Colloids and Surfaces A: Physicochem. Eng. Aspects 498 (2016) 248–257

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Synthesis and characterization of the epoxy-functionalized quaternary ammonium chloride

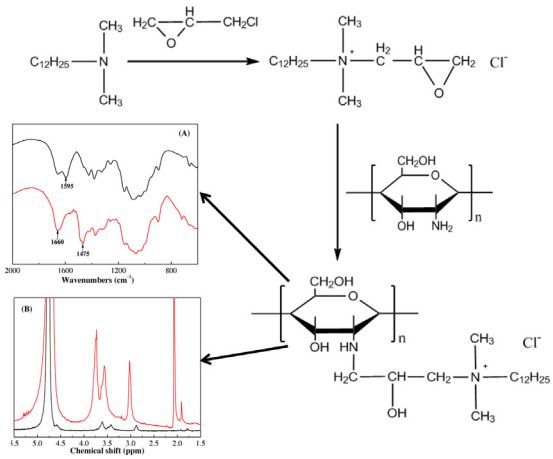
Yingwei Liu[a,1], Xiaodeng Yang[a,*], Yan Li[a], Yijian Chen[b], Xiangzhu Zhou[a], Tianduo Li[a]

[a] Key Laboratory of Fine Chemicals (Shandong Province), Qilu University of Technology, Jinan 250353, PR China
[b] China University of Petroleum, School of Petroleum Engineering, Qingdao 266580, PR China

HIGHLIGHTS

- DDEAC shows higher activity than DTAC.
- The introduction of the epoxy group facilitates micellization of DDEAC.
- DDEAC shows high reactivity on the modification of chitosan.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form 16 March 2016
Accepted 25 March 2016
Available online 26 March 2016

Keywords:
N,N-dimethyl-N-dodecyl-N-(1,2-epoxy propyl) ammonium chloride (DDEAC)
Surface activity
Aggregation behavior
Thermodynamical property
Reactivity

ABSTRACT

A kind of surface active epoxy-functionalized quaternary ammonium salt, N,N-dimethyl-N-dodecyl-N-(1,2-epoxy propyl) ammonium chloride (DDEAC), was synthesized. The surface activity and aggregation behavior were investigated by surface tension, dynamic light scattering, conductivity, steady state fluorescence measurements and by molecular dynamics simulations. As a control, the surface properties of dodecyl trimethyl ammonium chloride (DTAC) were also studied. Compared to DTAC, DDEAC showed higher surface activity and more ready aggregation formation as well as larger Ca^{2+} and Na^{+} tolerance. The data from molecular dynamics simulations showed that the DDEAC hydrated more easily than DTAC. The conductivity results indicated that the micellization of DDEAC is enthalpy-driven, however that of DTAC is enthalpy-driven only at temperatures higher than 25 °C and entropy-driven at temperatures lower than 25 °C. The reaction between DDEAC and chitosan implied that DDEAC could endow chitosan both hydrophilicity and hydrophobicity by one step reaction method and expand the application of chitosan.

* Corresponding author.
E-mail address: yangxiaodeng@qlu.edu.cn (X. Yang).

[1] Yingwei Liu is an undergraduate student of Qilu University of Technology, majors in Applied Chemistry.

http://dx.doi.org/10.1016/j.colsurfa.2016.03.066
0927-7757/

1. Introduction

Cationic surfactants are an important class of amphiphilic molecules, which have attracted a great deal of research interest for decades due to their extensive utilization [1], such as in textiles [2,3], paper manufacturing [4,5], mining [6–8], the synthesis of micro- and nano-materials [9,10] and drug delivery [11]. For instance, dodecyltrimethylammonium chloride (DTAC), one kind of commonly used cationic surfactants, could enwrap and delivery diclofenac sodium [12], form vesicles [13], extract heavy metal [14], modulate morphology of nano-materials [15], and so on. Along with the conscious enhancement of environmental protection, the synthesis and characterization of biocompatible cationic surfactants with functional groups such as ester-functionalized [12–16], amide-functionalized [17–19], enzyme-inspired [20], styrylo-functionalized [21,22] surfactants have attracted increasing attention in recent years.

Functional surfactants usually display excellent specific properties compared to conventional ones. For instance, ester-functionalized surfactants show far better surface properties than those with similar hydrophobic alkyl chain lengths [16], which can be ascribed to the enhancement of the solubility of the ester-functional groups [17]. In addition, the decomposition temperature of ester-functionalized long chain imidazolium- (or pyridinium-) surfactants is lower than that of simple alkyl chain ionic liquid surfactants [18]. Phenol-keto surfactants are more tolerant of Ca^{2+} ions for chelating carbonyl oxygen groups, which suggests further research on Ca^{2+} tolerant surfactants [19]. Enzyme-inspired functional surfactants can catalyze the aerobic oxidation of activated alcohols to aldehydes under ambient conditions in water, which is usually difficult to achieve with nonenzymatic processes [20].

The epoxy group is widely used because of its high reactivity and good specific properties; therefore, epoxy functionalized compounds have merited much attention. For instance, Jayalakshmi et al. [21] synthesized high performance cellulose acetate membranes using epoxy functionalized poly(ether-sulfone), which improved the membrane morphology, pure water flux, water content porosity, hydrophobicity, as well as a remarkable effectiveness in removing chromium ions. Sydlik et al. [22] synthesized expoxy-functionalized multi-walled carbon nanotubes (EpCNTs) by multiple covalent functionalization method, which improved adhesive properties and notably increased lap shear strength compared to commercial epoxy. Dou et al. [23] prepared epoxy-functionalized magnetic polymer core-shell microspheres with high magnetic responsiveness and a single hydrophilic monomer. The combination of the epoxy group and magnetic properties introduces the microspheres to a wide range of applications in stabilizers, targeted drug delivery and biological detection [24]. In our previous studies, epoxypropyl dodecyl dimethyl ammonium chloride [25], diethyl-2,3-epoxypropyl-[3-methyldimethoxyl] silpropyl ammonium chloride and mono epoxy-terminated polydimethylsiloxane [26] were synthesized and applied to modify gelatin, a renewable and biodegradable material. It was found that ammonium salt modified gelatin shows strong antibacterial activity. However, the synthesis and property investigation of epoxy functionalized surfactants have seldom been reported.

In the present work, a kind of surface active epoxy-functionalized quaternary ammonium salt, N,N-dimethyl-N-dodecyl-N-(1,2-epoxy propyl) ammonium chloride (DDEAC) was synthesized. The aggregation behaviors of DDEAC were investigated by surface tension, dynamic light scattering, conductivity, steady-state fluorescence measurements and by molecular dynamics simulations. Furthermore, the reactivity of DDEAC was tested by reacting it with chitosan using 1-allyl-3-methylimidazolium chloride (AmimCl) as a homogeneous and green reaction medium. The data implied that DDEAC could endow chitosan both hydrophilicity and hydrophobicity by one step reaction method. The work is expected to progress and be applicable to epoxy based surfactants in the preparation of functionalized biopolymer derivatives.

2. Experimental

2.1. Materials

Dodecyltrimethyl ammonium chloride (DTAC) was purchased from Xiya Reagent (Chengdu, China) and freeze-dried for 48 h before the experiments. N,N-dimethyl-N-dodecyl-N-(1,2-epoxypropyl) ammonium chloride (DDEAC) was synthesized in our laboratory, and used before freeze-drying for 48 h.

N,N-dimethyldodecylamine, epichlorohydrin and tetraethyl ammonium bromide were purchased from Xiya Reagent (Chengdu, China). Anhydrous ethanol and anhydrous ether were purchased from Tianjin Fuyu Fine Chemical Co. Ltd. (Tianjin, China). Anhydrous methanol, chloroform and sodium hydrogen phthalate were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Glacial acetic acid was purchased from Tianjin Baishi Chemical Co., Ltd. (Tianjin, China). Silver nitrate was purchased from Tianjin Chemical Reagent Factory (Tianjin, China). Acetic anhydride, crystal violet and perchloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were A.R. grade, and used without further purification. Triply distilled water was used to prepare the solutions of DTAC and DDEAC.

Chitosan was purchased from Xiya Reagent (Chengdu, China) and dried in vacuum at 80 °C for 24 h before the experiments. The degree of de-acetylization, DD = 91.2% and $M_v = 5.2 \times 10^5$, was determined by elemental analysis and the Ubbelohde viscosity methods, respectively.

2.2. Methods

2.2.1. Synthesis of DDEAC

Nucleophilic substitution reactions were carried out in triple-neck flasks. Typically, 6 g anhydrous methanol, 10.67 g (0.05 mol) N,N-dimethyl dodecylamine and 4.65 g epichlorohydrin (0.05 mol) were added into a desiccative triple-neck flask of 100 mL with a magnetic stirrer. The flask was placed in an oil bath and heated at 30 °C for 10 h under stirring. The crude product was obtained after the solvent was distilled under vacuum distillation. The product was refined by washing with anhydrous diethyl ether 5 times and then freeze-dried for 48 h. The molecular structures of DDEAC and DTAC are shown in Fig. 1(A). The ^{1}H NMR spectrum of DDEAC (the sample is obtained at reaction temperature of 20 °C, and time of 10 h) is shown in Fig. S1. The area ratio of the peak at 3.212 to that at 3.358 ppm certifies the synthesis of DDEAC.

The effects of solvent type, molar ratio of epichlorohydrin to N,N-dimethyldodecylamine, reaction time and temperature on the nucleophilic substitution reaction were investigated. The reaction conversion rate (CR) and epoxy values (EV) of the product were measured through silver ion titration and perchlorate-tetraethyl ammonium bromide methods, respectively. The conversion rate and epoxy values for DDEAC synthesized under different conditions are listed in Table S1 in supporting information.

The Krafft temperature (T_k), determined by visual observation, is 8 °C and consistent with the theoretical results [27]. The decomposition temperature (T_{onset}) is 240 °C, determined with an SDT Q600 simultaneous thermal analyzer (TA Instruments, USA) from room temperature to 600 °C at a 10 °C/min heating rate under a nitrogen atmosphere (100 mL/min).