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Surface properties and thermodynamic properties of micellization of mono- and di-tetrapropylene diphenyl ether disulfonates

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ABSTRACT

Mono-tetrapropylene diphenyl ether disulfonate (C_{12}-MADS) and Di-tetrapropylene diphenyl ether disulfonate (C_{12}-DADS) were synthesized via three steps reactions: Friedel-Crafts alkylation, sulfonation and neutralization. The surface properties and thermodynamic properties of micellization of tetrapropylene benzene sulfonate (C_{12}-BAS), C_{12}-MADS and C_{12}-DADS were investigated by equilibrium surface tension, dynamic surface tension and electrical conductivity measurement. The result of surface tension shows that surface activity of gemini surfactant C_{12}-DADS is better than that of C_{12}-BAS and C_{12}-MADS. The dynamic surface tension data show that the diffusion coefficients values of C_{12}-MADS and C_{12}-DADS are lower than that of C_{12}-BAS, and the adsorption process of surfactants at air/water interface is a mixed diffusion-kinetic adsorption mechanism. In addition, the electrical conductivity result indicates that the C_{12}-DADS more readily form micelles than other two.

1. Introduction

Gemini surfactants are generally made up of two identical moieties having the structure of conventional (monomeric) surfactants connected by a spacer group, which have attracted considerable interest in both scientific and industrial aspects [1–4]. It is because that these surfactants possess more predominant properties than corresponding traditional single-chain surfactants, including a lower critical micelle concentration (cmc), a higher efficiency at reducing surface tension and oil/water interfacial tension, an unusual viscosity behavior, better wetting and emulsifying properties, superior biological activity and controllable responses for the gemini surfactants constructed by non-covalent bond [4–11].

Di-tetrapropylene diphenyl ether disulfonate (C_{12}-DADS) is an anionic gemini surfactants, which is composed of two tetrapropylene benzene sulfonates (C_{12}-BAS) connected by a oxygen spacer. Mono-tetrapropylene diphenyl ether disulfonate (C_{12}-MADS), the analogue of C_{12}-DADS, only possess one alkyl chain. Compared with C_{12}-BAS, C_{12}-MADS adds a sulfophenyl group and a oxygen spacer. Scheme 1 shows the structure of C_{12}-DADS, C_{12}-MADS and C_{12}-BAS. Most reports about alkyldiphenyl oxide disulfonates or analogues focused on synthesis and studied the effects of hydrophobic chain length, alkyl side chain branches and structure of spacer on surface properties [2,4–7,12–15]. Our previous work also synthesized and investigated the effect of alkyl chain length of mono- or di-alkyl diphenyl oxide disulfonates on surface properties [7,16–18]. However, for C_{12}-DADS, C_{12}-MADS and C_{12}-BAS, few paper systematically investigate the effect of their structure on the both surface properties and thermodynamic properties of micellization.

In this paper, the C_{12}-MADS and C_{12}-DADS were synthesized by three steps reaction, including Friedel-Crafts alkylation, sulfonation and neutralization [7,16,17]. The structure of C_{12}-MADS and C_{12}-DADS were confirmed by ^{1}H NMR and the electrospray ionization-mass spectrometry (ESI-MS). In order to study the differences of surface properties and thermodynamic properties of micellization of C_{12}-BAS, C_{12}-MADS and C_{12}-DADS, the surface tension, dynamic surface tension and electrical conductivity were measured in our experiment.

2. Experimental procedures

2.1. Materials

Sulfated zirconium catalyst was prepared according to the methods reported previously [17]. The C_{12}-BAS was obtained by neutralizing the tetrapropylene benzene sulfonic acid (Shaoxing Light Chemical Co., Ltd.) using sodium hydroxide aqueous solution. Tetrapropylene (≥98%) were supplied by Jiangsu Chemical Group Co., Ltd. P. R. China. Diphenyl oxide (≥99%) was obtained from Kelong Chemical Co., Ltd. P. R. China. Sulfuric acid (≥98%) and fuming sulfuric acid (containing 20% SO_3) were supplied by Beijing Chemical Reagent Co., Ltd. P. R. China.

2.2. Synthesis of C_{12}-MADS and C_{12}-DADS

The C_{12}-MADS and C_{12}-DADS were synthesized by Friedel-Crafts alkylation, sulfonation and neutralization as shown in Scheme 2. In detail,

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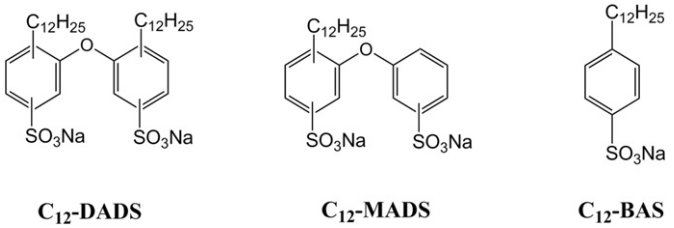


Scheme 1. Structure of C_{12}-DADS, C_{12}-MADS and C_{12}-BAS.

diphenyl oxide (68 g) was reacted with tetrapropylene (101 g) in presence of sulfated zirconium catalyst (6 g) at 160 °C for 3 h. After the reaction, the solid catalyst was separated from the mixture of products by decompress filter. The mono-tetrapropylene diphenyl ether was distilled between 180 °C and 220 °C under 10 mm Hg pressure. The di-tetrapropylene diphenyl ether was obtained by a silica gel chromatography, which uses petroleum ether as the mobile phase. The purity of the two intermediates determined by high performance liquid chromatography using methanol/dichloromethane (8:2, vol:vol) as the mobile phase, were 98.5% and 98.4%, respectively.

The fuming sulfuric acid (40 g) was used to sulfonate mono-tetrapropylene diphenyl ether (15 g) or di-tetrapropylene diphenyl ether (10 g) at 50 °C for 40 min. Then, a 30% sodium hydroxide aqueous solution was used to neutralize the sulfonated product until the pH reached 7. The obtained product was desalted in anhydrous ethanol by hot filtration. Unreacted dodecyl diphenyl ether was separated by extraction with petroleum ether. The aqueous layer was dried, and the light yellow power was obtained finally. The purity of C_{12}-MADS and C_{12}-DADS determined by two-phase titration, were 98.4% and 97.5%, respectively.

2.3. Measurement

2.3.1. Structure characterization

The electrospray ionization-mass spectrometry (ESI-MS) was employed to analyze structure of target product using a Waters ZQ2000 mass spectrometer with an electrospray interface (ESI). The mass spectra were recorded in negative mode.

^{1}H NMR spectra were measured in $CDCl_3$ at 25 °C with a JEOL JNM-GSX400 spectrometer (400 MHz; JEOL Limited, Tokyo, Japan).

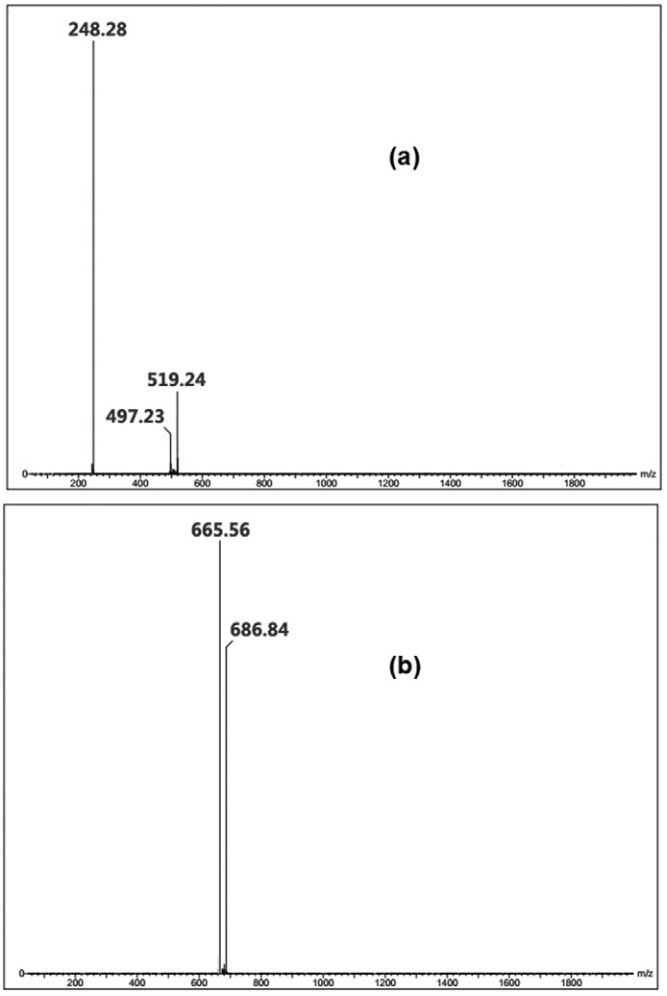
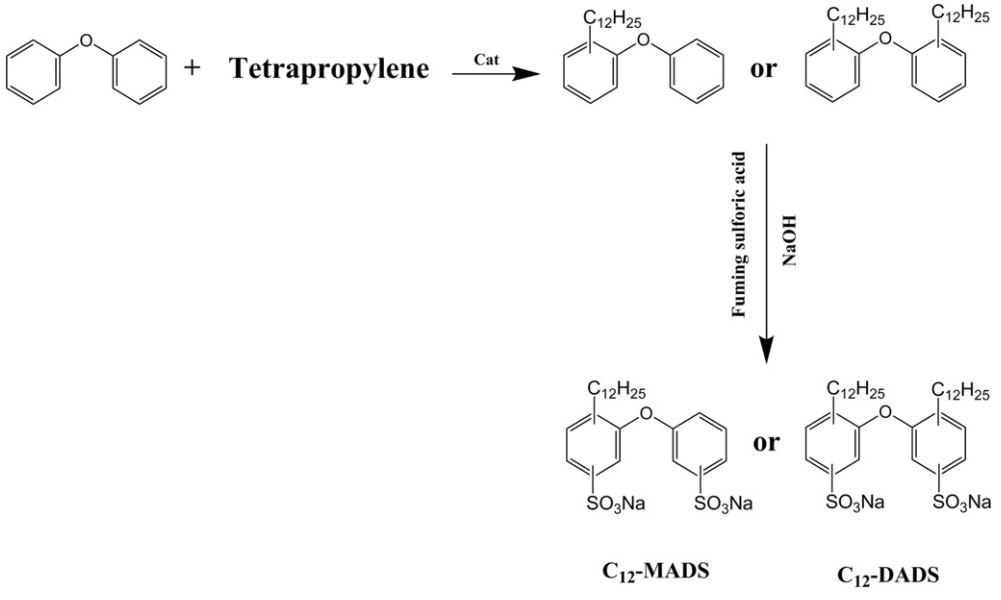


Fig. 1. ESI-MS spectrums of (a) C_{12}-MADS and (b) C_{12}-DADS.

2.3.2. Equilibrium surface tension

The KRŮSS K12 Processor Tensiometer (Germany) was employed to measure the equilibrium surface tension of surfactant aqueous solutions



Scheme 2. Synthesis of C_{12}-MADS and C_{12}-DADS.