si_4pyrCl decrease in the presence of organic salts and it drops with the increasing of the ionic strength.



ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form 29 August 2016
Accepted 31 August 2016
Available online 31 August 2016

Keywords:
Cationic silicone surfactant
Aggregation behavior
Organic salts effect

ABSTRACT

In this study, we synthesized the cationic silicone surfactant tri-(trimethylsiloxy)silylpropylpyridinnium chloride (Si_4pyrCl). We then systematically investigated the effects of organic salts such as sodium acetate, sodium oxalate, sodium citrate, sodium benzoate, and sodium salicylate on the aggregation behavior of Si_4pyrCl in aqueous solution through surface tension and electrical conductivity analyses, dynamic light scattering (DLS), and transmission electron microscopy (TEM). The addition of organic salts promoted surfactant aggregation. The aggregation ability was observed to be in the following order: s sodium salicylate > sodium benzoate > sodium citrate > sodium oxalate > sodium acetate. The measurement of electrical conductivity shows that the micellization of Si_4pyrCl in aqueous solution is spontaneous. Several spherical-like aggregates with a diameter of approximately 500 nm were observed via TEM.

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http://dx.doi.org/10.1016/j.colsurfa.2016.08.086

The diameter distribution was determined through DLS. This work will be of great significance for the understanding of cationic silicone surfactants and their applications in industrial production.

1. Introduction

Silicone surfactants are composed of hydrophobic silicon groups that are attached to one or more polar groups. They are extensively used in various fields, such as agriculture, textile manufacturing, and polyurethane foam manufacturing. They are also used as emulsifiers in cosmetics, wetting agents, and paint additives [1–6]. Owing to the low glass transition temperature, flexibility, and low cohesive energy of siloxane chains, silicone surfactants display surface activity both in aqueous and nonaqueous solutions [7,8]. In addition, silicone surfactants exhibit lower surface tension and toxicity compared with conventional hydrocarbon surfactants [9,10].

Silicone surfactants, especially trisiloxane surfactants, have been comprehensively studied in the past decades. Wang et al. reported that spherical vesicles self-assembled by carbohydrate-modified siloxane surfactants in aqueous solution could have potential applications as microsphere drug delivery systems [9,11,12]. To improve the spreading ability and hydrolysis resistance of trisiloxane surfactants, Peng et al. synthesized a series of surfactants: $RNRCH_2CH(OH)CH_2(OCH_2CH_2)_xOCH_3$. They concluded that the molar ratio of methyl to methylene in the hydrophobic groups, the shape of the hydrophobic groups, and the hydrophile/lipophile balance of twin-tail trisiloxane surfactants can affect the spreading ability of these surfactants [13].

Meanwhile, some researchers studied the aggregation behavior of cationic silicone surfactants in aqueous solution. Du et al. synthesized two trisiloxane-tailed cationic silicone surfactants with different head groups. They found that both surfactants are superior to conventional surfactants and observed vesicular-like aggregates with diameters ranging from 20 nm to 200 nm via TEM [14]. Hao et al. investigated the surface activity of organosilicon bola-form bi-quaternary ammonium amphiphiles with identical head groups and different hydrophobic linkages. They demonstrated that the length of siloxane spacers affects the aggregation behavior, physicochemical properties, and antimicrobial capacity of these surfactants [15]. Our group reported a series of cationic silicone surfactants with identical hydrophobic chains and different head groups (imidazolium cations, lammonium cations, and pyrrolidinium cations), with identical head groups and different hydrophobic groups (trisiloxane, tetrasiloxane, and tricarbonsilane), and with different counterions (nitrate anion and acetate anion) [16–18]. The head groups, hydrophobic chains, and counterions significantly affect the aggregation behavior of cationic silicone surfactants in aqueous solution. To the best of our knowledge, few systematic and detailed works have focused on the factors influencing the aggregation behavior of cationic silicone surfactants. The effects of salts on the aggregation behavior of surfactants in aqueous solution are vital to the broad applications of surfactants in various fields. Previous investigations revealed that the physicochemical properties and aggregation behavior of surfactants can be adjusted by adding various additives [19]. However, investigations on cationic silicone surfactants with organic salts are extremely limited.

In this work, we synthesized the cationic silicone surfactant tri-(trimethylsiloxy)silylpropylpyridinnium chloride (Si_4pyrCl). Five organic salts (sodium acetate, sodium oxalate, sodium citrate, sodium benzoate, and sodium salicylate) were selected to investigate their regulatory effects on the aggregation behavior of Si_4pyrCl in solutions. The effects of the nature and concentration of organic salts on the aggregation of Si_4pyrCl were investigated through surface tension and electrical conductivity analyses, dynamic light scattering (DLS), and transmission electron microscopy (TEM). A series of favorable parameters was assessed to understand the aggregation behavior of cationic silicone surfactants in the presence of organic salts.

2. Materials and methods

2.1. Materials

γ-Chloropropyltrimethoxysilane was purchased from Qufu Chengguang Chemical Co., Ltd. Trimethylchlorosilane was procured from Energy Chemical. Isopropyl alcohol, acetonitrile, pyridine, *n*-hexane, sodium acetate anhydrous, sodium oxalate, trisodium citrate dihydrate, sodium benzoate and sodium salicylate were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. All the solutions were prepared by triply distilled water.

2.2. Methods

Surface tension measurements were carried out on a model BZY-1 tensiometer (Shanghai Hengping Instrument Co., Ltd., accuracy $\pm 0.1\ mN\ m^{-1}$) by the ring method at 298.15 K.

Electrical conductivity measurements of cationic silicone surfactant solutions were carried out using a S230 SevenCompact^{TM} conductivity analyzer (Mettler Toledo Instrument Co., Ltd., accuracy ± 0.5%) with a thermostatic bath (DC-0506, Shanghai Hengping Instrument Co., Ltd.).

The dynamic light scattering (DLS) were performed by using Dynapro Titan system (Wyatt Technology, Santa, Barbara, CA) at a scattering angle of 90°.

The morphologies of the aggregates for Si_4pyrCl with or without organic salts in aqueous solution were examined by using a JEM-1011 TEM (JEOL, Japan) at 100 kV. The samples were prepared by placing the solutions on a carbon coated grid. A drop of phosphotungstic acid solution (2 wt%) was used to stain the samples when the grids were dried at room temperature.

2.3. Synthesis and characterization

The synthesis procedure for Si_4pyrCl is shown in Fig. 1.

2.3.1. Synthesis of γ-chloropropyltri(trimethylsiloxy)silane

The isopropanol (0.24 mol, 14.40 g) was added into the mixture of γ-chloropropyltrimethoxysilane (0.04 mol, 7.94 g) and trimethylchlorosilane (0.24 mol, 26.06 g) in a 100 ml flask, and then water (0.36 mol, 6.48 g) diluted. The organic phase was separated from the product and washed by water until it was neutral. The final product was distilled by rotary evaporation. ^1H NMR (300 M, $CDCl_3$): 0.066–0.130 ppm ($SiC\boldsymbol{H}_3$, 27H), 0.538–0.593 ppm ($SiC\boldsymbol{H}_2CH_2CH_2Cl$, 2H), 1.746–1.847 ppm ($SiCH_2C\boldsymbol{H}_2CH_2Cl$, 2H), 3.484–3.530 ppm ($SiCH_2CH_2C\boldsymbol{H}_2Cl$, 2H).

2.3.2. Synthesis of Si_4pyrCl

A mixture of γ-chloropropyltri(trimethylsiloxy)silane (0.01 mol, 3.73 g), pyridine (0.025 mol, 1.98 g) was added into