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Surface properties and synthesis of the cellulose-based amphoteric polymeric surfactant

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Abstract

A new family of amphoteric surfactant – 2-hydroxy-3-(*N*,*N*-dimethyl-*N*-dodecyl-ammonium)-propyloxy cellulose sulfate (GDCS) was synthesized by etherification of cellulose sulfate with glycidyl dodecyl dimethylammonium chloride (GDDMAC) in this paper. GDCS was characterized by FT-IR spectroscopy, ^{13}C NMR, elemental analysis and TG. The surface-active properties such as surface tension, critical aggregation concentration were determined by the Wilhelmy plate method. The micellar conformation of GDCS in aqueous solution at different concentration was investigated by environmental scanning electro microscopy (ESEM). Rheological measurements of GDCS indicated that the solution first behaved like a pseudoplastic property, the apparent viscosity decreased sharply, and then exhibited a Newtonian property, the apparent viscosity did not change obviously anymore.

Keywords: Cellulose; Amphoteric surfactant; ESEM; Micelle; Critical aggregation concentration

1. Introduction

The concept of polymeric surfactants is now some 50-years old. Strauss and co-workers studied "polysoaps" derived from poly (2-vinyl pyridine) in the early 1950s (Strauss & Jackson, 1951). Since that time, there has developed a substantial body of literature dealing with surface active and/or amphiphilic synthetic or natural polymers, particularly related to the concept of steric stabilization (Wingrave, 1980). A renewed interest in amphiphilic derivatives based on various commercial and non-commercial polysaccharides was evoked by the growing demand for natural and biodegradable surfactants (Bataille, Huguet, Muller, Mocanu, & Carpov, 1997; Hoogendam et al., 1998; Zhang, Zhang, & Li, 2000; Zhang, 2001a; Duval-Terrie, Huguet, & Muller, 2003; Duval-Terrie, Cosette, Molle, Muller, & Dé, 2003). Of particular interest are cellulose and its derivatives.

Water-soluble cellulosic derivatives can exhibit properties of biodegradable polymeric surfactants after an appropriate chemical modification. The hydrophobization of certain hydrophilic cellulose can be carried out by conversion to ethers or esters containing hydrophobic epoxide, halide, acyl halide, isocyanate or anhydride. The partial hydrophobization of water-soluble cellulosic derivatives such as hydroxyethyl cellulose (Landoll, 1982; Tanaka, Meadows, Phillips, & Williams, 1990; Meadows, Williams, & Phillips, 1994; Tanaka, Meadows, Williams, & Phillips, 1992), carboxymethyl cellulose (Sroková, Talába, Hodul, & Balázová, 1998; Sroková, Tomanová, Ebringerová, Malovíková, & Heinze, 2004; Charpentier et al., 1997; Merle, Charpentier, Mocanu, & Chapelle, 1999; Rosilio, Albrecht, Baszkin, & van Oss, 2000; Jiang & Zhou, 2000; Tang, Jiang, & Huang, 2000), sulfoethyl cellulose and cellulose sulfate (Talába, Sroková, Ebringerová, Hodul, & Marcincin, 1997) using alkyl or acyl halogenides was reported. The reaction conditions were governed to obtain products with a low degree of substituent and preserved water solubility. Prepared derivatives reduced the surface tension and

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had excellent emulsification. However, water-soluble amphoteric surfactants based on cellulose were reported hardly but by Li-ming Zhang (Zhang, 2001b).

In the present paper, a kind of amphteric surfactant – 2-hydroxy-3-(*N*,*N*-dimethyl-*N*-dodecyl-ammonium)propyloxy cellulose sulfate (GDCS) was synthesized by etherification of cellulose sulfate with glycidyl dodecyl dimethylammonium chloride (GDDMAC). The surface-active properties were determined, e.g. surface tension, critical micelle concentration. At the same time, the present work studied the conformation of micelle of the solution of GDCS at different concentration and the unique rheological properties.

2. Experimental section

2.1. Materials

Cellulose was purchased from Shijiazhuang Linter Co. Ltd. Chlorosulfonic acid was purchased from Shanghai Tingxin chemical reagent factory. Dimethyl formamide (DMF) was dried before use. Sodium hydroxide, methanol, acetone and epoxychloropropane were obtained from Tianjin University Kewei Co. Ltd. Dimethyl dodecyl amine was obtained from Tianjin Angel Chemicals Group Co. Ltd. Glycidyl dodecyl dimethylammonium chloride was prepared according to the literature (Jiang & Zhou, 2000).

2.2. Testing methods

Cellulose derivatives and cellulose were analyzed by using a Fourier transform infrared spectrometer. FT-IR spectra were recorded on a BIO-BAD EAALIBUR FTA-3000 Fourier transform infrared spectrometer. Transmittance measurements were conducted by using the KBr pellet method.

^{13}C NMR spectra of sample dissolved in D_2O (25 °C) was recorded using INOVA 500 MHz spectrameter. Tetramethyl silane (TMS) was an internal standard material.

A thermal gravimetric analyzer (TGA; TA Instruments ZRY-ZP) was used to measure the thermal degradation of the GDCS. Samples with a weight of ~10 mg were tested at a heating rate of 10 °C/min from 20 to 600 °C.

The degree of substitution of cellulosic derivatives was determined by inductively coupled plasma and elemental analysis.

Surface tension measurements of GDCS dissolved in doubly distilled water were performed by the Wilhelmy plate method with DCAT21 tensiometer (Germany) at 25 °C. The accuracy is 0.01 mN m^{-1}. Surface tension data were plotted against concentration in order to obtain the critical aggregation concentration (CAC) and corresponding surface tension ($\gamma_{\min}$).

ESEM images of micellar conformation were observed directly with environmental scanning electrical microscope (Quanta 200, USA). The aqueous solution was quenched at −10 to −20 °C, so the micelles in solution were frozen; Water in solution sublimed gradually under vacuum and then naked micellar particles were observed.

The steady shear rheological property of the solution of GDCS was obtained with rheometer (a Stress Tech ETC2, DE) with DC50 at 25 °C, using double concentric-cylinder geometry system. For rheological measurement, the sample was loaded onto the platen of the rheometer and sheared continuously from 0.1 to 180 s^{-1}.

2.3. Synthesis and purification of sodium cellulose sulfate

According to literature (Baumann, Richter, Klemm, & Faust, 2000), sodium cellulose sulfate was synthesized. The final whole mixture became the light yellow liquid. Afterwards the reaction mixture was cooled down to room temperature. The product was poured into a certain volume of 4% NaOH in methanol, filtered off and dissolved in ice water. At the same time the solution was neutralized with an aqueous NaOH solution. The solution was filtered to separate undissolved particles. The product gave a clear solution and was precipitated in a certain volume of methanol. The white product was dried under vacuum at 50 °C, dissolved product again in a little water and was subsequently freeze dried. The degree of substitution of sodium cellulose sulfate is 0.76 by calculating the data determined by the ICP ($S\% = 10.16$). IR:γ (O–H), 3452 cm^{-1}; γ (S=O), 1238 cm^{-1}; γ_s(O–S–O), 997 cm^{-1}; γ_{as}(O–S–O), 812 cm^{-1}. ^{13}C NMR: C-1 and C-1^1,AGU, 102.33 ppm and 100.52 ppm; C-2 and C-2^1,AGU, 73.98 ppm and 81.68 ppm; C-6 and C-6S,AGU, 60.02 ppm and 65.98 ppm.

2.4. Synthesis and purification of 2-hydroxy-3-(N,N-dimethyl-N-dodecylammonium)- propyloxy cellulose sulfate (GDCS)

Sodium cellulose sulfate (8 g) was added into 75 ml of isopropyl alcohol. Sodium hydroxide (1.34 g) dissolved in 5 ml

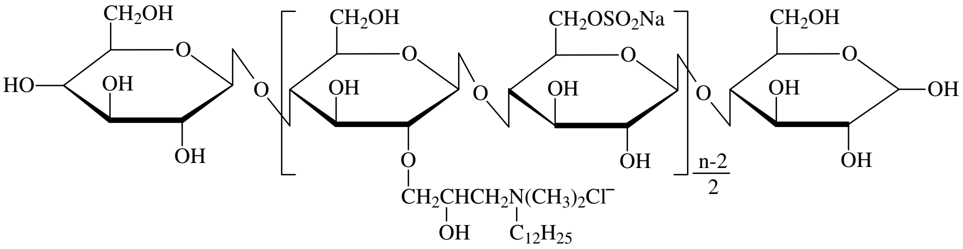

Fig. 1. Schematic diagram for GDCS.

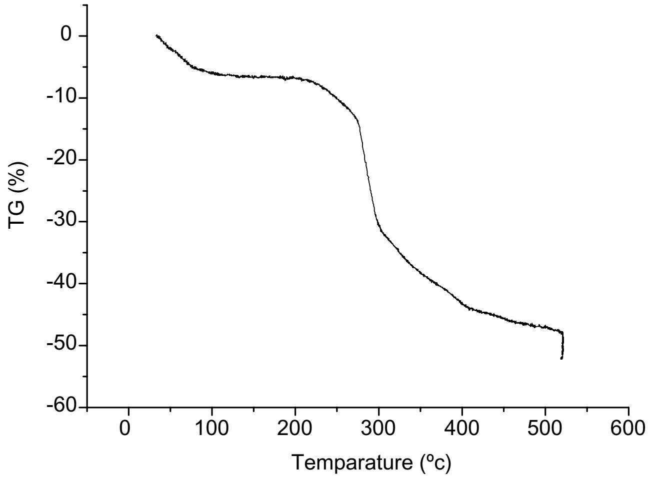

Fig. 2. Plot of TG curves of GDCS.

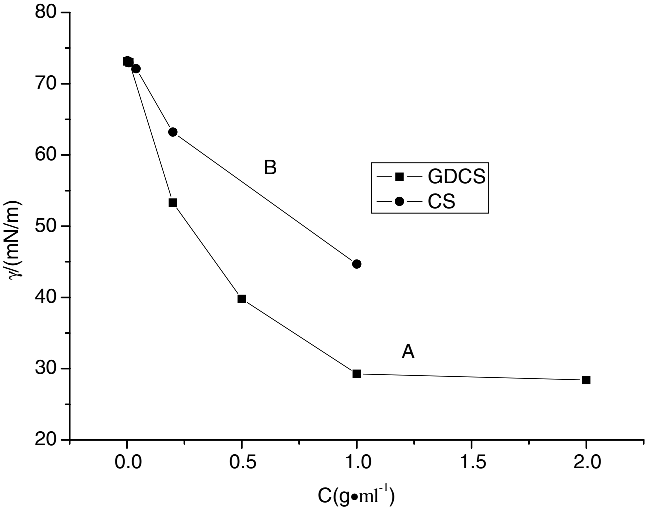

Fig. 3. Surface tension–concentration curve of GDCS.

of water was added dropwise over a period of 20 min. The mixture was stirred for another 1 h and then heated to 65 °C. The mixture was stirred for another 3 h at this temperature. A certain amount of GDDMAC dissolved in 15 ml aqueous isopropyl alcohol was added dropwise over 1 h. The reaction mixture was kept at 65 °C for another 6 h. The above liquid of the reaction mixture was removed. The cooled reaction mixture was dissolved with little water and neutralized with acetic acid. The clear solution of product was precipitated in a certain volume of acetone. The solid was washed with ethanol several times. Then, the solid was dissolved in a little water. The solution was filtered and dialyzed (MWCO 8000) against the distilled water. The solution was subsequently freeze dried. The products were named GDCS. The structure of it is shown in Fig. 1. Elemental analysis: C, 18.75; H, 3.71; N, 0.045 (Calc. $DS_N = 0.075$). IR: δ_s (CH_2), 1458 cm^{-1}; γ_{as}(C–O–C), 1135 cm^{-1}. ^{13}C NMR: C-6S,AGU, 65.98 ppm; – $(CH_2)_{11}CH_3$, 31.12–37.18 ppm; C-2,AGU, 73.16 ppm.

3. Results and discussion

3.1. Thermal properties of GDCS

The thermal property of GDCS is established from Thermal gravitic (TG). Fig. 2 is the plots of TG curve of GDCS. As shown in Fig. 2, the pyrolysis of GDCS proceeds in four parts: (1) the first weight loss that occurred below 100 °C, which was generally attributed to the evaporation of sorbed water from sample; (2) the second weight loss, which commenced at about 220 °C, was reflected in a slow weight decrease represented by a shoulder. This was the initial stage of pyrolysis by minor decomposition reaction; (3) a rapid weight loss, reflecting major decomposition, proceeded at 325 °C; and (4) a prolonged char oxidation stage. It is seen that the initial decomposition temperature of GDCS is lower than cellulose (Nada & Hassan, 2000). This can be attributed to the fact that the anion and cation introduced to cellulose decrease its crystallinity (Nada & Hassan, 2000). This leads to an earlier initial decomposition. But, the major decomposition temperature of GDCS is higher than cellulose (Nada & Hassan, 2000). This can be attributed the fact that the 2-hydroxy-3-(*N*,*N*-dimethyl-*N*-dodecyl-ammonium)-propyloxy chains attached to cellulose sulfate probably form a ring with the group – OH of AGU. The ring structure has a higher major decomposition temperature than the linear cellulose (Nada & Hassan, 2000).

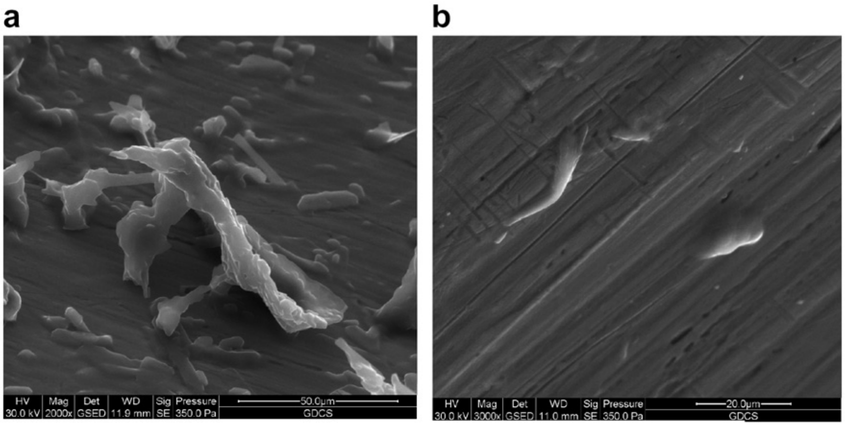

Fig. 4. ESEM of 0.04% GDCS in aqueous solution. (a) 0.04% 2000×; (b) 0.04% 3000×.

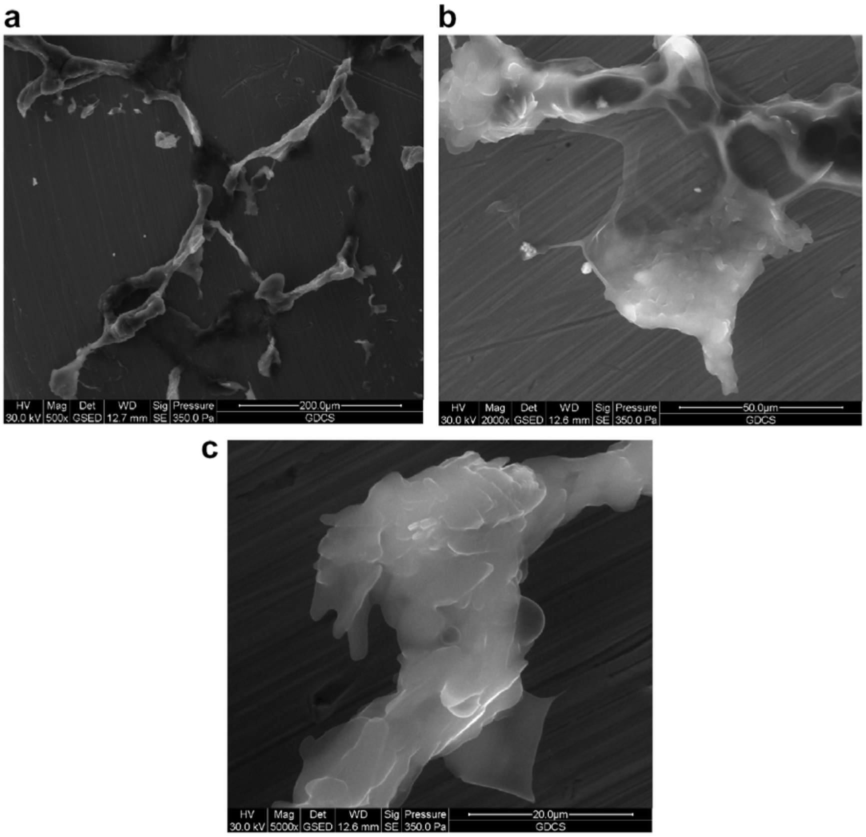

Fig. 5. ESEM of 0.2% GDCS in aqueous solution. (a) 0.2% 500×; (b) 0.2% 2000×; (c) 0.2% 5000×.

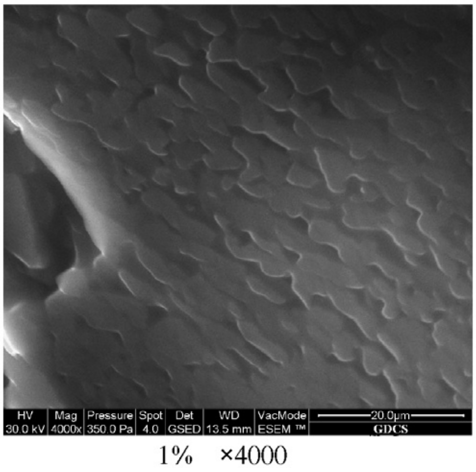

Fig. 6. ESEM of 1% GDCS in aqueous solution.

3.2. Critical aggregation concentration and micelle conformation of GDCS

Fig. 3 shows the isotherm of the surface tension of the GDCS and CS aqueous solution versus their concentration. According to Fig. 3, the curve A consists of two parts intersecting at the inflection point while there is no turning point in the curve B. The surface tension of the curve A decreased greatly in the low concentration regime. When its concentration was in high concentration regime, the surface tension slightly decreased. Finally, the surface tension was almost kept at constant. The plateau of surface tension means the micelle is formed in aqueous solution at corresponding concentration. The concentration at the inflection point denoted the critical aggregation concentration (CAC). The value of CAC was 0.6 (wt)%, corresponding value of surface tension at CAC was 34 $\mathrm{mN\,m^{-1}}$ ($\gamma_{\min}$). By comparison with reported results for other system, it is found that our value of $\gamma_{\min}$ at CAC is lower than the other reported data (Talába et al., 1997). This indicated that the capacity for reducing surface tension of GDCS was significantly enhanced in comparison with single cellulose sulfate. This also indicated that GDCS has the excellent surface activity and is comparable to that of low molecule weight surfactants.

The micellar conformation of GDCS in aqueous solution at different concentration was observed by ESEM (Figs. 4–6). As shown in Fig. 4, there were some sporadic club-shaped polymer molecule chains and the micelle could not be formed at concentration of 0.04 (wt)%. When the concentration was up to 0.2 (wt)% lower than CAC, the polymer molecules began to aggregate the dendritic micelle (Fig. 5(a)) and every polymer molecule was club-shaped shown in Fig. 5(b) and (c). As seen in Fig. 6, the polymer molecules had been aggregated strongly as to form the very thick network layer because the concentration of 1.0 (wt)% higher greatly than CAC.

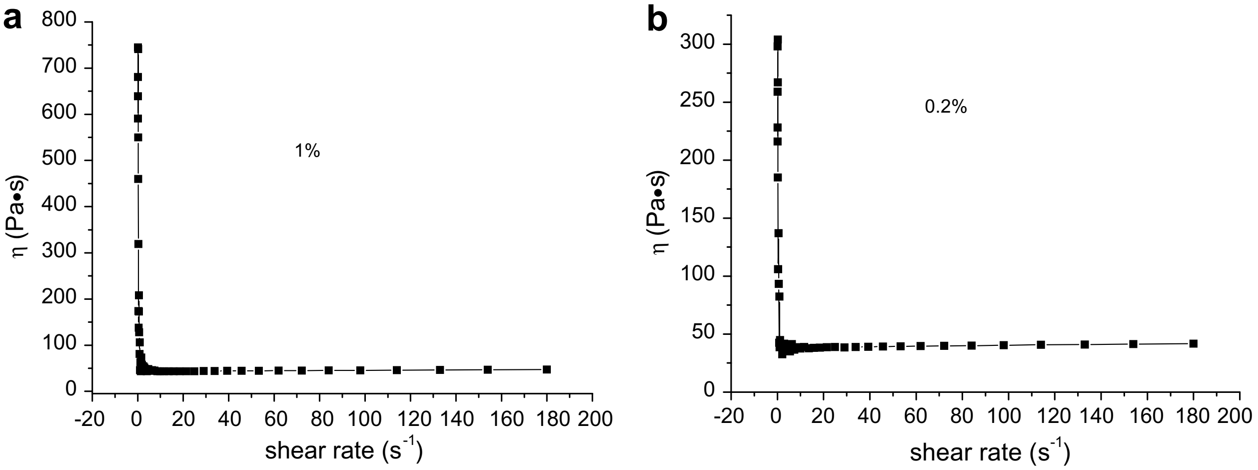

Fig. 7. Apparent viscosity of GDCS solution as function of shear rate.

3.3. Rheological properties of GDCS

Fig. 7 shows changes in apparent viscosity of the GDCS solution as a function of shear rate at different concentration. As shown in Fig. 7, the apparent viscosity of the GDCS solution decreased abruptly at different concentration, indicating rapid damage to molecular networks built up by the hydrophobic association. Then the apparent viscosity did not change anymore. The solution first behaved like a pseudoplastic property and subsequently a Newtonian property. When the shear was removed, the micelle networks could recover and were enhanced, which indicated that there was a kind of dynamic equilibrium between associating and not associating in the polymer molecules (Li, Ye, Cai, & Huang, 2006). At the same time, the highest apparent viscosity of GDCS could reach about 320 Pa s at a concentration of 0.2 (wt)% whereas it could reach about 750 Pa s at a concentration of 1.0 (wt)%. Generally speaking, in the meantime, there is intermolecular and intramolecular hydrophobic associations in the aqueous system of hydrophobically modified water-soluble cellulosic derivatives (Branham, Davis, Middleton, & McCormick, 1994). Below CAC, intramolecular associating dominated, the hydrodynamic volume of GDCS decreased because of the shrinkage of polymer molecules chains. Above CAC, intermolecular associating dominated, a wide range of molecules networks formed via nodes of hydrophobic microdomains, which significantly improved the hydrodynamic volume and leaded to a sharp increase in the apparent viscosity.

4. Conclusions

An amphoteric surfactant – GDCS with novel structure and significant surface-active properties was obtained in the paper. The obtained CAC value was about 0.6 (wt)% and the $\gamma_{\min}$ was 34 mN m^{-1} by the Wilhelmy plate method. It had significant surface-active properties comparable to the low weight surfactants. ESEM data indicated that there was no micelle in aqueous solution at low concentration and the dendritic micelle was formed gradually with the concentration up to 0.2 (wt)%. Finally, the very thick network layer was formed at 1.0 (wt)%. Rheological measurements of GDCS indicated that the solution first behaved like a pseudoplastic property, the apparent viscosity decreased sharply, and then exhibited a Newtonian property, and the apparent viscosity did not change obviously anymore.

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