Synthesis and evaluation of novel anionic polymeric surfactants based on polybenzoxazines

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ABSTRACT

A novel platform of anionic polymeric surfactants, poly(4HBA-oca$^-$Na$^+$), poly(4HBA-dea$^-$Na$^+$), and poly(4-HBA-doa$^-$Na$^+$), has been synthesized by polymerizing benzoxazine monomers that are synthesized by reacting an aliphatic amine of variable chain length (C$_8$, C$_{10}$ and C$_{12}$), with 4-hydroxybenzoic acid and para-formaldehyde. The structures of the monomers and polymeric surfactants are confirmed by NMR and FTIR. The ring-opening polymerization and thermal behavior of the benzoxazine monomers are studied by DSC and TGA. Size exclusion chromatography (SEC) coupled with Viscotek triple detection technique is used to characterize the molecular weight distribution of polybenzoxazine surfactants. The surfactants have low MW, varying from 2200 to 6000, and are fairly polydisperse. The influence of the structure on the surface activity is investigated by measuring the surface tension of aqueous solutions of the polymeric surfactants using the Wilhelmy plate method. The tensiometry results indicate that the adsorption at the air/water interface is similar for the octylamine, decylamine and dodecylamine-based surfactants. Increasing the alkyl chain length from C$_8$ to C$_{12}$ does not significantly affect the surface tension at the critical micelle concentration (γ_{cmc}), while the critical micelle concentration (cmc) gradually increases due to increasing hydrophobic effect. These polymeric surfactants give cmc values ranging from 0.12 g/L to 0.17 g/L, comparable to other polymeric surfactants reported in the literature. The influences of salt addition on the surface tension at the critical micelle concentration (γ_{cmc}) for these surfactants are studied. The minimum values of the γ_{cmc} are observed around 1 wt% NaCl for the polybenzoxazine surfactant solution.

1. Introduction

Surfactants constitute one of the most versatile and powerful class of materials used in the chemical industry. Their surface activity and self-assembly behavior make surfactants useful for many applications including detergents, coatings, inks, pharmaceuticals, personal care products, and advanced materials such as nanocomposites, for the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsions and microemulsions, as well as solid/liquid dispersions [1,2]. Polymeric surfactants may be used as an alternative to classical surfactants in most of the above applications, and based on the stability criteria, perform the best in dispersions [3,4]. The characteristic properties of polymeric surfactants originate from the formation of micellar aggregates in aqueous solution through the association of hydrophobic segments. The polymeric surfactants may form monomolecular-layer micelles or aggregate to form mul-

timolecular structures of various shapes [5]. The aggregation behavior of polymeric surfactants depends on the molecular structure of the amphiphile and on the solution conditions including concentration, temperature, pH and salinity [6–8]. Some studies on the synthesis and characterization of the surface activity of polymeric surfactants have been carried out via designing the molecular structure. For example, block copolymers were synthesized via ring opening reaction of cyclic imide [9], and comb-like copolymers were obtained using ethoxylated alkyl-phenol and formaldehyde for oil recovery applications [10]. Polymerizable surfactants have reactive functionalities that can exist in the hydrophobic tail or the polar headgroup. The most widely-used reactive group is a vinyl that can polymerize via thermal or photolytic initiation [11,12]. It is important to distinguish between polymeric surfactants from polymerizable surfactants such as used in microemulsion polymerization [13] and nanocomposites [14]. Polymerizable cationic surfactants such as vinylbenzyldimethyldodecylammonium chloride (VDAC) can homopolymerize as well as copolymerize with monomers like styrene [13].

This study illustrates the novel application of benzoxazine chemistry to make polymeric surfactants. In 1944, Holly and Cope reported the synthesis of 1,3-benzoxazines by combining a primary amine, a phenolic derivate, and formaldehyde [15]. The synthesis and characterization of polybenzoxazines was first reported by Ning and Ishida in 1994 [16]. Since then, extensive studies of the synthesis, characterization, and applications of benzoxazine monomers and polymers have been reported [17]. Benzoxazines exhibit various unusual properties, including near-zero shrinkage upon polymerization [18], fast property development at low conversion [19], high char yield [20], very low surface energy [21,22], and low water absorption despite having hydrophilic chemical repeat unit [23]. Of particular interest in the current study is the extremely versatile molecular design of benzoxazines [18]. While the majority of polybenzoxazines are hydrophobic, some show potential for applications in hydrophilic environment. Benzoxazines may have hydrophilic functionality such as carboxylic [24–27], amine [28–30], and hydroxyl groups [31,32], and a comonomer in the main chain, including polyether chain [33–35].Recently, Sawaryn et al. [36] synthesized nonionic benzoxazine polymerizable surfactants that were used to stabilize miniemulsions. High molecular weight nonionic benzoxazine surfactants, with hydrophilic polymeric blocks and benzoxazine moieties in the polymer backbone, have also been synthesized and used as protective colloids to stabilize o/w miniemulsions of benzoxazine resins [37]. However, the synthesis of anionic surfactants based on benzoxazine has not been described in the literature. This paper is the first to report anionic polybenzoxazine surfactants. The goals of this research are twofold: (a) the synthesis and characterization of carboxylic acid-functionalized benzoxazine monomers of various hydrophobe chain lengths, and (b) polymerization of these monomers to obtain anionic polymeric surfactants. The ability of the synthesized polymeric surfactants to reduce thewater/air surface tension and form micelles is evaluated by measuring the critical micelle concentration, cmc, and the surface tension at cmc, γ_{cmc}. Comparison of the cmc and γ_{cmc} of the new anionic polymeric surfactants with literature values for both low and high molecular weight surfactants are made to justify that these polybenzoxazines offer a superior alternative to conventional surfactants. Furthermore, the polymeric surfactants reported herein are thermally stable up to about 170 °C and do not contain sulfur, and therefore are more ecofriendly than many commercial surfactants.

2. Experimental

Paraformaldehyde (96%) was used as purchased from Acros Organics USA. 4-Hydroxybenzoic acid (99%), octylamine (99%), decylamine (95%), and dodecylamine (98%) were used as received from Sigma–Aldrich. 1,4-Dioxane was purchased from Fisher Scientific.

The benzoxazine monomers were prepared from 4-hydroxybenzoic acid, paraformaldehyde, and primary amines, including octylamine, decylamine and dodecylamine by using a modified solvent method reported in the literature [15].

2.1. Preparation of 3-octyl-3, 4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-oca)

In a 100 mL flask were mixed together octylamine (5 mmol, 0.646 g), 4-hydroxybenzoic acid (5 mmol, 0.69 g), and paraformaldehyde (12.5 mmol, 0.3877 g) and heated at 90 °C with magnetic stirring in dioxane (10 mL) for 24 h. The mixture was allowed to cool to room temperature and poured into 100 mL deionized water in a 200 mL flask to give a yellowish precipitate. The product was filtered and washed three times with deionized water and dried at 60 °C. The monomer was dissolved in chloroform and then

filtered by using filter paper to remove the dispersed material, followed by drying under vacuum in a rotary evaporator (yield: 72%).

^{1}H NMR (DMSO-d_6, frequency: 300 MHz, ppm: δ, 298 K): 1.31–1.48 (10H, CH$_2$—CH$_2$—CH$_2$), 3.96 (2H, Ar—CH$_2$—N), 4.89 (2H, O—CH$_2$—N), 6.76–7.66(3H, Ar—H).

FTIR (KBr, cm^{-1}): 1700 (the C=O stretching of the carboxylic group), 1240 (the stretching of Ar—O—C), 938 (out-of-plane vibration, benzene ring to which oxazine is attached).

2.2. Preparation of 3-decyl-3, 4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-dea)

4HBA-dea was prepared from decylamine (5 mmol, 0.786 g), 4-Hydroxybenzoic acid (5 mmol, 0.690 g), and paraformaldehyde (12.5 mmol, 0.387 g) as previously described for 4HBA-oca (yield: 73%).

^{1}H NMR (DMSO-d_6, frequency: 300 MHz, ppm: δ, 298 K): 1.31–1.47 (10H, CH$_2$—CH$_2$—CH$_2$), 3.96 (2H, Ar—CH$_2$—N), 4.87 (2H, O—CH$_2$—N), 6.77–7.68(3H, Ar—H).

FTIR (KBr, cm^{-1}): 1700 (the C=O stretching of the carboxylic group), 1240 (the stretching of Ar—O—C), 938 (out-of-plane vibration, benzene ring to which oxazine is attached).

2.3. Preparation of 3-dodecyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carboxylic acid (abbreviated as 4HBA-doa)

4HBA-doa was prepared from dodecylamine (5 mmol, 0.945 g), 4-Hydroxybenzoic acid (5 mmol, 0.690 g), and paraformaldehyde (12.5 mmol, 0.387 g) as previously described for 4HBA-oca (yield: 78%).

^{1}H NMR (DMSO-d_6, frequency: 300 MHz, ppm: δ, 298 K): 1.31–1.47 (10H, CH$_2$—CH$_2$—CH$_2$), 3.95 (2H, Ar—CH$_2$—N), 4.87 (2H, O—CH$_2$—N), 6.77–7.68(3H, Ar—H).

FTIR (KBr, cm^{-1}): 1700 (the C=O stretching of the carboxylic group), 1240 (the stretching of Ar—O—C), 938 (out-of-plane vibration, benzene ring to which oxazine is attached).

2.4. Polymerization of benzoxazine monomers and ionization of polymeric benzoxazines

1.0 g Of each monomeric benzoxazine, 4HBA-oca, 4HBA-dea, and 4HBA-doa, was polymerized on separate glass plates by following the same heating procedure in an air circulating oven at 160 °C for 30 min.

1.0 g Of each polymerized benzoxazine monomer, abbreviated as poly(4HBA-oca), poly(4HBA-dea) and poly(4HBA-doa), was weighed separately into a 50 mL beaker. Since the starting monomers are monofunctional benzoxazines, the polymers formed are at best small oligomers with molecular weight in the range of 2000–6000 [38]. The designated amount of NaOH (to neutralize all carboxylic acid groups) was dissolved in 20 mL of deionized water, and then added to the polybenzoxazine oligomer. The beaker containing polybenzoxazine oligomer sample and base solution was placed in an ultrasonic bath until the solid was dissolved. The solution was then filtered with a filter paper and cooled to room temperature. The resulting polymer was dried overnight at 60 °C in an air circulating oven to a constant weight.

3. Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Varian Gemini 2000 NMR operating at a proton frequency of 300 MHz. All samples were dissolved in deuterated dimethylsulfoxide (DMSO-d_6).