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Original article

# Synthesis of anionic sulphonate-crown ether surfactants

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ABSTRACT

Two sulphonate-crown ether surfactants (sodium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate, ammonium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate) were designed and synthesized *via* a two-step continuous method. The products were purified and characterized by IR, $^1$H NMR and elemental analysis. The physicochemical properties of the surfactants were studied by fluorescence, conductivity and dynamic light scattering techniques.

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## 1. Introduction

Crown ether surfactants have the ability of forming micelles and recognizing cations simultaneously, which distinguishes them from the normal surfactants, and thus have great potentials in several applications [1–5]. Up to now, to the best of our knowledge, almost all crown ether surfactants are non-ionic, in which a lipophilic long-chain alkyl group is attached onto a crown ether [6,7]. However, their low solubility in water and the obvious temperature effect (*i.e.*, cloud point) limited their applications in some fields. In this study, we designed and synthesized two kinds of surface-active sulphonate-crown ether to improve the solubility of the crown ether surfactants in water. Moreover, their insensitivity to temperature allowed them to have a wider working temperature range than nonionic crown ether surfactants.

## 2. Experimental

### 2.1. Synthesis of anionic sulphonate-crown ether surfactants

*Acylation of dibenzo-18-crown-6 (DB18C6):* DB18C6 (2.19 g, 6 mmol) was added to polyphosphoric acid (PPA) with vigorous stirring. When the mixture was heated to 90 °C, lauric acid (1.56 g, 7.8 mmol) was added slowly, and the reaction mixture was mechanically stirred for 3 h. Then, the hot solution was cooled and decomposed with an ice-water mixture. After stirring for 4 h, the resulting pale yellow precipitates were collected by filtration, washed with water until a neutral pH value was achieved, and dried in vacuum at room temperature. The reaction was monitored by thin-layer chromatography (silica thin-layer plate, petroleum ether/dichloromethane/ethanol = 1/1/0.2, v/v/v).

*Sulfonation of 4′-dodecanoyl-DB18C6*: The dried mixture of mono- and didodecanoyl-DB18C6 (3.28 g) was dissolved in anhydrous dichloromethane (20 mL). At −10 °C, chlorosulfonic acid (2 mL, 30.4 mmol) was added dropwise. Later, the reaction mixture was warmed to room temperature gradually, and was stirred for 24 h. Then, the reaction mixture was cautiously poured into an ice-water mixture, the pH value was adjusted to 9 using a saturated sodium carbonate solution (or ammonia), and the mixture was stirred overnight. After being centrifugated, the aqueous phase was separated from the dichloromethane phase. The aqueous phase was lyophilized in vacuum to provide a solid powder, which was washed with hot petroleum ether to remove the residual reactant. The residue was extracted with ethanol at room temperature. The extracts were dried by vacuum rotary evaporation. After being washed by a small amount of cold water to remove the residual inorganic salts and dried in vacuum at room temperature, the final product was obtained. With respect to dichloromethane phase, didodecanoyl-DB18C6 was obtained after the removal of solvent and the following recrystallization from ethanol. The synthetic methods used to prepare the target anionic sulphonate-crown ether surfactants are outlined in Scheme 1.

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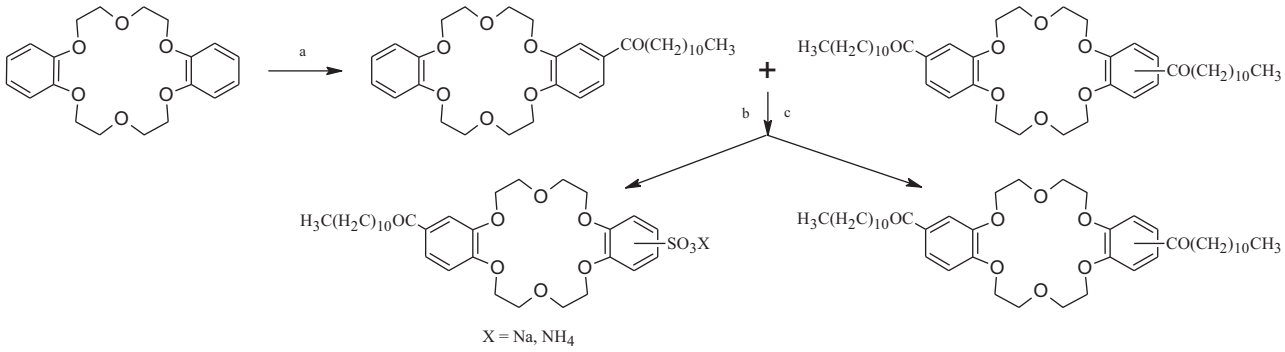


**Scheme 1.** Synthetic route of anionic sulphonate-crown ether surfactants: (a) lauric acid, PPA; (b) $HSO_3Cl$, $CH_2Cl_2$; (c) $H_2O$, $Na_2CO_3/NH_3{\cdot}H_2O$.

### *2.2. Physicochemical characterization of the anionic sulphonate-crown ether surfactants*

The fluorescence spectra were measured on an F-4500 Fluorescence Spectrometer (Hitachi, Japan). The excitation and emission slit widths were 10 nm and 5 nm, respectively, and the scanning speed was 240 nm/min. Conductivity measurements were carried out at 25.0 °C using a FE30 conductivity meter (Mettlet Toledo, Switzerland). The conductivity meter was calibrated by measuring the conductivity of $1.0 \times 10^{-2}$ mol $L^{-1}$ potassium chloride. The dynamic light scattering (DLS) experiment was carried out at 25.0 °C *via* a Zetasizer Nano ZS90 (Malvern Instruments, U.K.) laser light scattering spectroscopy (wavelength: 633 nm) with a scattering angle of 90°. The intensity autocorrelation functions were analyzed to obtain the hydrodynamic radii ($R_h$) of micelles with methods of Contin and Cumulant.

## 3. Results and discussion

### *3.1. Synthesis of anionic sulphonate-crown ether surfactants*

In the acylation of benzo-crown ether, carboxylic acid-PPA is always used [8,9]. According to Grebenyuk's method [9], DB18C6 was acylated. However, the results of $^1$H NMR analysis showed that the ratio of hydrogen atoms in the crown ether to those in the long chain was between 16:23 and 16:46, indicating that the products were a mixture of mono- and didodecanoyl-DB18C6. Different feed ratios of lauric acid to DB18C6 ranging from 1.1:1 to 1.9:1 were used. It was found that the increased feed ratio could not avoid the formation of didodecanoyl-DB18C6 while the lower feed ratio led to the residue of DB18C6 as well as the generation of didodecanoyl-DB18C6. The feed ratio of 1.3:1 was found to be proper to ensure the complete consumption of DB18C6. Due to the extremely similar properties of mono- and didodecanoyl-DB18C6, it was difficult to separate them. To solve this problem, we used a two-step continuous method, *i.e.*, the neutralized and dried acylated product was directly used in the second step without any separation. After sulfonation, the segregation of didodecanoyl-DB18C6 from the target product became much easier.

In addition, it is worthwhile to notice that the usage of chlorosulfonic acid is necessary. Sulfate salt-PPA is a mild sulfonating reagent in the sulphonation of benzo-crown ether [10]. Nevertheless, in our work, when $Na_2SO_4$-PPA was used, the FTIR spectra of the product showed that the absorption peaks at *ca.* 2920 $cm^{-1}$ and 2850 $cm^{-1}$, corresponding to the stretching vibration of C–H group, were extremely weak, suggesting that the dodecanoyl group was lost at the reaction temperature of 75 °C. While concentrated sulfuric acid was tried, the dodecanoyl group was still lost even the reaction temperature was maintained −20 °C. Thus, chlorosulfonic acid was used to sulphoacylate the monododecanoyl-DB18C6, and then the product was hydrolyzed in a basic solution to produce the desired sulphonate. Using this strategy, the sulphonated products were finally obtained.

The products were characterized by IR, $^1$H NMR and elemental analysis and the following data agree well with the structure of sodium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate and ammonium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate.

Sodium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate: Yellow powder, 0.86 g (22.2%), IR (KBr, $cm^{-1}$): $\nu$ 2924 ($CH_2$, $\nu_{a(CH_2)}$), 2852 ($CH_2$, $\nu_{s(CH_2)}$), 1672 (ArCO, $\nu_{c=o}$), 1595 (Ar, $\nu_{carbon\ skeleton}$), 1514 (Ar, $\nu_{carbon\ skeleton}$), 1456 (Ar, $\nu_{carbon\ skeleton}$), 1431 ($COCH_2$, $\delta_{CH_2}$), 1267 ($SO_3Na$, $\nu_{a(SO_2)}$), 1138 ($CH_2OCH_2$, $\nu_{a(C-O-C)}$), 1041 ($SO_3Na$, $\nu_{s(SO_2)}$), 694 ($SO_3Na$, $\nu_{(S-O)}$). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.849 (t, 3H, $CH_3$), 1.235 (m, 16H, $CH_2$), 1.578 (q, 2H, $COCH_2CH_2$), 2.953 (t, 2H, $COCH_2$), 3.917 (m, 8H, $ArOCH_2CH_2$), 4.109 (m, 4H, $ArOCH_2$), 4.196 (m, 4H, $ArOCH_2$), 6.913 (d, 1H, ArH), 7.085 (d, 1H, ArH), 7.163 (s, 1H, ArH), 7.185 (s, 1H, ArH), 7.451 (d, 1H, ArH), 7.647 (d, 1H, ArH). Elem. anal. calcd. % for $C_{32}H_{45}NaO_{10}S$: C 59.61, H 7.03; found: C 59.55, H 7.17.

Ammonium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate: Yellow powder, 0.91 g (23.5%), IR (KBr, $cm^{-1}$): $\nu$ 2924 ($CH_2$, $\nu_{a(CH_2)}$), 2852 ($CH_2$, $\nu_{s(CH_2)}$), 1674 (ArCO, $\nu_{c=o}$), 1593 (Ar, $\nu_{carbon\ skeleton}$), 1512 (Ar, $\nu_{carbon\ skeleton}$), 1456 (Ar, $\nu_{carbon\ skeleton}$), 1429 ($COCH_2$, $\delta_{CH_2}$), 1267 ($SO_3NH_4$, $\nu_{a(SO_2)}$), 1138 ($CH_2OCH_2$, $\nu_{a(C-O-C)}$), 1063 ($SO_3NH_4$, $\nu_{s(SO_2)}$). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.850 (t, 3H, $CH_3$), 1.237 (m, 16H, $CH_2$), 1.578 (q, 2H, $COCH_2CH_2$), 2.939 (t, 2H, $COCH_2$), 3.857 (m, 8H, $ArOCH_2CH_2$), 4.146 (m, 8H, $ArOCH_2$), 7.040 (d, 1H, ArH), 7.083 (d, 1H, ArH), 7.181 (s, 1H, ArH), 7.367 (s, 1H, ArH), 7.428 (d, 1H, ArH), 7.610 (d, 1H, ArH). Elem. anal. calcd. (%) for $C_{32}H_{47}NO_{10}S{\cdot}1H_2O$: C 58.61, H 7.53, N 2.14; found: C 58.83, H 7.52, N 2.19.

### *3.2. Physicochemical properties of the anionic sulphonate-crown ether surfactants*

It was found that the two kinds of synthesized surfactants had good solubility in ethanol and dimethyl sulfoxide (DMSO), but were difficult to be dissolved in dichloromethane. The solubility of the ammonium salt of the surfactants in water was lower than $5.0 \times 10^{-5}$ mol $L^{-1}$, while their sodium salt can reach $2.0 \times 10^{-3}$ mol $L^{-1}$ at least. This phenomenon indicates that the cations have a great impact on the solubility of the synthesized anionic sulphonate-crown ether surfactants. Therefore, the physicochemical characterization was focused on the sodium salt. Moreover, with the increase of the temperature, a cloud point phenomenon in the aqueous solution of the sodium salt was not observed.

When the ethanol solution of the sodium salt was excited at 322 nm, an obvious fluorescence emission peak appeared at *ca.*

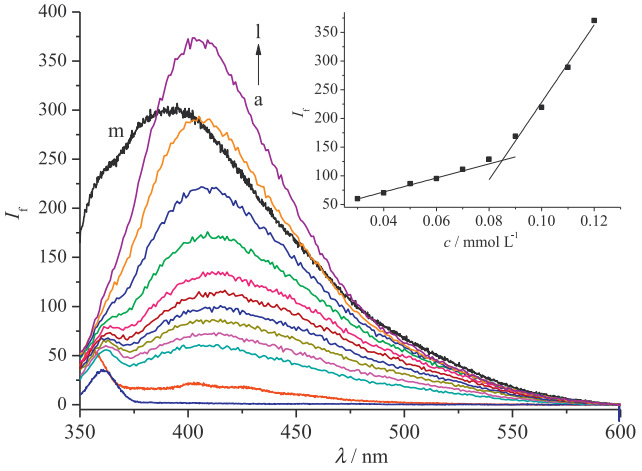


**Fig. 1.** Emission spectra of water (a), ethanol (b), surfactant in the aqueous solution of 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12 mmol L$^{-1}$ (from *c* to l), surfactant in ethanol solution of 0.10 mmol L$^{-1}$ (m), $\lambda_{ex}$ = 322 nm. The inset shows the relationship between the relative fluorescence intensity at 404 nm ($I_f$) and the concentration of the surfactant in aqueous solution.

395 nm (curve m in Fig. 1). When water was used as the solvent, the fluorescence emission peak was red-shifted to *ca.* 404 nm (curves *c*–l in Fig. 1). With the increase of the concentration of the sodium salts in aqueous solution, the fluorescence emission was enhanced, which could be ascribed to the aggregation of the surfactant and the formation of micelles. The plots of the relative fluorescence intensity *vs* the concentration of sodium salt (inset, Fig. 1) shows that a significant inflexion appears at the concentration of $8.5 \times 10^{-5}$ mol L$^{-1}$, which divides the plots into two linear regions. It can be concluded that the critical micelle concentration (*cmc*) of the surfactant is about $8.5 \times 10^{-5}$ mol L$^{-1}$. The results of the conductivity measurements (Fig. 2) indicated that the *cmc* of the surfactant is about $7.8 \times 10^{-5}$ mol L$^{-1}$, close to the result of fluorescence analysis.

Fig. 3 shows the DLS results of size distributions of the aqueous solution of the sodium salt. When the concentration of the sodium salt is 0.08 mmol L$^{-1}$, close to the *cmc* value, there already exist two peaks. The first peak ($R_h$ = 25 nm) is assigned to the formed small micelles, and the second peak ($R_h$ = 160 nm) is assigned to the formed large micelles. As the concentration of the sodium salt

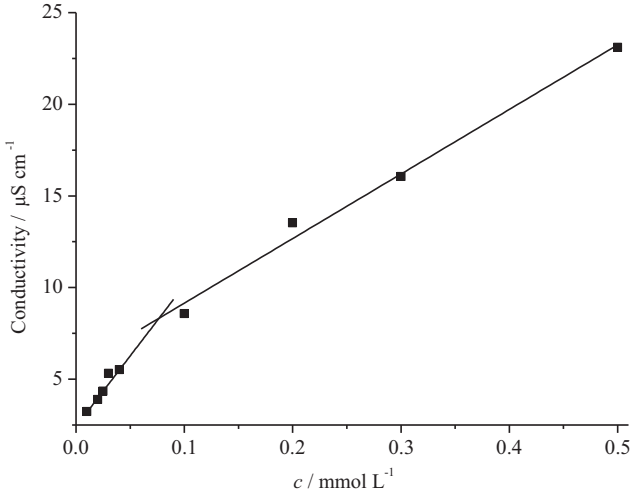


**Fig. 2.** Dependence of the conductivity on the concentration of the surfactant at 298.2 K.

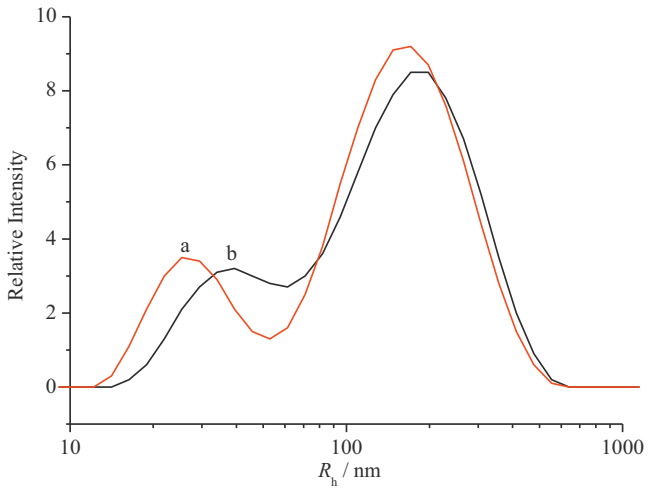


**Fig. 3.** DLS results of the aqueous solutions of the surfactant with different concentration: (a) 0.08 mmol L$^{-1}$; (b) 0.10 mmol L$^{-1}$.

increases to 0.10 mmol L$^{-1}$, the $R_h$ value of the two kinds of micelles increase to 35 nm and 190 nm, respectively.

## 4. Conclusion

A novel series of anionic sulphonate-crown ether surfactants, *i.e.*, sodium (4′-dodecanoyldibenzo-18-crown-6)-4″(5″)-sulphonate and ammonium (4′-dodecanoyl-dibenzo-18-crown-6)-4″(5″)-sulphonate, were successfully synthesized in high purity in this work. The structures of these surfactants were elucidated by IR, $^1$H NMR and elemental analysis. The experimental results indicated that the sodium salt was temperature insensitive, and had improved water solubility than nonionic crown ether surfactants. These properties allow them to have potential applications in several fields.

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