Synthesis, aggregation behavior of novel cationic silicone surfactants in aqueous solution and their application in metal extraction

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ABSTRACT

Two cationic silicone surfactants, 3-[tri-(trimethylsiloxy)]silylpropylpyridinium chloride (Si_4pyrCl) and *N*-methyl-3-[tri-(trimethylsiloxy)]silylpropylpiperidinium chloride (Si_4pipCl), were synthesized. Their aggregation behavior in aqueous solution was investigated through analyses of surface tension, electrical conductivity, dynamic light scattering (DLS), and transmission electron microscopy (TEM). Surface-tension measurements showed that the two cationic silicone surfactants decreased the surface tension of water to almost 20 mN m^{-1}. This result indicated the surfactants' remarkable surface activity. The effects of inorganic salts, sodium chloride, sodium bromide, sodium iodide and sodium sulfate, on the aggregation behavior of Si_4pyrCl and Si_4pipCl were systematically explored. Results showed that the aggregation of Si_4pyrCl and Si_4pipCl was promoted by the addition of salts and that aggregation ability followed the order of NaI > NaBr > Na$_2$SO$_4$ > NaCl. Thermodynamic parameters obtained from electrical-conductivity measurements indicated that the micellization of Si_4pyrCl and Si_4pipCl was entropy driven. Spherical aggregates with diameters ranging from 200 nm to 600 nm were observed by TEM, and the aggregates' diameter distribution was obtained by DLS. The extraction behavior on several metal ions (Co (II), Mn (II), Fe (III), Ni (II), Cu (II), Al (III), Sn (IV), Zn (II), Ce (III), Li (I), Mg (II), Au (III), and Pd (II)) in chloroform by the surfactants in chloroform was studied for the first time. Results showed that Si_4pipCl and Si_4pyrCl had good extraction ability for Au (III) and Pd (II).

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1. Introduction

Surfactants form various kinds of aggregates in aqueous solution, including worm-like micelles, spherical micelles, vesicles, and bilayers [1, 2,3,4,5]. The conformations of these highly ordered aggregates are related to their wide-ranging applications in many fields. Meanwhile, silicone surfactants are novel efficient surfactants and consist of silicone groups as hydrophobic groups coupled to one or more polar groups. Silicone surfactants form abundant aggregates in aqueous solution. They have wide industrial applications, such as in textile and polyurethane foam manufacturing. Silicon surfactants are also used as agricultural adjuvants, as cosmetics emulsifiers, as wetting agents, and as paint additives [6,7,8,9,10,11,12]. Compared with hydrocarbon surfactants, silicone surfactants exhibit lower surface tension and lower toxicity, which are mainly attributed to the low cohesive energy, good flexibility, and low glass transition temperature of the siloxane chain [13,14,15,16]. Silicone surfactants have remarkable surface activity in both water and organic liquids and can decrease the surface tension of water to approximately 20 mN m^{-1} [17,18].

The aggregation behavior in aqueous solutions of silicone surfactants with different chemical structures has been widely studied in the past decades, especially trisiloxane surfactants. Wang et al. reported that the carbohydrate-modified siloxane surfactants could self-assemble into spherical vesicles, which may have potential applications as microsphere drug delivery systems [19,20,21]. Kunieda et al. hypothesized that the self-organized structures or liquid crystals of silicone surfactants with ethylene oxide (EO) groups were highly related to total surfactant concentration and to dimethylsilicone unit and ethylene oxide (EO) ratios [22].

Meanwhile, some researchers had investigated the synthesis of cationic silicone surfactants and their aggregation behavior in aqueous solution. Schmaucks et al. investigated a series of silicone surfactants, $((Me_3SiO)(SiMe_2O)_n SiR^1 R^2 (CH_2)_3N^+Me_2 R3 X^-$ (R^1, R^2 = Me, Me_3SiO; n = 0, 1; R3 = alkenyl or alkyl; X = halogen)), and found that the interfacial behavior of the isomerically quaternary ammonium compounds strongly depended on the number of silicon atoms [23]. Hao et al. studied the surface activity of silicone bi-quaternary ammonium amphiphiles, $[OH_5C_3(C_2H_5)_2N^+-(CH_2)_3-Si(CH_3)_2-O-(Si(CH_3)_2O)_n-Si(CH_2)_3\cdots(CH_2)_3-N^+(C_2H_5)_2C_3H_5O]Cl_2$- ($Si_nN_2Cl_2$, n = 0, 4, 6, 8). Their study demonstrated that the length of the siloxane spacer greatly affected the surfactants' physicochemical properties, aggregation

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behavior, and antimicrobial ability [14]. He et al. studied the aggregation behavior of cationic siloxane surfactants, $(Me_3SiO)_2Si(Me)(CH_2)_3N^+$-$Me_2(CH_2)_2OH\ X^-$ (X = Cl, Br, and I). Their study reported that vesicles were present at low concentrations, but they transformed to liquid crystal sheet structures (LLC) and lamellar solids as surfactant concentration increased [24]. Recently, our group also investigated a series of cationic silicone surfactants [18,25,26] and found that head groups (imidazolium cations, lammonium cations, and pyrrolidinium cations), hydrophobic chains, and counterions (nitrate anion and acetate anion) had a significant effect on the aggregation behavior of cationic silicone surfactants. To our knowledge, few systematic and detailed investigations had reported the influence of various factors, including molecular architecture, temperature, and additives, on the aggregation behavior of cationic silicone surfactants.

Metal extraction by silicone surfactants is a vital application based on the unique properties of silicone surfactants. Silicone surfactants with special structures as side groups, such as imidazole and pyridine groups, could interact with metal ions and extract them from aqueous solutions. Related research on metal extraction by extractants containing imidazole or pyridine groups had already been published. Wang et al. utilized $[C_{14}\text{-}4\text{-}C_{14}im]Br_2$ as both as a surfactant and an extractant in the preparation of W/O microemulsion for gold extraction [27]. Tong et al. had successfully utilized [Hpy]Cl to extract palladium in chloroform [28]. These studies indicate a promising future for the application of silicone surfactants in metal extraction. Meanwhile, we believe that compared with conventional hydrocarbon surfactants with the same molecular weight, the introduction of the Si atom could enhance the lipophilicity of surfactants, which might strengthen the hydrophobicity of extractant-metal complexes and improve the extraction and separation of certain metals. The application of silicone surfactants in metal extraction could improve the extraction process, as well as expand the extraction theory system and provide novel approaches for metal separation. However, no studies on metal extraction by silicone surfactants have been reported so far.

In this study, we synthesized two novel cationic silicone surfactants, Si₄pyrCl and Si₄pipCl, and systematically investigated their aggregation behaviors in an aqueous solution with and without additives. We conducted surface tension and conductivity measurements, DLS, and TEM visualization to investigate the aggregation behavior of the synthesized surfactants. We explored the influence of the head groups on the aggregation behavior of cationic silicone surfactants. The study of metal extraction on (Co (II), Mn (II), Fe (III), Ni (II), Cu (II), Al (III), Sn (IV), Zn (II), Ce (III), Li (I), Mg (II), Au (III) and Pd (II)) by the two silicone surfactants could improve our understanding and expand the potential application of silicone surfactants.

2. Experimental section

2.1. Materials

γ-Chloropropyltrimethoxysilane was purchased from Qufu Chenguang Chemical Co., Ltd. N-methylpiperidine, sodium chloride, trimethylchlorosilane, sodium bromide, sodium iodide and sodium

sulfate were procured from Energy Chemical. Isopropyl alcohol, acetonitrile, pyridine, n-hexane, chloroform, ether and alcohol were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. The feed solutions were prepared by dissolving metal chlorides in hydrochloric acid solutions: $PdCl_2$, Guangfu Institute of Fine Chemical (Tianjin, China); $HAuCl_4 \cdot 4H_2O$, Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China); $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ and $SnCl_4 \cdot 5H_2O$, Kermel Chemical Reagent Tianjin Co., Ltd. (Tianjin, China). Triply distilled water was used to prepare all the solutions. The structures of the cationic silicone surfactants are shown in Fig. 1.

2.2. Methods

2.2.1. Surface tension

Surface tension measurements were carried out on a model BZY-1 tensiometer (Shanghai Hengping Instrument Co., Ltd., accuracy ± 0.1 mN m⁻¹) by Du Nouy ring method at 298.15 K. All measurements were repeated until the values were reproducible.

2.2.2. Electrical conductivity

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

2.2.3. Dynamic light scattering measurements

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

2.2.4. TEM measurements

The morphologies of cationic silicone surfactant aggregates in aqueous solution were examined by using a JEM-1011 TEM (JEOL, Japan) at 100 kV. The samples were prepared by placing cationic silicone surfactants 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 of the products

2.3.1. γ-Chloropropyltri(trimethylsiloxy)silane

A mixture of γ-chloropropyltrimethoxysilane (0.04 mol, 7.94 g) and trimethylchlorosilane (0.24 mol, 26.06 g) was mixed into a 100 mL flask and the isopropanol (0.24 mol, 14.40 g) was slowly added. Then, water (0.36 mol, 6.48 g) was added dropwise into the product of alkoxylate reaction. The organic phase was obtained separated from the product and water was used to wash the organic layer until it was neutral. The final product was distilled by rotary evaporation. ¹H NMR (300 M, CDCl₃): 0.066–0.130 ppm (SiC$\textbf{\textit{H}}_3$, 27H), 0.538–0.593 ppm (SiC$\textbf{\textit{H}}_2$CH₂CH₂Cl, 2H), 1.746–1.847 ppm (SiCH₂C$\textbf{\textit{H}}_2$CH₂Cl, 2H), 3.484–3.530 ppm (SiCH₂CH₂C$\textbf{\textit{H}}_2$Cl, 2H).

Si₄pyrCl   Si₄pipCl
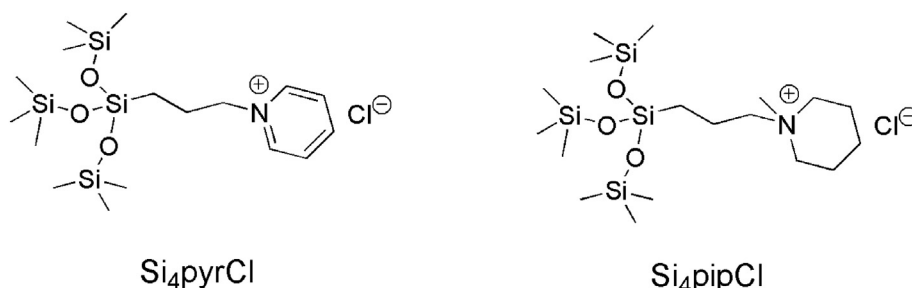
Fig. 1. Chemical structures of the cationic silicone surfactants.