



Synthesis of core–shell composites using an *inverse surfmer*

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ABSTRACT

Anilinium dodecylsulfate was prepared from aniline and sodium dodecylsulfate. The critical micellar concentration of the salt was determined using electrical conductimetry, which revealed that the change of counteraction, sodium by anilinium, reduced the critical micellar concentration with respect to the conventional counterpart, sodium dodecylsulfate. The anilinium dodecylsulfate was used as the surfmer in the synthesis of polystyrene/polyaniline core–shell composites, first performing as the surfactant to stabilize the emulsion polymerization of styrene, and later as the monomer to synthesize polyaniline via oxidative polymerization. Here, the surfmer function was directed toward the external phase instead of to the internal phase, as with conventional surfmers with carbon–carbon double bonds. Consequently, the term *inverse surfmer* is proposed. Analyses of its composite microstructure using electron microscopy and thermogravimetric analysis confirmed the core–shell arrangement.

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1. Introduction

Perhaps the most studied surfactants with special functions are polymerizable surfactants, also known as surfmers. These compounds are especially attractive because, aside from acting as conventional emulsifiers, they can link covalently to a latex particle surface [1,2]. This feature avoids surfactant desorption from the polymer particles and improves resistance to freezing and to shearing of the latex [3]. Most surfmers are susceptible to homopolymerization and copolymerization [4]. However, maleic surfmers are only able to copolymerize [5,6]. Numerous reports have described state of the art over the years [3,7–10]. For this reason, their various aspects will not be detailed here.

Herein, we describe results of anilinium dodecylsulfate (DS-AN) used as a new concept of reactive surfactant. In this case, functionality lies on the anilinium group and not on a polymerizable carbon–carbon double bond. The reactive site is not located in the organic phase of the emulsion as found with traditional surfmers [11–17]. These features greatly distinguish DS-AN from the traditional surfmer concept. However, the intention is similar that DS-AN performs as a surfactant because it exhibits a critical micellar concentration and stabilizes emulsion polymerization, and it performs as a monomer because polyaniline is obtained from it

by oxidative polymerization. Therefore, DS-AN and other analog molecules can be regarded as a new approach to generating surfmers.

As described, because of its amphiphilic nature, DS-AN presents a number of potential applications. For instance, in the stabilization of emulsion polymerizations (macroemulsion, suspension, miniemulsion or microemulsion) and by combining the function as a monomer for the synthesis of electrically active polyaniline, DS-AN presents the possibility of obtaining electrically conductive polymer composites. Consequently, in this first approach, we applied DS-AN in the synthesis of polystyrene/polyaniline core–shell composites to demonstrate the feasibility and versatility of this class of reactive surfactants. It is noteworthy that several approaches to produce core–shell colloidal polymer composites of vinyl or acrylic polymers with polyaniline have been reported in the literature [18–25].

2. Experimental section

2.1. Materials

Aniline, sodium dodecylsulfate (SDS), ammonium persulfate (APS) and hydrochloric acid (Nacalai Tesque Inc.) were used as received. Styrene monomer (Nacalai Tesque Inc.) was distilled under vacuum. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (WAKO pure Chemical Industries, Ltd.) was recrystallized from a saturated aqueous solution at 60 °C.

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2.2. Synthesis of anilinium dodecylsulfate (DS-AN)

DS-AN salt was synthesized as follows. First, the salt of anilinium hydrochloride was obtained by reacting aniline and hydrochloric acid in a 1:1 molar ratio. The amount of water sufficient to dissolve the salt was added. Next, an aqueous solution of sodium dodecylsulfate (SDS) corresponding to 1:1 molar ratio with respect to aniline was mixed with the salt of anilinium hydrochloride. The interchange of ions produced the precipitation of the sulfate salt of anilinium because of the much lower solubility of this salt in water at room temperature. Salt purification was performed by saturating an aqueous solution at ca. 50 °C. Then the solution was allowed to cool in laboratory conditions and then refrigerated at 4 °C for 12 h. The solid was recovered by filtration on a filter paper and dried under vacuum at 60 °C. ^1H RMN (400 MHz, δ , $(\text{CD}_3)_2\text{S}=\text{O}$) 0.85 (3H), 1.23 (18H), 1.26 (2H), 1.42 (2H), 3.65 (2H), 7.26 (2H), 7.44 (3H). FTIR (cm^{-1} , ATR) 3300–2850, 2940, 2850, 2920, 2620, 1500, 1623, 1600, 1478, 1470, 1374, 1200, 1214, 1056, 963, 950, 814, 740, 720. The critical micellar concentration (cmc) (mmol dm^{-3} , electrical conductimetry) was 2.99.

2.3. Determination of critical micellar concentration

The critical micellar concentration (cmc) of DS-AN and SDS was determined using electrical conductimetry. The procedure was the following. An aqueous concentrated solution of the salts was prepared in laboratory conditions. In a glass vessel, 100 ml of demineralized water, with electrical conductivity of $1.8 \mu\text{S cm}^{-1}$, was loaded and tempered at 35 °C. The cell of the conductivity meter was fixed 1 cm above the vessel bottom. Progressive additions of 1 ml each time of the solution were achieved. The evaluation consisted of measuring the increase of electrical conductivity as a function of the salt concentration. Gentle magnetic stirring was used to homogenize the solution.

2.4. Emulsion polymerization

Styrene emulsion polymerization, as the first step of the method, was performed as follows. First, an aqueous solution of DS-AN containing 10, 20 or 40 mmol dm^{-3} was loaded into the reactor and left to stabilize for 20 min at 70 °C. Then $0.00184 \text{ mol dm}^{-3}$ of 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50) was loaded into the reactor. The emulsion was prepared by injecting the monomer into the reactor. The relation of the monomer to water was 20/80 (wt/wt). Monomer addition was regarded as the initiation of the polymerization. Therefore, the first sample to determine polymerization kinetics was taken 3 min after monomer feeding. All polymerizations were performed at 70 °C, with stirring of 300 rpm and permanent flux of nitrogen. A series of samples were taken during the polymerization to determine the kinetics.

2.5. Oxidative polymerization

Polyaniline (PAni-DS) shell synthesis, as the second step, was conducted as follows. First, 50 ml of polystyrene latex was loaded into a glass vessel. In a separate container, an aqueous solution of DS-AN was prepared at 50 °C. Afterward, the solution and the latex were mixed together while maintaining gentle magnetic stirring and temperature for 4 h to allow the salt to absorb onto the polymer particles. After this time, the system was left to cool at room conditions. Then, an aqueous solution of ammonium persulfate (APS), corresponding to a molar ratio of 1.2:1 (DS-AN:APS), was poured dropwise to launch DS-AN polymerization. Once the initiator was fed, the reaction system was transferred to a refrigerator to complete oxidative polymerization at $-2 \text{ }^\circ\text{C}$ for 24 h.

2.6. Characterization

Proton nuclear magnetic resonance (^1H NMR) spectra of DS-AN and SDS were obtained using an FT-NMR (JNM GX400; JROL) in deuterated DMSO ($(\text{CD}_3)_2\text{S}=\text{O}$) at 60 °C. Infrared spectroscopy (FTIR) analyses were run in an IR Fourier Transform Spectrophotometer (IR Prestige-21 FTIR-8400s; Shimadzu Corp.). Before analyses, DS-AN was recrystallized from a saturated aqueous solution heated at 50 °C and then cooled to 4 °C.

Scanning electron microscopy in transmission mode (STEM) was performed in a field emission electron microscope (JSM-7401F; JEOL) at 30 kV. To prepare the samples, two drops of latex were dispersed using sonication for 5 min in 30 ml of tridistilled water. Subsequently, a drop of latex was placed and left to dry on a holey carbon copper grid. By this procedure, the latexes, the core-shell composites and samples of pure PAni-DS were analyzed.

3. Results and discussion

3.1. ^1H NMR and infrared spectroscopy

The ^1H NMR spectra of DS-AN and SDS, were run in deuterated DMSO ($(\text{CD}_3)_2\text{S}=\text{O}$; $\delta = 2.49 \text{ ppm}$). The most relevant difference between the spectra of DS-AN and SDS were the multiplets at $\delta = 7.44 \text{ ppm}$ and at $\delta = 7.28 \text{ ppm}$ corresponding to the protons of the anilinium cation. This difference indicated the presence of the anilinium group in DS-AN (Fig. S1).

The FTIR spectra of SDS presented the following bands (Fig. S2). The peaks at 2940 cm^{-1} and 2850 and 2920 cm^{-1} correspond to the symmetric stretching of the C–H bond of CH_3 groups and to the symmetric and asymmetric stretching bands of C–H bond of CH_2 groups, respectively. The bands at 1374 and 1478 cm^{-1} were assigned to bending vibration of C–H bonds of CH_3 groups. The peaks at 1200 and 1214 cm^{-1} and 1056 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations, respectively, of the S=O₂ bond. The peaks at 814 and 963 cm^{-1} , respectively, stand for the symmetric and asymmetric stretching of S–O bond. Finally, the band at 720 cm^{-1} corresponds to the rocking vibration of the C–H bond of CH_2 groups. On the other hand, the spectrum of DS-AN presented the same set of bands described for SDS. In addition, the following are also present (Fig. S2). A wide band at 2620 cm^{-1} corresponds to an overtone of the $^+\text{NH}_4$ group, whereas the bands at 1500 and 1600 cm^{-1} , respectively, correspond to the symmetrical and asymmetrical vibrations of N–H bonds of this group. The peak at 1623 cm^{-1} corresponds to the scissoring vibration of bond NH_2 of $^+\text{NH}_4$ group. The peaks at 1470 cm^{-1} , and 950 and 740 cm^{-1} , respectively, correspond to waving and out of plane bending vibrations of C–H bonds of the anilinium group. This set of bands confirms the presence of the countercation in DS-AN. Literature is available to consult functional group frequencies [26–29].

3.2. Critical micellar concentration

The cmc of DS-AN was determined using electrical conductimetry. This technique is specially applied with ionic surfactants because the electrical conductivity of soluble ionic compounds in water depends directly on the concentration [30]. Some reports have described the surface activity of “aniline–organosulfonic acid” complexes (aniline–dodecylbenzenesulfonic acid), during polyaniline synthesis in aqueous or organic phase, or in emulsified systems [31–35]. However, the characterization and determination of the cmc of analog compounds to DS-AN have not been reported. The curves of electrical conductivity (k) ($\mu\text{S cm}^{-1}$) versus the surfactant concentration (mol dm^{-3}) of SDS and DS-AN are shown in

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