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ORIGINAL ARTICLE

Synthesis, Characterization and Surface Activity of Hexadecyl *o*-Xylene Sulfonate Isomers

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Abstract This paper deals with the synthesis of a series of hexadecyl *o*-xylene sulfonate isomers (with the *o*-xylene ring located at different positions along the *n*-hexadecyl chain) by a Friedel–Crafts reaction, and the Grignard reaction followed by a hydrogenation. The structure was confirmed by ^{1}H NMR. All analytical methods indicated high levels of purities of the isomers with the orthoxylene ring located at the first, third, fifth and seventh carbon atom on the *n*-hexadecane chain. The critical micelle concentration (CMC), surface tension and maximum surface excess concentration at CMC and area per molecule at the interface were determined. As the *o*-xylene sulfonate group is shifted toward the center of the hexadecyl chain, the branching degree is enhanced and the surfactant molecule tends to produce a much looser packing at the gas–liquid interface. Accordingly, at CMC, the adsorption density decreases, the CMC increases and the tension reduction is weakened.

Keywords Alkyl *o*-xylene sulfonate · Isomerization · Surface activity

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Introduction

Chemical flooding is an important method for Enhanced Oil Recovery (EOR) [1, 2]. Surfactants play an important role in chemical flooding. The main function of the surfactant is to reduce the interfacial tension between the oil and water to an ultra-low value ($<10^{-3}$ mN m^{-1}). Most surfactants used in EOR are mixtures of different compounds, such as the petroleum sulfonates and the heavy alkyl benzene sulfonates which are mainly composed of alkyl benzene sulfonates with different molecular weights and alkyl chain lengths. Because of the complex components and unidentified structures, it is difficult to elucidate the relationship between the structures and properties in theory. This enables the researchers to synthesize the alkyl aryl sulfonates with definite structures. A considerable number of investigations have been reported on the synthesis and surface properties of alkylbenzene sulfonate with the definite structures. Baumgartner [3, 4] synthesized the isomers of dodecyl benzene sulfonate with the benzene ring attached at different positions on the dodecyl chain for the first time. The detergence and wetting properties were reported and related with different structures and much work was focused on the foaming, wetting, surface tension. Doe [5, 6] and Wade [7] studied the interfacial tension between *n*-alkane and an aqueous solution of hexadecyl benzene sulfonate isomers, and characterized the surfactants by the concept of the preferred alkane carbon number ($n_{\min}$) to attain minimum tension. They found that when the benzene ring point of attachment is shifted to the center of the *n*-hexadecane chain, the surfactant becomes more hydrophobic, although it is also more water soluble, an apparently paradoxical association of properties. In recent years, Yang [8, 9] and Zhao [10] synthesized a series of the hexadecyl benzene sulfonates. Zhang [11] synthesized multi-*n*-alkyl benzene sulfonates and reported characteristic parameters such as the critical micellar concentration (CMC), and the surface and interfacial tension at CMC. However, the synthesis and surface properties of alkyl *o*-xylene sulfonates were not reported. In this paper we present the synthesis of a series of isomers of hexadecyl *o*-xylene sulfonates and we report on some of their properties.

The correct name of the sulfonate final product in which the sulfonated *o*-xylene group is attached to the 3rd carbon atom of the *n*-hexadecane chain could be *n*-hexadecane 3-*o*-xylene sulfonate or 3-hexadecyl *o*-xylene sulfonate and it is abbreviated in what follows as C16-3OXS. The same kind of abbreviation is used for the other isomers, with the number before OXS indicating the point of attachment of the aryl group on the *n*-hexadecane chain. The routes to attain the synthesized compounds are illustrated in Schemes 1 and 2. The details are discussed later in the experimental section. Because of the steric hindrance, the acylation cannot take place in the *ortho* position of one of the methyl groups of the xylene ring, as a consequence, there is only one possible final isomer of the alkyl orthoxylene sulfonate. It means that the only isomeric variation is due to the attachment position of the *o*-xylene ring on the *n*-hexadecane chain.

Experimental Procedures

Materials

The purity of all the chemicals used was high grade. Hexadecanoyl chloride, tetradecanoyl chloride, dodecanoyl chloride, decanoyl chloride were from Shalong (Huzhou Zhejiang Province China). *n*-Bromoethane, *n*-bromobutane, *n*-bromohexane were from Yancheng (Jiangsu Province China). *o*-Xylene, ethyl ether, magnesium strips, anhydrous calcium chloride and sodium hydroxide were obtained from Kemiou (Tian Jin China). All reagents were distilled prior to use. Pd/C catalyst (5%) was provided by the Dalian Institute of Chemical Physics (Dalian China). Hydrogen and nitrogen were of high grade purity from XueLong (>99.99% purity, Daqing China). After some optimization trials, the hexadecyl *o*-xylene sulfonate (C16OXS) different isomers was carried out through the following steps.

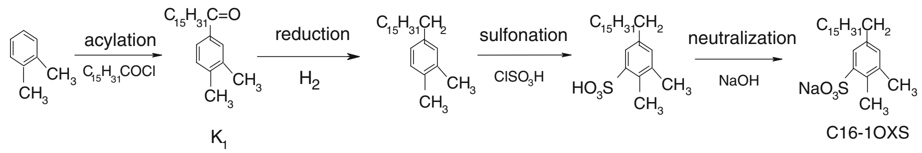
Synthesis of Hexadecyl *o*-Xylene Ketones

Acyl chloride (0.10 mol) was added dropwise to a stirred solution of anhydrous $AlCl_3$ (17.33 g, 0.13 mol) and *o*-xylene (42.47 g, 0.40 mol), the mixture was cooled in an ice-water bath for 30 min and then heated at a reflux for 3 h. The mixture was then cooled and decomposed with ice-cooled dilute hydrochloric acid (100 mL). After the phase separation, the upper layer was washed with a $NaHCO_3$ solution and deionized water until it became neutral, and finally dried over anhydrous calcium chloride. The excess of *o*-xylene was removed by distillation and the solvent was evaporated under reduced pressure. The above-mentioned procedure lead to ketones labeled K_1, K_3, K_5 and K_7 in 79.20, 84.82, 80.27, and 79.63% yields, respectively. K_1 was used to synthesize the hexadecane *o*-xylene alkane directly by hydrogen addition reduction without the two following steps.

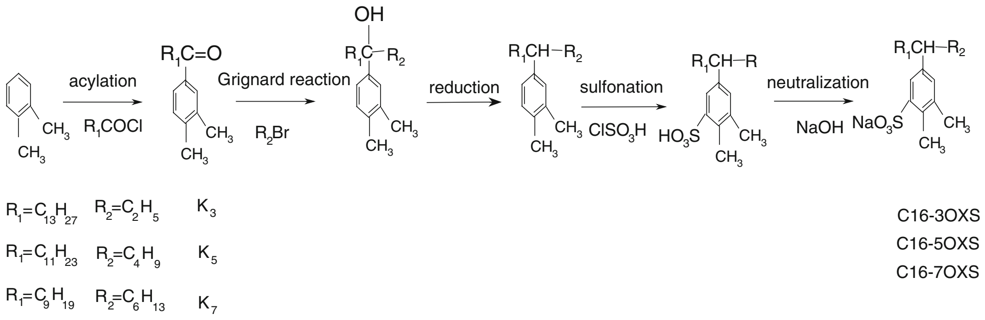
Synthesis of Hexadecyl *o*-Xylene Tertiary Alcohols

The reaction was conducted under nitrogen. Traces amount of iodine were used to initiate the Grignard reaction. Alkyl bromide (0.1 mol) was added dropwise to the mixture of the magnesium strips (50.4 g, 2.1 mol) and Et_2O (50 mL), then the reaction was placed in reflux until the magnesium

Scheme 1 Synthesis route of C16-1OXS



Scheme 2 Synthesis route of C16-3OXS, C16-5OXS, C16-7OXS



strips had disappeared. A suspension of alkyl *o*-xylene ketone (0.05 mol) in Et_2O (50 mL) was added dropwise over 30 min to the Grignard reagent and heated at reflux for 2 h. The resulting mixture was decomposed by ice-cold dilute hydrochloric acid (100 mL). After the phase separation, the aqueous solution was extracted three times with ether. All extracts were combined, washed with deionized water until neutral and dried over anhydrous calcium chloride. The hexadecyl *o*-xylene alcohol was distilled under reduced pressure.

Synthesis of Hexadecyl *o*-Xylene Isomers

The hexadecyl *o*-xylene isomers were synthesized by hydrogenation of the corresponding tertiary alcohols (20.0 g) in glacial acetic acid (50 mL) and perchloric acid (1.0 mL) using 1.0 MPa H_2 and 1.0 g Pd/C (5%) catalysts. Pd/C catalyst was filtered off and washed with petroleum ether. The filtrate was then decomposed with water. The aqueous solution was extracted twice with petroleum ether. The solvent was washed with $NaHCO_3$ solution and distilled water, respectively, until neutral, and dried over anhydrous calcium chloride. The hexadecyl *o*-xylene isomers were obtained after distillation under reduced pressure.

Synthesis of Hexadecyl *o*-Xylene Sulfonates

Chlorosulfonic acid was added dropwise to the hexadecyl *o*-xylene (molar ratio 1.5:1). The reaction proceeded for 2 h at 20 °C. The sulfonation product was neutralized with a sodium hydroxide solution. After the phase separation, the mixture was recrystallized three times with anhydrous ethanol. The final product was filtered and dried in a vacuum oven at 80 °C. The purity of the product was determined by the two-phase titration methods. The structure was confirmed by ^1H NMR.

Analytical Methods

^1H-NMR spectra were obtained with a Bruker FT-200 spectrometer using $CDCl_3$ as solvent. Chemical shifts (δ) were reported in ppm related to internal tetramethylsilane.

The surface tension was measured by the drop-volume technique in a water bath with thermostat control at 298 ± 0.1 K. The time scale for one drop was 3–50 min depending on the time required to attain equilibrium. The surface tension was then measured three times for each sample with a 3–50 min interval between each reading to ensure equilibrium data. The surface tension (γ) is given by

$$\gamma = \frac{FV\Delta\rho g}{R}$$

where R is the tip's radius, $\Delta\rho$ the difference of the two phases, g the local gravity acceleration, V the volume of one drop, $F(R/V)^{1/3}$ is a correction factor which accounts for the nonsphericity of the drop. Each surface tension value was determined from the average at least five measurements.

Results and Discussion

Properties and Purity of Intermediates and Final Products

C16-OXS isomers were prepared following Scheme 1 and Scheme 2. The boiling points of the intermediates are listed in Table 1. It can be seen that the *o*-xylene group position on the hexyldecyl chain has little effect on the boiling point. The purity of the C16-OXS isomers was determined by two-phase titration methods. C16-3OXS and C16-5OXS form crystals and may be filtered, and their purity is high, i.e. 98.5 and 97.0% (Table 2). C16-1OXS and C16-7OXS are brown and tacky semi-solids, may be because of the isomer structure, or because of their lower purity, i.e. 96.7 and 93.4%, respectively.

Table 1 Boiling stage of the intermediates

R_1	R_2	Boiling stage (°C)	Pressure (MPa)
Hexadecyl *o*-xylene ketone			
C_9H_{19}		314–317	0.080
$C_{11}H_{23}$		285–288	0.080
$C_{13}H_{27}$		227–230	0.082
$C_{15}H_{31}$		189–194	0.081
Hexadecyl *o*-xylene alcohol			
C_9H_{19}	C_6H_{13}	304–312	0.076
$C_{11}H_{23}$	C_4H_9	302–305	0.080
$C_{13}H_{27}$	C_2H_5	312–315	0.078
Hexadecyl *o*-xylene alkane			
C_9H_{19}	C_6H_{13}	284–286	0.078
$C_{11}H_{23}$	C_4H_9	290–292	0.080
$C_{13}H_{27}$	C_2H_5	304–306	0.078
$C_{15}H_{31}$		282–286	0.082

Table 2 Purity of the products

Products	C16-1OXS	C16-3OXS	C16-5OXS	C16-7OXS
Purity (wt%)	96.7	98.5	97.0	93.4

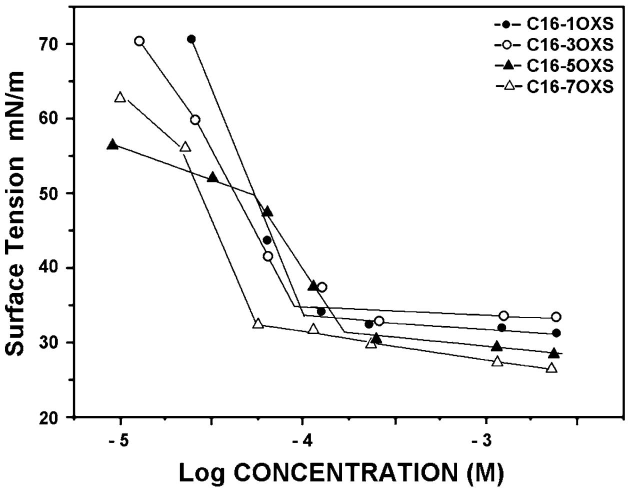


Fig. 1 Surface tension versus aqueous molar concentration (log scale) of synthesized C16-OXS isomers

^{1}H-NMR Characterization of the Products

The structures of C16-1OXS, C16-3OXS, C16-5OXS and C16-7OXS were confirmed by ^{1}H-NMR spectral analyses.

C16-1OXS ^{1}H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.860$–0.903 (t, $-\mathrm{CH_3}$, 3H), 1.061–1.328 (b, $-\mathrm{CH_2}-$, 24H), 1.411 (t, Me–$\mathrm{CH_2}$–, 4H), 1.783 (s, Ar–CH_3^1, 3H), 2.082 (s, Ar–CH_3^2, 3H), 2.751 (t, Ar–$\mathrm{CH_2}$–, 2H), 6.799 (s, Ar–H^1, 1H), 7.432 (s, Ar–H^2, 1H).

C16-3OXS ^{1}H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.637$–0.685 (t, $-\mathrm{CH}_3^1$, 3H), 0.758 (t, $-\mathrm{CH}_3^2$, 3H), 1.040–1.239 (b, $-\mathrm{CH_2}-$, 22H), 1.492 (m, Me–$\mathrm{CH_2}$–, 4H), 1.902 (s, Ar–CH_3^1, 3H), 2.151 (s, Ar–CH_3^2, 3H), 2.227–2.305 (m, –CH–, 1H), 6.948 (s, Ar–H^1, 1H), 7.567 (s, Ar–H^2, 1H).

C16-5OXS ^{1}H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.864$–0.907 (t, $-\mathrm{CH}_3^1$, 3H), 1.068 (t, $-\mathrm{CH}_3^2$, 3H), 1.250 (b, $-\mathrm{CH_2}-$, 22H), 1.391 (m, Me–$\mathrm{CH_2}$–, 4H), 1.750 (s, Ar–CH_3^1, 3H), 2.066 (s, Ar–CH_3^2, 3H), 2.719 (m, –CH–, 1H), 6.770 (s, Ar–H^1, 1H), 7.377 (s, Ar–H^2, 1H).

C16-7OXS^{1}H NMR [300 MHz, ($\mathrm{CDCl_3}$)] $\delta = 0.701$–0.722 (t, $-\mathrm{CH}_3^1$, 3H), 0.790–0.840 (t, $-\mathrm{CH}_3^2$, 3H), 1.050–1.211 (b, $-\mathrm{CH_2}-$, 22H), 1.492 (m, Me–$\mathrm{CH_2}$–, 4H), 1.938(s, Ar–CH_3^1, 3H), 2.165 (s, Ar–CH_3^2, 3H), 2.348 (m, –CH–, 1H), 6.974(s, Ar–H^1, 1H), 7.594(s, Ar–H^2, 1H).

All analytical methods indicated a high level of purity of all the isomers.

Surface Tension Studies of Different C16-OXS

Figure 1 shows the plot of surface tension versus concentration of C16-OXS isomers (on log scale) showing a break point which correspond to a well-defined CMC beyond which it remains essentially constant. As the *o*-xylene sulfonate group is shifted toward the center of the hexadecyl chain, the CMC increases probably because of a reduction in the hydrophobic effects, the minimum tension (at CMC) gradually decreases, thus indicating enhanced surface activity.

Area per Molecule and Efficiency of Adsorption

The surface excess, Γ at the air–water interface was calculated by applying the Gibbs adsorption isotherm equation. The area per molecule at the interface was estimated from the corresponding value of Γ. Table 3 summarized the CMC, γ_{CMC}, Γ, A, pC_{20} values. As the *o*-xylene sulfonate group is shifted toward the center of the hexadecyl chain, there is an increase in the branching, the surface area per molecule becomes larger, and Γ and γ_{CMC} decrease, and the branched hydrophobic chain tends to reduce the packing density at the gas–liquid interface.

A convenient measurement of the efficiency of adsorption at the gas–liquid interface is the pC_{20} parameter introduced by Rosen [12], which is the negative of the logarithm of the surfactant concentration in the bulk phase required to produce a 20 mN m^{-1} reduction in the surface tension of the solvent. As shown in Table 3, pC_{20} decreases as the *o*-xylene sulfonate group is shifted toward the center of the hexadecyl chain. The results indicate that energetically speaking, the increase in branching of the hydrophobic chain inhibits the transfer of a surfactant molecule from the bulk to the interface.

Table 3 γ_{CMC} and CMC values of hexadecyl *o*-xylene sulfonates

Surfactant	CMC (10^{-4} mol L^{-1})	γ_{CMC} (mN m^{-1})	Γ (10^{-10} mol cm^{-2})	A (nm^2)	pC_{20}
C16-1OXS	0.7975	33.76	6.291	0.2640	4.099
C16-3OXS	1.125	33.44	3.506	0.4738	3.949
C16-5OXS	2.391	29.68	2.085	0.7967	3.622
C16-7OXS	2.555	26.64	1.870	0.8883	3.594

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