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ORIGINAL ARTICLE

Synthesis and Solution Properties of Carbohydrate-Modified Polysiloxane Bola Surfactants

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Abstract Three carbohydrate-modified polysiloxane bola surfactants (ATPS-GA) were synthesized using a two-step method. Their chemical structures were characterized by infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Their surface properties and aggregation properties in aqueous solution were determined using surface tension measurements and transmission electron microscopy (TEM). Surface tension measurement results indicated that the three bola surfactants are under 25 mN m^{-1}, and much lower than those of conventional hydrocarbon bola surfactants due to the siloxane moiety at the end of the hydrophobic chains. TEM analysis results indicated that the ATPS-GA can self-assemble into spherical micelles with a wide range of average diameters from 100 nm to above 600 nm.

Keywords Carbohydrate · Bola surfactant · Polysiloxane · Synthesis · Properties

Introduction

Bola surfactants consisting of two or more hydrophilic groups connected by a hydrophobic spacer have attracted great attention because of their fundamental importance and their potential applicability [1, 2]. Most of these bola surfactants have been studied for their aggregate behavior in water as a function of their structure [3, 4]. In an aqueous environment, these bola surfactants often self-assemble into unilamellar vesicles, which are stable over a long period of time and could be used as membrane models [5].

The hydrophilic groups of bola surfactants can be nonionic, anionic, cationic or zwitterionic. Recently, bola surfactants involving carbohydrate as the hydrophilic group have attracted increasing attention because they provide the required hydrosolubility to the aggregates and reduce toxicity [6–10]. The hydrophobic chains of bola surfactants can be hydrocarbon or heteroatom in nature. However, most of research publications have focused on the hydrocarbon-tailed bola surfactants. Only a few reported studies of heteroatom-tailed bola surfactants are available [9].

Siloxane-tailed surfactants, as heteroatom-tailed surfactants, have been widely used in many industrial fields such as foam stabilizers, emulsifying agents, detergents and antifoaming agents due to their thermal stability, lower surface tension, and excellent spreading and wetting properties [11]. Most commonly, the hydrophilic groups in siloxane-tailed surfactants consist of polyethers [12]. Because the polyethers are often produced from nonrenewable petrochemical ethylene oxide and propylene oxide, the polyether siloxane-tailed surfactants are not environmental-friendly surfactants [13, 14]. Recently, siloxane surfactants with carbohydrate as hydrophilic group have been synthesized and studied [15–29]. Compared with hydrophilic polyether groups, carbohydrates possess important properties such as biodegradability, biocompatibility, good hydrophilicity and better environmental.

It is therefore of particularly advantageous to combine carbohydrate-modified bola surfactants with carbohydrate-modified siloxane surfactants to develop novel carbohydrate-modified polysiloxane bola surfactants. Compared

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with conventional bola surfactants, changing the hydrocarbon-tailed group to a siloxane-tailed group and the use of a carbohydrate hydrophilic group may lead to significant variations to the surface properties and aggregate behavior.

In this paper, carbohydrate-modified polysiloxane bola surfactants of different molecular weight were synthesized by two-step reactions as shown in Fig. 1. Their chemical structures were confirmed by FT-IR and ^{1}H NMR. Surface activity and aggregation properties of the three bola surfactants were investigated to compare with conventional hydrocarbon-tailed bola surfactants.

Experimental Procedures

Materials

Octamethylcyclotetrasiloxane (D_4), tetramethylammonium hydroxide (TMAH), gluconolactone (GA) were purchased from Energy Chemical Co. Ltd. 1,3-bis(aminopropyl)tetramethyldisiloxane (AT) was purchased from Alfa Aesar (Tianjin) Chemical Co. Ltd. Absolute methanol was obtained from Nanjing Chemical Reagent Co. Ltd. All regents were used as received without any further purification.

Synthesis of Amine-Terminated Polysiloxanes (ATPS)

The reaction was carried out in a 250-mL four-neck round-bottomed flask, equipped with a magnetic stirrer, a thermometer, and a reflux condenser. The mixture of D4 (14.83 g, 50.0 mmol), AT (12.43 g, 50.0 mmol) and TMAH (0.68 g, 7.5 mmol) were added based on the ingredients and stirred for 3 h at 90 °C under a nitrogen atmosphere. The resulting TMAH was then deactivated by heating to a temperature of 140 °C for 1 h. To remove unreacted starting materials and the low weight oligomer, the liquid product was subjected to fractional distillation. The amine-terminated polysiloxanes (ATPS-1) was obtained as a colorless liquid with a yield of 94.8 % (25.85 g). The amine value of ATPS-1, which was determined as reported earlier [30], was 3.89 mmol g^{-1}. The molecular weights of ATPS-1, which was determined by end-group titration also as reported earlier [31], was 517 g mol^{-1}.

The ATPS-2 and ATPS-3 were obtained using the same procedure as for ATPS-1. ATPS-2 was colorless liquid with a yield of 98.6 %. The amine value and molecular weight of ATPS-2 were 3.35 mmol g^{-1} and 596 g mol^{-1}, respectively. ATPS-3 was a colorless liquid with a yield of 96.8 %. The amine value and molecular weight of ATPS-3 were 2.98 mmol g^{-1} and 691 g mol^{-1}, respectively.

Synthesis of Carbohydrate-Modified Bola Polysiloxane Surfactants (ATPS-GA)

The ATPS-1 (25.71 g, 0.1 mol NH_2) and gluconolactone (17.81 g, 0.1 mol) were put into a three-neck round-bottom flask equipped with a magnetic stirrer and refluxing condenser. The mixture was stirred and heated to reflux temperature for 12 h using methanol as solvent. After removal of the solvent, a solid residue was obtained and dried under reduced pressure to a constant mass. The carbohydrate

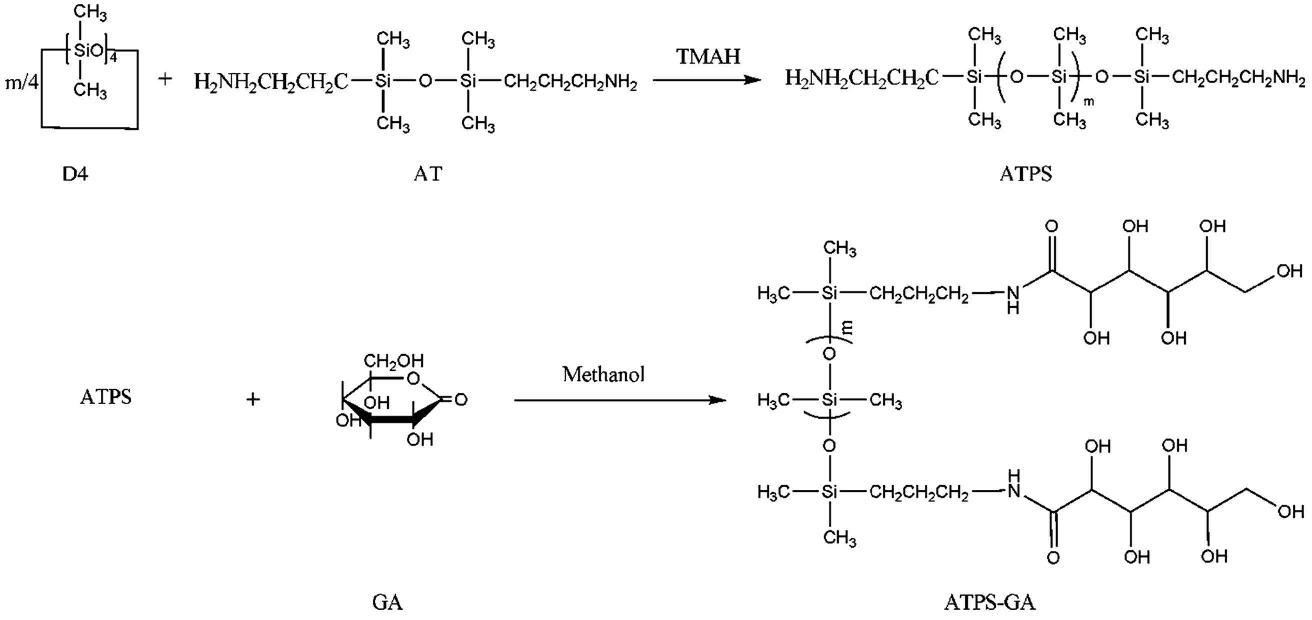

Fig. 1 Synthetic routes and acronyms of ATPS-GA surfactants

modified bola polysiloxane surfactants (ATPS-GA-1) were obtained as a white powder with a yield of 94.6 % (39.5 g).

The ATPS-GA-2 and ATPS-GA-3 were synthesized using the same procedure as for ATPS-GA-1. ATPS-GA-2 was a white powder with a yield of 95.3 %. ATPS-GA-3 was a white powder with a yield of 93.8 %.

Characterization

Results of Fourier transform infrared spectroscopy (FT-IR) of ATPS and ATPS-GA were recorded using a Nicolet 380 (Thermo, USA) Spectrometer. The ATPS were smeared directly onto a KBr plate, whereas the ATPS-GA were mixed with KBr and pressed onto a plate for measurement.

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) of ATPS and ATPS-GA were performed on a Bruker Avance DPX-300 Hz spectrometer. $CDCl_3$ and D_2O were used as solvent, respectively.

Measurement of Surface Tension

The surface tensions of aqueous solutions of the bolaform surfactants were measured on a KRUSS K12 Processor Tensiometer by the Wilhelmy plate method at 25 ± 0.1 °C.

Because aqueous solutions of the surfactants were prepared in doubly distilled water, before measurement, the surface tension of water was confirmed to be in the range of 72.0 ± 0.3 mN m^{-1}.

Transmission Electron Microscopy

The aggregation behaviors of the bola surfactants in solutions were studied by a negative-staining method using JEM-1011 transmission electron microscopy (TEM) at 100 kV. One drop of the aggregates solution was laid on a 400-mesh copper grid coated with a thin film of carbon. The grids were negatively stained using 1.5 wt% phosphortungstic acid. The excess liquid was also tapped with filter paper.

Results and Discussion

Synthesis and Characterization of ATPS-GA Surfactants

Results from the synthesis indicated that the amine values of the three ATPS copolymers gradually decrease with increasing of the feed of D_4, and the molecular weights increase with increasing of the feed of D_4.

The structures of ATPS and ATPS-GA were determined by FT-IR and ^{1}H NMR. The FT-IR spectra of ATPS and ATPS-GA are shown in Fig. 2. As illustrated in Fig. 2a, the peaks at 1259.2 and 800.2 cm^{-1} were attributed to Si–C group, the peaks at 1022.1, 1089.6 cm^{-1} were assigned to the Si–O–Si group, and the peaks at 3353.0 and 1579.2 cm^{-1} were ascribed to the NH_2 group. As shown in Fig. 2c, the successful chemical incorporation of GA with ATPS was proved through the obtained of amide bond peak at 1643.8 and 1552.6 cm^{-1}, and the disappearance of ester peak of gluconolactone at 1725.9 cm^{-1}. Figure 3 shows the ^{1}H NMR spectrum of ATPS and ATPS-GA. As illustrated in Fig. 3a, the peak at 0.07 ppm was assigned to $–Si–\mathbf{CH}_3$, the peak at 0.47 ppm was attributed to $–Si–\mathbf{CH}_2$, the peak at 1.42 ppm was ascribed to $–Si–CH_2–\mathbf{CH}_2$, and the peak at 2.63 ppm was attributed to $–N–\mathbf{CH}_2$. Compared with the ^{1}H NMR spectrum of the ATPS copolymer in Fig. 3a, the spectrum of ATPS-GA in Fig. 3b indicated that the new peaks in the range from 3.50 to 4.60 ppm were assigned to protons of the incorporated GA, and the peak for $–N–\mathbf{CH}_2$ shifted to 3.30 ppm. Based on the FT-IR and ^{1}H NMR analyses, indicating that ATPS-GA surfactants were successful synthesized using two-step reactions.

Equilibrium Surface Tension and Critical Micelle Concentration

To evaluate the surface activity of the bola surfactants, the aqueous solution equilibrium surface tension was determined. As illustrated in Fig. 4, the surface tension was plotted against the aqueous solution concentration of ATPS-GA-1, ATPS-GA-2 and ATPS-GA-3. It is clearly seen that the surface tension of bola surfactants gradually decrease with the increasing in logarithmic scale concentration and then level off. The critical micelle concentrations (CMC) of these three bola surfactants are shown as

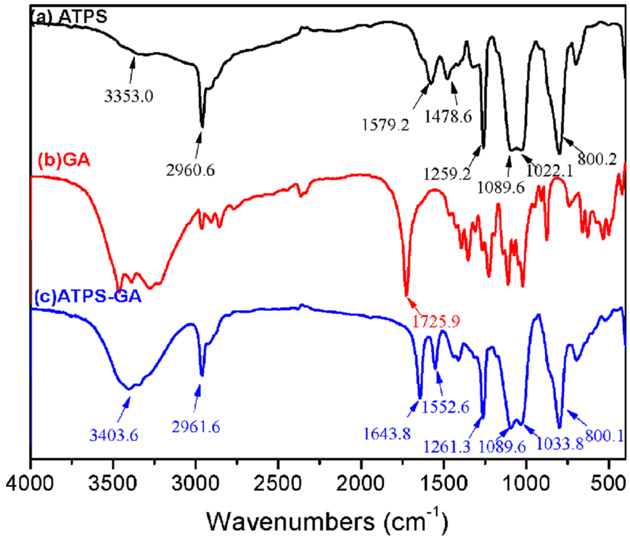

Fig. 2 FT-IR of (*a*) ATPS, (*b*) GA and (*c*) ATPS-GA

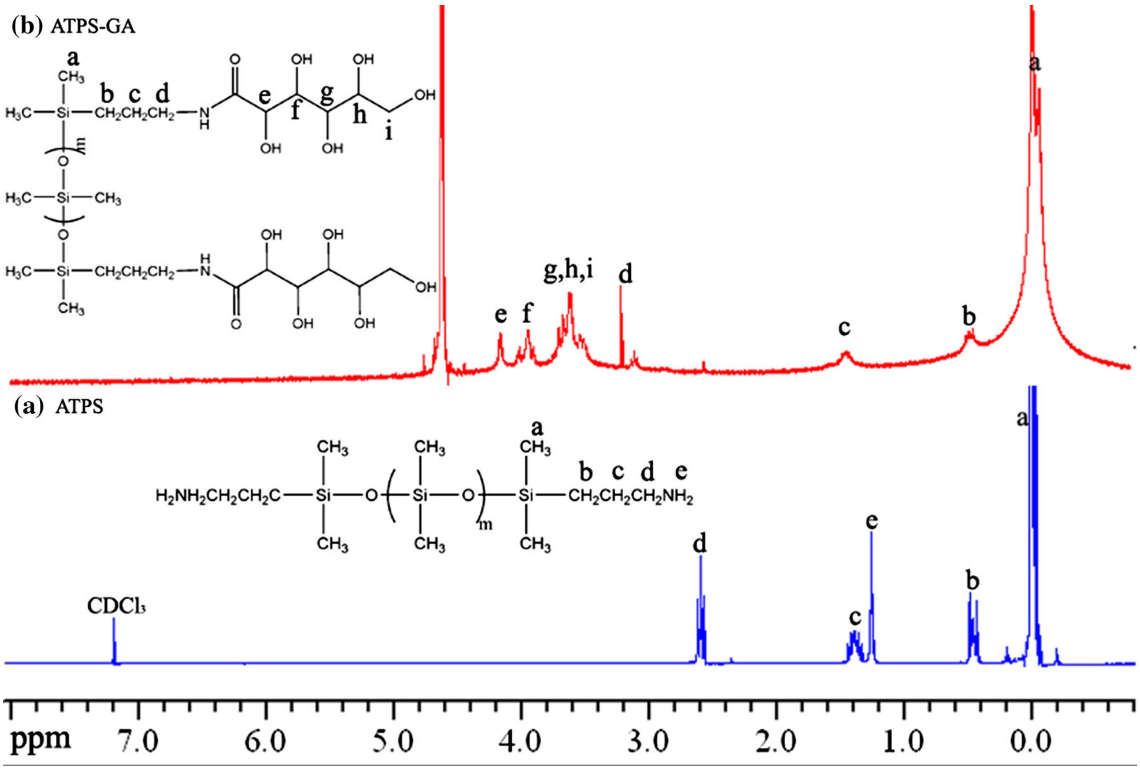

Fig. 3 ^{1}H NMR of (*a*) ATPS, (*b*) GA, (*c*) ATPS-GA

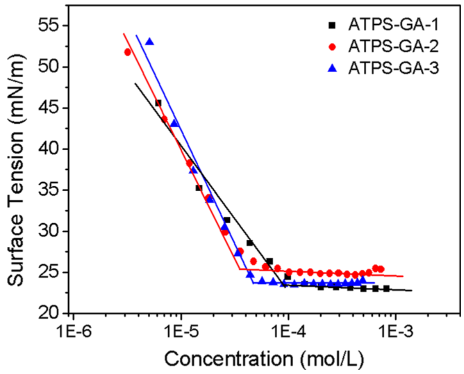

Fig. 4 Surface tension of aqueous solutions of the three bola surfactants as a function of the concentration at 25 °C. *Filled black squares* = ATPS-GA-1, *filled black circles* = ATPS-GA-2 and *filled black triangles* = ATPS-GA-3

sharp bends in the curves. The CMC and the surface tension at the CMC (γ_{CMC}) results of these three bola surfactants are summarized in Table 1. The CMC of ATPS-GA-1, ATPS-GA-2, and ATPS-GA-3 are 9.63, 3.35 and 4.52 10^{-5} mol L^{-1}, respectively. The γ_{CMC} of ATPS-GA-1, ATPS-GA-2 and ATPS-GA-3 are 23.2, 24.5 and 23.6 mN m^{-1}, respectively. It can be seen that these three bola surfactants significantly reduced the surface tension at low concentration, indicating that these molecules adsorbed strongly at the air–water interface. γ_{CMC} values are 23–25 mN m^{-1}, significantly lower than those conventional hydrocarbon-based bola surfactants [1, 2]. This result may be attributed to the siloxane methyl groups in the hydrophobic part lying flat at the air–water interface [32–34].

Table 1 The CMC and γ_{CMC} of ATPS-GA surfactants with different molecular weight

Surfactants	CMC (10^{-5} mol/L)	γ_{CMC} (mN/m)
ATPS-GA-1	9.63	23.2
ATPS-GA-2	3.35	24.5
ATPS-GA-3	4.52	23.6

Aggregation Properties

The aggregation behaviors of conventional hydrocarbon bola surfactants in aqueous solutions have been widely reported [10, 35, 36]. Hill et al. investigated the aggregation behavior of ABA and comb-type siloxane surfactants using optical microscopy, cryo-TEM and X-ray scattering [37, 38]. However, studies on the aggregation behaviors of the carbohydrate-modified polysiloxane bola surfactants in aqueous solution are rare. As reported in Table 1, the critical micelle concentration of the bola surfactants is very low due to the extreme hydrophobicity of polysiloxanes,

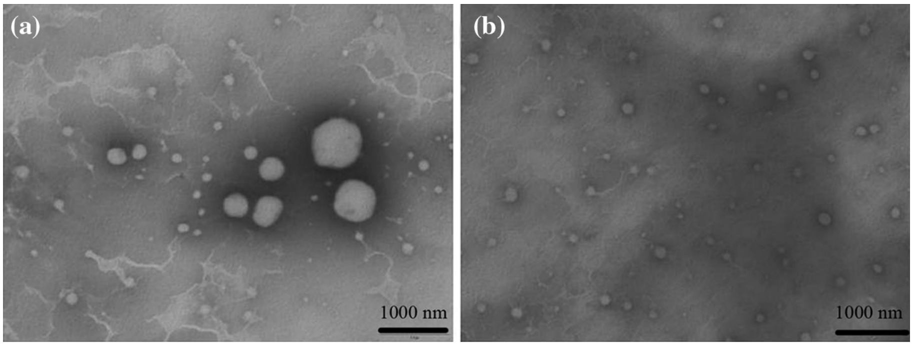

Fig. 5 Negative-stained TEM images of aggregates formed in ATPS-GA-1 solutions (**a**) 1 wt%; (**b**) 2 wt%

indicating that the bola surfactants are easy to self-assemble into aggregates in water. In order to evaluate the size and shape of aggregates formed in the bola surfactant solutions, the TEM measurements was conducted by negative-staining methods. Figure 5 shows the TEM images of the ATPS-GA-1 in aqueous solution. As shown in the TEM images, spherical micelles with a wide range of average diameters from 100 nm to above 600 nm were observed and found to be bigger than conventional polymeric micelles usually with a diameter of less than 100 nm. The majority of smaller micelles are less than 200 nm in diameter, whereas large ones can reach more than 600 nm in diameter. Based on the literature reports, the formation of larger complex micelles is attributed to he further aggregation of simple micelles, which is induced by hydrogen bonding or van der Waals interactions among the hydrophilic shell [39, 40].

Conclusions

Three novel carbohydrate-modified polysiloxane bola surfactants were successfully synthesized using two-step reactions and characterized by FT-IR and ^{1}H NMR spectrometry. The surface activity of the three surfactants, ATPS-GA-1, ATPS-GA-2 and ATPS-GA-3, in water was determined by surface tension measurements and found to have excellent efficiency in surface tension reduction due to the incorporation of a polysiloxane moiety. TEM analysis of ATPS-GA aqueous solutions revealed that ATPS-GA can self-assemble into micelles with a wide range in diameter.

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