

Synthesis, micellization behavior and alcohol induced amphipathic cellulose film of cellulose-based amphiphilic surfactant



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ABSTRACT

This paper presented a novel preparation method of the cellulose-based amphiphilic surfactant, and the surfactant was used to prepare amphipathic cellulose membrane. The native cotton cellulose was tailored to cellulose segments in ionic liquid 1-butyl-3-methylimidazolium chloride. Then, the hydrophobic and hydrophilic modification of cellulose segments were carried out by esterification and graft polymerization of the ϵ -caprolactone (ϵ -CL) monomer onto the hydroxyl group of cellulose as well as sulphonation with sulfamic acid. The amphipathic cellulose membrane was made by cellulose-based amphiphilic surfactant cross-linking with glutaraldehyde. The molecular structure of amphipathic cellulose surfactant was confirmed by FT-IR, and its surface active properties were investigated by Wilhelmy plate method and Steady-state fluorescence probe method, respectively. Experimental results showed that cellulose-based amphiphilic surfactant caused low interfacial tension of 48.62 mN/m and its critical micelle concentration (cmc) value was 0.65 wt% when the grafting ratio of cellulose-g-PCL (poly-caprolactone) was 25.40%. The contact angle between a droplet of water and the surface of membrane was 90.84°, and the surface free energy of the alcohol induced cellulose membrane was 15.7 mJ/m². This study may help increase using natural and biodegradable surface-activity materials with improved properties as surfactants.

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1. Introduction

Cellulose, consisting of 10000–25000 β -(1→4)-linked glucopyranosyl repeating units has attracted the considerable attraction of research community all around the globe owing to their unique intrinsic properties such as biodegradability [1,2], easy availability [3], environmental friendliness [4,5], flexibility [6], easy processing and impressive physico-mechanical properties [7–9]. Using renewable materials, more eco-friendliness can be achieved relative to the conventional toxic synthetic polymer composites materials [10–12]. But the strong inter- and intra-molecular hydrogen bonding between the hydroxyl groups in the glucopyranose units, the nature homopolymer has not only higher degree of polymerization (DP) but also higher crystallization, which is not favorable for reagents accessing to the hydroxyl groups [13]. Cellulose therefore has limited modification. There is a demand for cellulose with lower molecular weight and smaller polydispersity index (PDI). The crystallinity of cellulose can be decreased by mechanical grinder [14] or dissolution in special solvent [15,16]. Marcel Meiland had tailored

microcrystalline cellulose in H₃PO₄ medium at room temperature for 3 weeks and obtained samples with degree of polymerization of 35 and a PDI of 1.58 [17]. The room-temperature ionic liquids (ILs) are recently considered as green solvent and successfully used to dissolve and process cellulose [18]. It promotes the further study of low molecular weight of cellulose with a narrow molecular weight distribution, and provides a new direction of modification on cellulose segment. Nevertheless, there is very little research about the stepwise separation of cellulose fractions from ILs.

Landoll [19,20] et al. prepared cellulose surfactant by the method of hydrophobic modification of hydroxyethyl cellulose. In addition, they reported the method of partial hydrophobization of O-(2-sulfoethyl) cellulose using 1-bromododecane, 1-bromodecane, and 1-bromododecane with cellulose sulfate [21]. Wei et al. [22] reported another method in which microcrystalline cellulose was esterified with C₈, C₁₂ or C₁₈ acyl chloride in DMAc/LiCl solution, and then the hydrophobic cellulose derivatives were hydrophilic modified by chlorosulfamic acid.

Since hydrophobic modification reagent has good biodegradability, caprolactone has been employed in biodegradable polyester, polymer-covered and controlled drug delivery [23–26]. Qiu et al. prepared an amphiphilic biodegradable oligosaccharide-based graft copolymer with the method that hydrophobic

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poly-caprolactone (average length $DP \approx 6$) was controlled grafting ratio onto the 3-position hydroxyl group of the short and water soluble maltoheptaose (MH, $DP = 7$) backbone [27].

There is a new development about blending other materials with cellulose to get cellulose composite films. Zhang et al. [28] prepared the regenerated cellulose/graphene nanocomposite film by dispersing graphene into cellulose solution in DMAC/LiCl. When the cellulose/montmorillonite platelet film was fabricated from LiOH/urea/cellulose solution, its surface property was turned from hydrophilic to hydrophobic, because the orientation of cellulose chains on the film surface changed in the composite [29].

This work presented a novel approach for preparation of cellulose-based amphiphilic surfactant with following procedures. The cotton cellulose was tailored to cellulose segments with lower molecular weight polydispersity index in 1-butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid. Then hydrophobic esterification was carried out by the graft polymerization of the ϵ -caprolactone (ϵ -CL) monomer onto the hydroxyl group of cellulose. In addition, hydrophilic sulfonation was performed with sulfamic acid and then neutralized with sodium hydroxide. After various trials under different conditions and the optimal conditions for synthesis of cellulose-based amphiphilic surfactant were developed.

Cellulose-based amphiphilic surfactant still belongs to the macromolecular compound. The surface active properties of cellulose-based amphiphilic surfactant and its micellization behavior were investigated, respectively. After the mixture solution of cellulose-based amphiphilic surfactant and glutaraldehyde was cast on a plastic plate and dried, a new modified cellulose membrane could be prepared. The surface hydrophobicity of the membrane was produced by orientating aggregation of cellulose-based amphiphilic surfactant molecules with adding alcohol. The amphiphilic surface-active property and directional arrangement ability of hydrophilic and hydrophobic groups were also discussed in this paper.

2. Experimental methods

2.1. Materials

Cotton cellulose powder with average degree of polymerization of 3600 was supplied by Hubei Xiangtai Cellulose Co. Ltd. The above raw material was first dried in vacuum oven at 80°C overnight to remove moisture. N-methylimidazole (99% purity), butyl chloride (99.5% purity), ϵ -caprolactone (99.9% purity), sulfamic acid (97% purity), stannous (II) octanoate $\text{Sn}(\text{Oct})_2$ (95% purity) were purchased from Tianjin Kermel Chemical Reagents Company, China. The fluorescence probe pyrene (AR grade) was supplied by the Sigma-Aldrich Co. and recrystallized from ethanol and acetone, respectively. Deionized water was used in the preparation of all the solutions.

2.2. Preparation of 1-butyl-3-methylimidazolium chloride (BMIMCl)

The ionic liquid BMIMCl was synthesized according to the reference [30]. N-methylimidazole (20.53 g, 0.25 mol) and 1-butyl chloride (27.78 g, 0.30 mol) were carefully mixed in a three neck flask equipped with a reflux condenser by dropwise method under magnetically stirring. The reaction time was 48 h, and the temperature of mixed reagents was 87°C . The product, a colorless liquid, was first cooled to room temperature and then washed with 25 ml ethyl acetate for three times. Furthermore, the excessive ethyl acetate was removed by a rotation evaporator under vacuum condition at 80°C for 4 h. The resulted liquid product was BMIMCl.

2.3. Tailor the cotton cellulose to cellulose segments

The typical procedure for tailoring the cotton cellulose is summarized as follows. 1 g cotton cellulose dispersed into 20 g BMIMCl in a three neck flask, and then the above mixture was heated in an oil bath at 120°C for 12 h under mechanically stirring and nitrogen atmosphere. Then, a clarified polymer solution about 5 wt% concentration of tailored cellulose was obtained.

Ionic liquid BMIMCl and deionized water were mixed with a proportion of 25:1 (w/w). Then the mixture of BMIMCl/water was dropwise added into cellulose/BMIMCl solution with mechanically stirring. Subsequently, the viscous solution with regenerated cellulose was obtained. The heterogeneous system was separated by filtration using a funnel. The partly precipitated cellulose was left on the funnel, and the solubilized cellulose solution was sucked into suction flask. The mixture of ionic liquid and water with different proportions were added into the solubilized cellulose solution, and stepwise separation of the cellulose segments was carried out by different solubilities in mixture solution according to the order of the extraction process, the fractions were named cellulose segment A, B and C. All of the fractions were washed out by large quantities of deionized water separately.

The molecular weight distribution (MWD) of the cellulose segments was examined with gel permeation chromatography (GPC) method, after the cellulose samples dissolved in the 0.5% (w/v) solvent of lithium chloride/N,N-dimethylacetamide (LiCl/DMAC) according to the usual solvent exchange procedure [31]. GPC analysis was performed with a high-performance liquid chromatography system (HPLC) (Shimadzu LC-20AD) equipped with a StyragelHT4 column (Waters WAT044211). The temperature of column compartment was 80°C and temperature of refractive index detector (RID) was 40°C . MWD of cellulose segments was evaluated according to Waters Polystyrene STD KIT SM-105 polystyrene standards with different molecular weight (7350, 16500, 52500, 153000, 370000, 809000, the polydispersity index was 1.02). The calculation was based on the principle of universal calibration in 0.5% LiCl/DMAC.

XRD measurements of the cellulose segments and the native cotton cellulose were performed on a Max-2000 Rigaku powder diffractometer (Shimadzu, Japan). The diffracted intensity of Cu K α radiation ($\lambda = 0.15406 \text{ nm}$; 40 kV and 40 mA) was measured in a 2θ range between 5° and 80° .

2.4. Preparation of cellulose-based amphiphilic surfactant

The cellulose-based amphiphilic surfactants were synthesized according to the procedure in Fig. 1. After the raw material drying for 24 h in a vacuum drying oven, the cellulose segments with low molecular weight were carefully dispersed in 15 ml fresh anhydrous toluene in a 3-necked flask equipped with a mechanical stirring. Then, ϵ -caprolactone (ϵ -CL) pre-sett concentration was

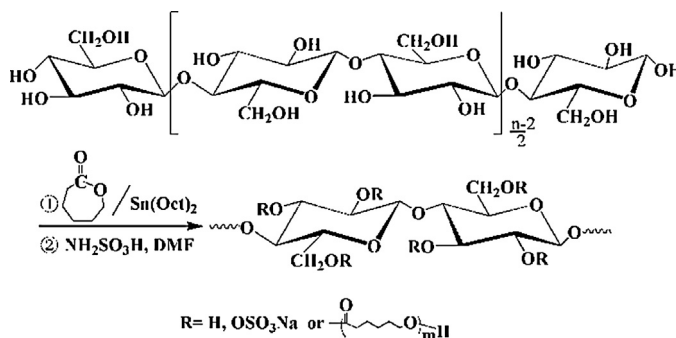


Fig. 1. Synthetic procedure of cellulose-based amphiphilic surfactant.

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