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The interactions between cationic cellulose and Gemini surfactant in aqueous solution

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ABSTRACT

Due to the extensive application of cationic cellulose in cosmetic, drug delivery and gene therapy, combining the improvement effect of surfactant–cellulose complexes, to investigate the properties of cellulose in aqueous solution is an important topic from both scientific and technical views. In this study, the phase behavior, solution properties and microstructure of Gemini surfactant sodium 5-nonyl-2-(4-(4-nonyl-2-sulfonatophenoxy)butoxy)phenyl sulfite (9-4-9)/cationic cellulose (JR400, the ammonium groups are directly bonded to the hydroxyethyl substituent with a degree substitution of 0.37) mixture was investigated using turbidity, fluorescence spectrophotometer and shear rheology techniques. As a control, the interaction of corresponding monovalent surfactant, sodium 2-ethoxy-5-nonylbenzenesulfonate (9-2) with JR400 in aqueous solution was also studied. Experimental results showed that 9-4-9/JR400 mixture has lower critical aggregation concentration (CAC) and critical micelle concentration (CMC) (about one order of magnitude) than 9-2/JR400 mixture. A low concentration of Gemini surfactant 9-4-9 appeared to induce an obvious micropolarity and viscosity value variation of the mixture, while these effects required a high concentration of corresponding monovalent one. Furthermore, dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements illuminated the formation and collapse procedure of network structure of the 9-4-9/JR400 mixture, which resulted in the increase and decrease of viscosity. These results suggest that the molecular structure of the surfactant has a great effect on its interaction with cationic cellulose. Moreover, the Gemini surfactant/cationic cellulose mixture may be used as a potencial stimuli-responsive drug delivery vector which not only load hydrophilic drugs, but also deliver hydrophobic substances.

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1. Introduction

Cellulose is a natural linear chain polysaccharide produced by plant. It is the main composition of the herbal cells wall and tissues. Owning to its outstanding merits, such as easy acquired, readiness for modification, good water solubility and favorable biocompatible, cellulose and its semi-synthetic derivatives are extensively applied in veterinary foods, fibers and clothes, wood and paper, cosmetic and pharmaceutical industries. In addition, cationic cellulose derivatives contain amino/ammonium groups which enable them with high affinity for negatively-charged molecules, while the glucosidic backbone may bring about hydrophobic interactions. It is demonstrated that the cationic cellulose mix with the oppositely charged surfactant together may improve their favorite features or to avoid undesirable problems. In the other hand, Gemini surfactant is a type of surfactant consisting of two hydrophobic chains and two polar head groups which are covalently attached through a spacer at the level of the head groups. (Menger & Littau, 1991; Menger & Littau, 1993; Hait & Moulik, 2002; Tyagi & Tyagi, 2009). This unique molecular structure attributes to Gemini surfactant exhibit special properties compared to its corresponding monovalent one, such as lower critical micelle concentration value (CMC) and C_{20} value (surfactant concentration in the solution phase that will reduce the surface tension of the solvent by 20 mN m^{-1}) (Azum, Naqvi, Akram, & Kabir-ud-Din, 2008), better lime-soap dispersing properties and wetting properties (Zhu, Masuyama, & Okahara, 1990; Zhu et al., 1993). Furthermore, Gemini surfactant with hydrophilic spacers possess low Krafft temperature and thus can be used directly in cold water (Kim, Kida, Nakatsuji, Hirao, & Ikeda, 1996; Manet, Karpichev, Dedovets, & Oda, 2013). Some Gemini surfactants with short spacer group have especially unusual rheological properties (Kern, Lequeux, Zana, & Candau, 1994; Xu, Lin, Wu,

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& Han, 2004). These unique properties make them attractive for use in a number of applications, including detergent, shampoo, enhancing oil recovery, drug delivery, and the construction of high-porosity materials (McGregor, Perrin, Monck, Camilleri, & Kirby, 2001; Romero, Jiménez, Huc, & Oda, 2004; Yu, Zhao, & Bayly, 2008; Tang et al., 2012; Zhao, 2014). Since Bunton, Robinson, Schaak, and Stam, (1971) reported the first cationic type Gemini surfactant in 1971, many efforts have been devoted to synthesizing novel Gemini surfactants and investigating their associated behavior including CMC, micelle aggregation number (Rosen & Song, 1996; Bai, Yan, & Thomas, 2001), micelle micropolarity and microviscosity (Alami, Levy, Zana, & Skoulios, 1993; Zana, In, & Lévy, 1997; Mathias, Rosen, & Davenport, 2001; Wang et al., 2014b), solution rheology (Geng, Hu, Jia, & Luo, 2014) and microstructure (Danino, Talmon, & Zana, 1995; In, Bec, Aguerre-Chariol, & Zana, 2000; Zana & Xia, 2004).

The interactions between polymer and surfactant have been extensively studied over the past few decades (Mel'nikov, Sergeyev, & Yoshikawa, 1995; Nilsson, Goldraich, Lindman, & Talmon, 2000; Qiu, Cheng, Xie, & Shen, 2004; Muzzalupo et al., 2007; Wang et al., 2009; Han & Wang, 2011; Azum, Asiri, Rub, Al-Youbi, & Khan, 2012; Mirgorodskaya, Yatskevich, Zakharova, & Konovalov, 2012). Mixing of surfactant with polymer always generates many unexpected properties and new applications, such as improving oil recovery, loading and releasing of drugs, isolating and purifying DNA, providing a simplified model for bio-process and tuning stability and regulating the rheology of composites. For instance, using the anionic surfactant Aerosol OT (AOT) and the polysaccharide polymer alginate as a soft template, Chavanpatil et al. developed a novel polymer–surfactant nanoparticle formulation for sustained release of water-soluble drugs. The concentrations of AOT and alginate have a great impact on the drug encapsulation and release efficiencies (Chavanpatil et al., 2007). Zhou et al. (2013) reported the mono molecular condensation of plasmid DNA and effective cell transfection by imidazolium Gemini surfactant, which acted as a potential non-viral vector for gene therapy. Recently, Wang et al. has found that the Gemini surfactant (12-6-12) has a stronger ability to decrease the critical micelle temperature of the polymer than the traditional single-chain ionic surfactant. This can be attributed to the stronger aggregation and lower critical micelle concentration of the Gemini surfactant than the monovalent (Wang, Tian, & Wang, 2014). Moreover, a number of cosmetic and household products and drug delivery system, surfactant and polymer have also been formulated using Gemini surfactant (Somasundaran et al., 2005; Faustino, Calado, & Garcia-Rio, 2009; Vongsetskul et al., 2009). These co-formulations have engendered innovative functions that individual surfactant or polymer cannot achieve. Obviously, revising the influence of cellulose and surfactant molecular structure on their interaction is of particular importance in biological and industrial purposes (Kumar & Tyagi, 2014).

Rodríguez et al. reported that the chemical structure of the cationic cellulose has great effect on the interactions with surfactant. Two cationic hydroxyethyl celluloses, polyquaternium-4 (PQ-4) and polyquaternium-10 (PQ-10), and sodium dodecylsulfate were used as the models. They found that PQ-4 is easier to establish of a three-dimensional network after addition of the surfactant, while PQ-10 is susceptible to form precipitation. These different behaviors of the two cationic celluloses may be originated from their distinctive molecular structures: PQ-4 has less ammonium groups, in small chains grafted to the cellulose backbone, and more free hydroxyethyl substituent than PQ-10 (Rodríguez, Alvarez-Lorenzo, & Concheiro, 2003a) Furthermore, the authors systematically evaluated the association processes of sodium ibuprofen (an amphiphilic drug) with four cationic celluloses which have different chemical structures, and their repercussions on the properties of the aqueous dispersions and cross-linked hydrogels (Rodríguez, Alvarez-Lorenzo, & Concheiro, 2003b). They found that the association phenomena are directly related to the self-aggregation of the drug molecules. Especially when the concentration of drug is above the CMC, the associate interaction could be dramatically enhanced. More importantly, in the presence of surfactant (SDS), the diffusion coefficient value was reduced almost 50%. This encouraging research provided by these studies is particularly useful in the design of novel pH control drug delivery-release systems.

In order to further explore the influence of surfactant structure on its interaction with cellulose; more information concerning the interaction process between cellulose and surfactant is required. Here we selected a Gemini surfactant (9-4-9, sodium 5-nonyl-2-(4-(4-nonyl-2-sulfonatophenoxy)butoxy)phenyl sulfite), a monovalent surfactant (9-2, sodium 2-ethoxy-5-nonylbenzenesulfonate), and cationic cellulose JR400 as the model. (Zhu, Cheng, Zheng, & Yu, 2004; Zhu, Cheng, Wang, & Yu, 2006; Cao et al., 2009). The molecular structure of the surfactants and their synthetic routes were shown in Fig. 1a. The ammonium groups of the cationic cellulose JR400 are directly bonded to the hydroxyethyl substituent with a degree substitution of 0.37 (Fig. 1b). The phase behavior, solution and microstructure properties of the surfactant/cellulose mixture were studied by turbidity, fluorescence spectrophotometer and shear rheology techniques. We expect this work could provide some fundamental data on the surfactant/cellulose mixture which may be favor to design novel and controllable drug deliver-release systems.

2. Experimental

2.1. General materials and methods

Iodoethane (99%) was purchased from Alfa Aesar. Pyrene (98%) was purchased from Acros Organics Chemical Ltd. and recrystallized with ethanol. JR400 which has been cationically modified with an average molecular weight of 300,000 g/mol and a degree substitution (calculated by the nitrogen content) of 0.37 was purchased from Spec-Chem Industry, China, the chemical structure was shown in Fig. 1b. The aqueous solution of 1% (w/v) JR400 bears 12 mM quaternary ammonium. Nonylphenol was purchased from Tianjin Synthetic Detergent, Ltd. Chlorosulfonic acid (HSO_3Cl) was purchased from Shanghai Tianlian Fine Chemicals, Ltd. Tetrahydrofuran (THF) was distilled from CaH_2 under nitrogen. All other chemicals and reagents were AR grade and used without further purification. Deionized water was used in all experiments.

2.2. Syntheses of 9-4-9 and 9-2

The Gemini surfactant 9-4-9 was synthesized and purified according to the method described in our previous papers. The synthetic routes of 9-4-9 and 9-2 were shown in Fig. 1a. The synthesis procedure of surfactant 9-2 was shown as below.

KOH (4.0 g, 71 mM) solid was added to 40 mL dry THF solution containing nonylphenol (5.5 g, 25 mM). The mixture was stirred at room temperature for 15 min and then heated to 80 °C. Then iodoethane (4.1 g, 26 mM) was slowly added into the reaction mixture with syringe. After refluxing at 80 °C for 2 h, the mixture was cooled to room temperature. THF was poured out and the yellow oil liquid was added into 100 mL diethyl ether. The solution was washed sequentially by dilute NaOH aqueous solution and water. The organic layer was dried with anhydrous $MgSO_4$ for 48 h. After removal of the solvent, the residue was purified by column chromatography to give 1-ethoxy-4-nonylbenzene (compound B, 5.0 g, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ 0.52–1.73 (m, 22*H*), δ 3.74–4.05 (t, 2*H*), δ 6.83–6.93 (d, 2*H*), δ 7.06–7.18 (m, 2*H*).

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