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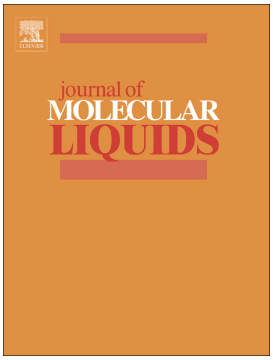

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Synthesis and Surface Properties of Alkyl *β-D*-thioglucopyranoside

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Abstract

Alkyl thioglycosides are a class of nonionic sugar-based sulfur-containing surfactants and bioreagents. The surfactants 1,2-trans alkyl *β-D*-thioglucopyranosides with different alkyl chain length (n = 6–12) were stereoselectively prepared by the Helferich method. Their properties including *HLB* number, log*P* value, water solubility, foam property, emulsifying property, surface property and thermotropic liquid crystal property were mainly investigated. The results showed that their *HLB* numbers and water-solubility decreased as the related log*P* values increased with increasing the alkyl chain length. Alkyl *β-D*-thioglucosides were already insoluble in water with n ≥ 10. Both *β-D*-thioglucopyranosides (n = 8, 9) reduced the surface tension of the related aqueous solution to nearly 29 $mN \cdot m^{-1}$ at the critical micelle concentration (*CMC*), they also had excellent foaming ability and foam stability. Nonyl *β-D*-thioglucopyranoside had good emulsifying properties for both n-octane/water system and toluene/water system. Alkyl *β-D*-thioglucopyranosides (n = 6–12) were observed to have the thermotropic liquid crystal properties.

Keywords: Alkyl *β-D*-thioglucopyranoside; Water solubility; Sugar-based surfactants; Surface activity; Thermotropic liquid crystalline

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1. Introduction

It is well-known that the glycosylic bonds can be classified as *O*-glycosylic bond [1], *S*-glycosylic bond [2], *Se*-glycosylic bond [3], *N*-glycosylic bond [4], *C*-glycosylic bond [5]. Indeed, the uncountable glycosides were found in nature [3, 6].

Alkyl (poly)glycosides (APGs) are a very interesting kind of multifunctional nonionic polyhydroxy surfactants, which contain a hydrophilic glycosyl head (such as glucosyl, maltosyl and xylosyl group) and a hydrophobic alkyl tail (saturated or unsaturated chain) [7–9]. As a kind of well-known industrial products, APGs and their anomerically pure 1,2-cis or 1,2-trans alkyl glycosides all have bestowed excellent surface activity, foaming, emulsifying properties, biodegradability, little-to-no toxicity and antibacterial properties [7, 10–13], and thereof they are used in a broad range of scientific research, industrial and consumer applications, such as membrane protein [14], textile industry [15], agrochemicals [16], functional materials [17], detergent, emulsifier, food, cosmetics and so on[18]. In addition, some alkyl glycosides can form a micellar so that they would be expected to encapsulate drug molecules to exercise drug carriers in the pharmaceutical industry [19, 20].

Compared with well-known alkyl (poly)glycosides and the related anomerically pure glycosides [21–23], there are not so many researches on preparation, properties and the related application of alkyl thioglycosides [2, 24, 25]. As a class of sugar-based nonionic sulfur-containing surfactants, alkyl thioglycosides are also amphipathic, biodegradable, low-to-no hydrolase activity and low toxicity, which

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should be practically used in detergents and other fields [25].

In the field of life science, alkyl thioglycoside can be used as a the effective medium to extract the membrane protein to stabilize further the structure and function of the extracted protein. For instance, although octyl *β*-thioglucoside (OTG) (**4c**) has an anomical structure and a critical micelle concentration (*CMC*) similar to octyl *β*-glucoside (OG) (OTG: *CMC*, 9 mM; OG: *CMC*, 23–25 mM [26]), OTG was considered as a highly efficient and mild nonionic detergent superior to OG because the OTG-solubilized membrane protein bacteriorhodopsin (BR) was high structural stability with the specific BR trimeric complexes in the dark and under light illumination since the apparent activation energy of denaturation of the OTG-solulized BR was calculated approximately twice as high as that of denaturation of the OG-solulized BR, and the subsequent removal of OTG was readily performed by dialysis in the reconstitution process into the related lipid bilayer membrane since OTG had enough high *CMC* value (9.0×10^{-3} mol·L^{-1}) [27, 28].

As is known to all, the hydrophile-lipophilic balance (*HLB*) number and the water solubility of alkyl glycosides would be gradually reduced with increasing the alkyl chain length [29]. However, with the higher *HLB* number and bigger water-solubility, the related surfactants were found to arrange difficultly in the air-solvent interface so that it would be easy to cause their poor surface activities and low practical applicable value as surfactants/detergents. As the other side of a coin, the longer alkyl chain would cause the lower *HLB* number and poor water-solubility, such surfactants/detergents would be not easy to construct spontaneously the

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oil-in-water (O/W) micellar microstructure by supramolecular self-assembly, therefore their practical application would be obviously restricted to some extent as well [30, 31]. In general, a glycoside should be used as a good stabilizer for O/W emulsions as *HLB* = 8–15; on the opposite, and it should be applied to stabilize water-in-oil (W/O) emulsions as *HLB* = 3–6. In the comparison, it should be used as detergent as well.

Since alkyl thioglycosides haven't been well studied for their preparation [25, 32], surface activity [33], phase behavior [34], thermotropic liquid crystal property [35], therefore their research should be explored further to disclose their struture-property relationships convenient for their application in science, life and functional materials.

In the paper, we planned to prepare a series of 1,2-trans alkyl *β-D*-thioglucopyranosides (also called as alkyl *β-D*-1-thioglucopyranosides, alkyl 1-thio-*β-D*-glucopyranosides [36], 1-*S*-alkyl *β-D*-thioglucopyranosides [37] or alkylthio *β-D*-glucopyranosides [38]) with different alkyl chain length (**Scheme** 1) by the glycochemistry method [36], and investigate their physicochemical properties involving in *HLB* number, log*P* value, water solubility, surface activity and thermotropic liquid crystal property to further disclose their structure-properties relationships. The investigation should provide valuable theoretical parameters for scientific research and applicable prospects as nonionic sugar-based sulfur-containing surfactants/detergents.

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2. Experimental

2.1 Materials and instruments

All detailed chemical reagents and the instruments used for the preparation and characterization of the target thioglycosides were presented in the Elemenary Supporting Information (ESI).

The corresponding chemical structures were confirmed by ^{1}H NMR spectroscopy which was recorded by Bruker Avance 400 spectrometers when the products were dissolved in $CDCl_3$, D_2O or DMSO-d6. Surface tension was obtained with a DP-A precision digital manometer. Differential scanning calorimetry (DSC, TA-Q10, TA Instruments) was used for tracking the thermal transitions of the samples through a heating and cooling procedure at a scanning rate of 10 ^{o}C/min with nitrogen as sweeping fluid. Benzoic acid and indium were used as the standard sample to calibrate the heat flow and temperature. The samples with 3 ~ 5 mg were encapsulated in the sealed aluminum pans. The liquid crystal textures of the samples were carried out by a polarized optical microscopy (POM, Leica DM-LM-P) equipped with a Leica heating stage (FP82HT) under the different temperatures. The samples were heated and cooled at 5 ^{o}C/min.

2.2 Synthesis

Alkyl *β-D*-thioglucopyranosides (**4a ~ 4f**, n = 6, 7, 8, 9, 10, 12) (**Scheme 1**) were synthesized with *D*-glucose and mercaptans (n = 6, 7, 8, 9, 10, 12) as the raw materials by the literature method [36]. The detailed synthetic processes can be available in the ESI.

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2.3 General methods

2.3.1. Hydrophile-lipophilic balance (HLB) and octanol-water coefficient (logP)

The *HLB* numbers of the prepared alkyl *β-D*-thoglucopyranosides were calculated from Eq. (1) by the Griffin method [1, 10].

$$HLB=\frac{20H}{H+O} \quad (1)$$

In the equation, *H* and *O* represented the quality of hydrophilic sugar part (including sulfur atom) and lipophilic alkyl chains, respectively.

The octanol-water partition coefficient (log*P*) values of alkyl *β-D*-thioglucopyranosides were calculated by ChemBioDraw (Ultra 14.0) to estimate their hydrophobicity and hydrophilicity [1, 29].

2.3.2 Solubility

The solubility of alkyl *β-D*-thioglucopyranosides in water or ethanol was determined at room temperature (25 °C) with the described methods [10, 39].

2.3.3 Surface tension

The surface tension of alkyl *β-D*-thioglucopyranosides was determined by maximum bubble pressure method (MBPM) [10, 40–42]. First, a series of different concentrations of aqueous solution of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) were prepared to record the related maximum additional stress (Δ*p*) respectively. With distilled water as a reference, the constant *K* was readily calculated according to the Laplace formula (Eq. (2)) and surface tension (*γ*) of the water at 25 °C. The surface tension of a series of different concentrations were next calculated out respectively. The obtained data were drawn to show the relationship between the surface tension

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and the concentration. The slope ($d\gamma/dlnC$) was obtained by fitting the curves of surface tension and concentration below *CMC*. According to Eq. (3), the surface excess concentration of monolayer saturated adsorption (Γ_{max}) was calculated out. The average molecular cross-sectional area (A_{min}) was calculated by Eq. (4) [8]. Herein, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$ and n = 1 since such thioglucopyranoside is classified as a nonionic surfactant; *T* is the thermodynamic temperature (K).

$$\gamma = K\Delta p \tag{2}$$

$$\Gamma_{\max} = -\frac{1}{RT} \cdot \left(\frac{d\gamma}{d\ln C}\right)_p \tag{3}$$

$$A_{\min} = \frac{1}{N_A \Gamma_{\max}} \tag{4}$$

The effectiveness of reducing surface tension (π_{CMC}) was obtained by Eq. (5). The efficiency of reducing surface tension (pC_{20}) was calculated by Eq. (6) [8].

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{5}$$

$$\mathrm{p}C_{20} = -\lg C_{20} \tag{6}$$

Herein, γ_0 represented the surface tension of the distilled water, γ_{CMC} was the surface tension of aqueous solution at the *CMC*, C_{20} was the concentration of the aqueous surfactant solution while the surface tension was reduced by 20 $mN \cdot m^{-1}$ in the aqueous solution.

The standard micellization free energy (ΔG_{mic}) and surface adsorption free energy (ΔG_{ads}) of alkyl *β-D*-thioglucopyranosides in aqueous solution were also calculated out by Eq. (7) and (8) respectively [42, 43].

$$\Delta G_{\mathrm{mic}} = RT\ln(C_{\mathrm{CMC}}) \tag{7}$$

$$\Delta G_{\mathrm{ads}} = \Delta G_{mic} - \frac{\pi_{\mathrm{CMC}}}{\Gamma_{\max}} \tag{8}$$

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2.3.4 Foaming property

According to the literature[42], the foaming property of the aqueous solution of alkyl *β-D*-thioglucopyranosides was determined at 25 °C. An aqueous solution of alkyl *β-D*-thioglucopyranosides with mass fraction of 0.25% and volume of 10 mL was obtained and placed in 100-mL graduated cylinder with a plug. The initial volume of foam (V_0) was recorded just after 60 seconds of intense shock, and the foaming performance was evaluated according to the initial volume of foam. Just after the solution kept in static state for 5 min, the foam volume (V_5) was recorded, the foam stability was evaluated according to the foam disappearance rate (υ) which was calculated by Eq. (9).

$$\upsilon = \frac{V_0 - V_5}{t} \qquad (cm^3/s) \tag{9}$$

2.3.5 Emulsifying property

An aqueous solution of alkyl *β-D*-thioglucopyranosides with mass fraction of 0.25% was prepared. A 20 mL aqueous solution of alkyl *β-D*-thioglucopyranosides was put into 100-mL cylinder with a plug, then 20 mL of n-octane or toluene as the oil phase was added, the mixture was strongly shocked for 60 sec. After the solution kept in static state for 1 h, the volumes of the water layer, the emulsion layer and the oil layer were recorded respectively. The emulsifying strength was determined according to the volume of the emulsion layer [42].

2.3.6 Thermotropic phase behavior

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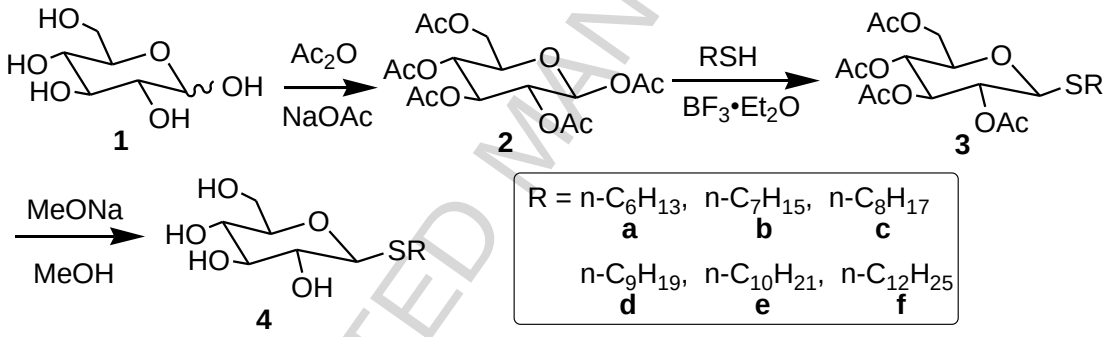
The thermal phase transition behavior of alkyl *β-D*-thioglucopyranoside was observed by polarizing microscopy (POM) during the heating and cooling process, and rate of temperature changed was controlled at 5 $^{o}C \cdot min^{-1}$. The phase transition temperature of alkyl *β-D*-thioglucopyranosides was measured by differential scanning calorimeter (DSC) [1, 29].

3. Results and discussion

3.1 Synthesis and characterization of alkyl *β-D*-thioglucopyranoside



Scheme 1. Synthesis of alkyl *β-D*-thioglucopyranoside

In fact, alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) were prepared by a lot of glycochemistry method. Saito [24] prepared some *β-D*-thioglucopyranosides by thiourea method. Glycosyl bromide was reacted with thiourea and subsequent reaction with alkylbromide and the final deacetylation was taken to obtain the related thioglycoside. The procedure was rather complex and glycosyl bromide wasn't stable in spite of proper yield without using any expensive reagent. Li's group [24] reported better thioglycosylation of 1,2-cis-glycosyl acetates to obtain the related compounds

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aryl *β*-thioglycosides with boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) as Lewis acid catalyst rather than other Lewis acid catalysts. Gurudutt's group also reported thioglycosylation using glcosyl halides and zinc salts of thiol in reflux to obtain the mixture of proportional variable α/β anomers since the direct condensation of peracetylsugar with mercaptans was not smooth/effective and led to unexpected results because the initially formed alkyl *β*-thioglycosides anomerized under the influence of the catalyst (zinc chloride, tin (IV) chloride, boron trifluoride or *p*-toluene sulfonic acid) to give a 7:3 α/β mixture [37]. They also found that the *S*-glycosidation of Me_3CSH and AllSH was much strange and failed to yield the corresponding glucosides, probably due to their inability to form the ion-quadruplet intermediate. Doren's group [36] investigated that the direct condensation of peracetylated monosaccharides and the appropriate n-alkylanethiol by the $BF_3 \cdot Et_2O$ method had the advantage over a Königs-Knorr type of route.

In the paper, the homologous series of kinetically controlled alkyl *β-D*-thioglucopyranosides (n = 6, 7, 8, 9, 10, 12) were prepared by the direct glycosylation method [36], and the method should be reasonable since the acetoxy group on C-2 would provide anchimeric assistance for the loss of the acetoxy group at the anomeric centre and lead to form an acyloxonium ion intermediate, and then such cyclic intermediate was most easily attacked by the thiol on the *β*-side to obtain 1,2-trans protected alkyl thioglycoside. As described in **Scheme 1**, *D*-glucose (**1**) was acetylated to afford 1,2,3,4,6-penta-*O*-acetyl-*β-D*-glucopyranose (**2**), the latter was condensated with mercaptan (n = 6, 7, 8, 9, 10, 12) with boron trifluoride diethyl

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etherate ($BF_3 \cdot Et_2O$) as Lewis acid catalyst to provide alkyl 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-thioglucopyranoside (**3**). The protected thioglycoside (**3**) was deacetylated to obtain the target poduct alkyl *β*-*D*-thioglucopyranoside (**4**).

The condensation reaction should produce a mixture (*β* (main) and *α* (less)) of two anomers whose configuration differs completely from each other at C1 position. Since the column separation was introduced to make a successful attempt to obtain anomerically pure 1,2-trans protected alkyl *β*-*D*-thioglucopyranosides (**3a** ~ **3f**). The characterization of the anomeric configuration was further confirmed by ^{1}H NMR method. For example, the chemical shift (coupling constant, $J_{1,2}$) of hexyl 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-thioglucopyranoside (**3a**) was 4.48 ppm (10.0 Hz). Hexyl 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-thioglucopyranoside (**3a**) was deacetylated to get alkyl *β*-*D*-thioglucopyranoside (**4a**) without change of anomeric configuration. Other alkyl *β*-*D*-thioglucopyranosides (**4b** ~ **4f**) also were successfully prepared with the same glycochemical procedure.

The 1,2-trans anomeric configurations of alkyl 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-thioglucopyranosides (**3a** ~ **3f**) were readily characterized with ^{1}H NMR spectral analysis (in the ESI) since their H-1 chemical shifts (coupling constants $J_{1,2}$) in $CDCl_3$ all were 4.48 ppm (10.0 Hz, D_2O) (**3a** ~ **3f**). Meanwhile, the 1,2-trans anomeric configurations of alkyl *β*-*D*-thioglucopyranosides (**4a** ~ **4f**) all were readily characterized with ^{1}H NMR spectral analysis (in the ESI) since their H-1 chemical shifts (coupling constants $J_{1,2}$, deuterium solvent) were 4.47 ppm (9.8 Hz, D_2O) (**4a**), 4.48 ppm (9.9 Hz, D_2O) (**4b**), 4.43 ppm (9.9 Hz, D_2O) (**4c**), 4.20 ppm (9.7

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Hz, DMSO-d6/D_2O) (**4d**), 4.20 ppm (9.7 Hz, DMSO-d6/D_2O) (**4e**), 4.20 ppm (9.7 Hz, DMSO-d6/D_2O) (**4f**).

Indeed, 1,2-trans *O*-glucopyranoside generally showed the coupling constant $J_{1,2}$ = 4–8 Hz, for instance, H-1 chemical shifts (coupling constants $J_{1,2}$) of alkyl *β-D*-glucopyranoside were 4.20–4.51 ppm ($J_{1,2}$ = 6.3–7.9 Hz)) [44]. However, a lot of 1,2-trans *S*-glucopyranosides had higher coupling constants $J_{1,2}$. (n-propyl 2,3,4,6-tetra-*O*-acetyl-*β-D*-thioglucopyranoside 10.0 Hz [38], n-propyl 2,3,4,6-tetra-*O*-acetyl-*α-D*-thioglucopyranoside 5.7 Hz [38], S-Trifluoromethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-*β-D*-glucopyranoside 9.9 Hz [45], 2,3-di-*O*-Acetyl-1-*S*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-1-thio-*β-D*-glucopyranose 10.5 Hz [46], cyclohexyl 2,3-di-*O*-acetyl-4,6-bis-*O*-(4-bromobenzoyl)-1-thio-*β-D*-glucopyranoside 10.1 Hz [46]). Therefore, the results elucidated that the 1,2-trans *β*-anomer alkyl *β-D*-thioglucopyranosides (n = 6, 7, 8, 9, 10, 12) were successfully formed.

3.2 *HLB* number, log*P* and solubility

The *HLB* number of alkyl *β-D*-thioglucopyranosides (n = 6–12) (**4a** ~ **4f**) was calculated by the Griffin method on condition that the hydrophilic part contained sulfur atom, and the results were listed in **Table 1**. From **Table 1**, the *HLB* number (13.9 → 10.7) of alkyl *β-D*-thioglucopyranoside (n = 6 → 12) was bigger than the *HLB* number (13.6 → 10.3) of alkyl *β-D*-glucopyranoside (n = 6 → 12) with the same alkyl chain length.

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On the opposite, the log*P* value (0.78 → 3.29) of alkyl *β-D*-thioglucopyranoside (n = 6 → 12) was bigger than the log*P* value (0.06 → 2.57) of alkyl *β-D*-glucopyranoside (n = 6 → 12) with the same alkyl chain length from **Table 1**. The data should be considered as right and rather valuable since the hydrophilicity of sulfur atom is weaker than that of oxygen atom, i.e. the lipophilicity of sulfur atom is stronger than that of oxygen atom. Since log*P* > 0, alkyl *β-D*-thioglucopyranoside (n = 6, 7, 8, 9, 10, 12) had different degrees of lipophilicity although there was somewhat hydrophilicity due to its hydrophilic glucopyranosyl head [1]. In addition, the longer the alkyl group and the stronger the lipophilicity.

Table 1 *HLB* number and log*P* value of alkyl *β-D*-glucopyranoside [44] and *β-D*-thioglucopyranoside

Alkyl *β-D*-gluco-pyranoside (n)	log*P*	*HLB* number	Water solubility	Alkyl *β-D*-thiogluco-pyranoside (n)	log*P*	*HLB* number	New *HLB* number	Water solubility
6	0.06	13.6	high	6	0.78	13.9	11.7	high
7	0.48	12.9	high	7	1.20	13.3	11.2	high
8	0.90	12.3	soluble	8	1.62	12.7	10.6	soluble
9	1.31	11.7	soluble	9	2.04	12.1	10.2	low
10	1.73	11.2	low	10	2.45	11.6	9.8	insoluble
12	2.57	10.3	insoluble	12	3.29	10.7	9.0	insoluble

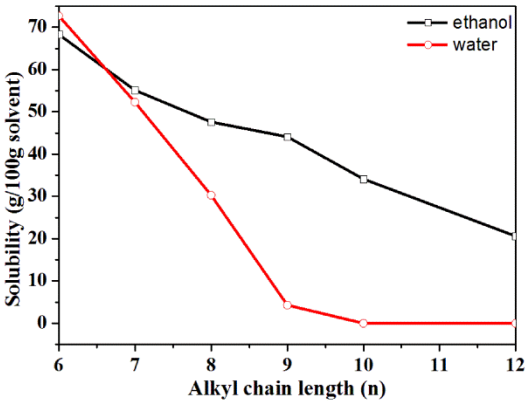

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Fig. 1 Solubility of alkyl *β-D*-thioglucopyranoside in water or ethanol

The results of the solubility of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) were shown in **Fig. 1**. Their solubility in water and ethanol decreased gradually with increasing the alkyl chain length. At the beginning, the solubility of hexyl *β-D*-thioglucopyranoside (**4a**) in water is slightly higher than that in ethanol. The solubility (44.1 g) of nonyl *β-D*-thioglucopyranoside (**4d**) in ethanol is obviously higher than that in water (4.3 g). While n ≥ 10, the related *β-D*-thioglucopyranosides (**4e** ~ **4f**) are soluble in ethanol and insoluble in water.

Whilst inspecting again the calculated *HLB* number in **Table 1** by Eq. (1), such data should be naturally considered as really accessible/convenient but rather strange since the electronegativity of sulfur atom is 2.58, which is obviously less than the strong electronegativity of oxygen atom (3.44), almost equivalent to the electronegativity of carbon atom (2.55), i.e. the sulfur atom was considered to have stronger lipophilicity and weaker hydrophilicity. Therefore, a new idea/whim was introduced to recalculate *HLB* number (called as a new *HLB* numbr) by Eq. (10) from the Griffin method on condition that the hydrophilic part only involved partially sulfur atom.

$$HLB=\frac{20(S+1.08)}{T} \quad (10)$$

In the new *HLB* equation, *S* represented the quality of hydrophilic sugar part (without sulfur atom), and *T* represented total molecular quality. The value 1.08 was a calculated result from 0.03*32.07/0.89 since the difference between electronegativity

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of oxygen atom (3.44) and electronegativity of carbon atom (2.55) was 0.89 and the difference between electronegativity of sulfur atom (2.58) and electronegativity of carbon atom (2.55) was 0.03, and as well 32.07 was mass of sulfur atom.

The calculated data (the new *HLB* numbers) were also listed in **Table 1**. It was interesting that the new equation was effectively supported according to the experimental data although the equation was somewhat curious. The new *HLB* number (11.7 → 9.0) of alkyl *β-D*-thioglucopyranoside (n = 6 → 12) was smaller than the *HLB* number (13.6 → 10.3) of alkyl *β-D*-glucopyranoside (n = 6 → 12) with the same alkyl chain length. Meanwhile, the related thioglucopyranoside (n = 6–9) had water solubility on condition that the new *HLB* number > 10, for instance, nonyl thioglucopyranoside (**4d**) still had small water solubility; and the new *HLB* number < 10, the related thioglucopyranosides (n = 10 (**4e**), 12 (**4f**)) did not have water solubility.

3.3 Interfacial Property

The maximum bubble pressure method (MBPM) was used to measure the surface tension of different concentration of aqueous alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) solution at 25 °C. On the opposite, the surface tension of alkyl *β-D*-thioglucopyranosides (**4e** ~ **4f**) weren't investigated because their solubility in water was too low to be measured.

The relationship curve between the surface tension and the concentration was shown in **Fig. 2**, and the resulting data were summarized in **Table 2**. From **Fig. 2** and

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Table 2, alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) were observed to reduce significantly the surface tension (γ) of their aqueous solutions. The surface tension value (γ_{CMC}) decreased with increasing the alkyl chain length at the *CMC*, the γ_{CMC} data of octyl *β-D*-thioglucopyranoside (**4c**) and nonyl *β-D*-thioglucopyranoside (**4d**) aqueous solutions at their *CMC* reached the lowest (29.63 $mN \cdot m^{-1}$). Furthermore, the *CMC* value showed a decreasing trend with increasing the alkyl chain length.

In addition, the related molecular cross-sectional area (packing area, A_{min}) was found to have a downward trend (42.48 $Å^2 \rightarrow$ 23.82 $Å^2$) with increasing the alkyl chain length (n = 6 → 9). On the contrary, the surface excess concentration (Γ_{max}) tended to increase ($3.91x10^{-6}$ $mol \cdot m^{-2} \rightarrow 6.97x10^{-6}$ $mol \cdot m^{-2}$) with increasing the alkyl chain length (n = 6 → 9). The reason should be that there was a repulsive force between hydrophobic alkyl chain and water and as well an attractive force between hydrophilic glycosyl head and water. The increase of the alkyl chain length made it easier for alkyl *β-D*-thioglucopyranoside to adsorb on the air/water interface and further form the related interface layer *via* the ordered alignment and self-assembling behavior since more hydrocarbon units should increase the hydrophobicity and increase the distance with water. Compared with the short alkyl chain in a homologous series, the long alkyl chain should indeed enhance effectively the microphase separation of the thioglycosidic molecules and their close alignment each other involving in several forces such as the hydrophobic-hydrophobic interactions (Van der Waals forces, dispersion forces, London dispersion forces) of the alkyl chain and the hydrophilic-hydrophilic interactions (hydrogen bonds) of the glycosyl head at

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the air/water interface. In addition, such sulfur atom with somewhat amphipathicity perhaps also gave the special contribution to the microphase separation and the stability of the two dimensional (2D) and/or three dimensional (3D) supermolecular network structure newly formed since it has higher atomic number, bigger atomic radius, smaller electronegativity, weaker electron-binding ability, lower ionization energy and better polarizability/deformability than oxygen atom with high hydrophilicity (also considered as poor amphipathicity and no lipophilicity). The experimental results, based just on the multifunctional interactions, showed that they had monotonic changes for the related *CMC*, γ_{CMC}, Γ_{max} and A_{min} data in the range of alkyl chain (n = 6-9), such gradation in their surface phenomenon is really typical of a homologous series.

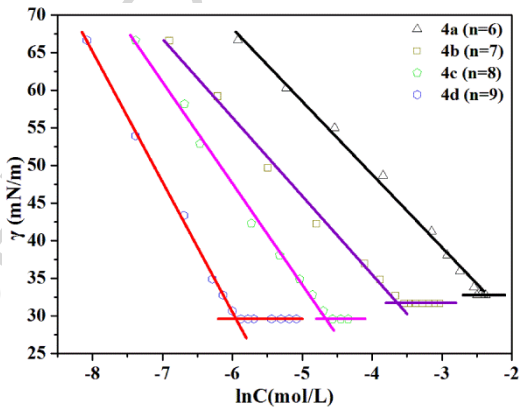

Fig. 2 Surface tension of alkyl *β-D*-thioglucopyranoside (**4a** ~ **4d**)

Table 2 Interfacial property of alkyl *β-D*-thioglucopyranoside

Thioglycoside (n)	**6**	**7**	**8**	**9**
CMC (mol·L^{-1})	8.21×10^{-2}	2.72×10^{-2}	1.04×10^{-2}	2.80×10^{-3}
γ_{CMC} (mN·m^{-1})	32.80	31.75	29.63	29.63
Γ_{max} (10^{-6} mol·m^{-2})	3.91	4.21	5.43	6.97

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A_{min} (Å^2)	42.48	39.46	30.59	23.82
pC_{20} (mol·L^{-1})	1.88	2.42	2.74	3.15
π_{CMC} (mN·m^{-1})	39.17	40.22	42.34	42.34
ΔG_{mic} (kJ·mol^{-1})	-6.20	-8.94	-11.33	-14.59
ΔG_{ads} (kJ·mol^{-1})	-16.22	-18.49	-19.18	-20.66

In **Table 2**, the related efficiency (pC_{20}) of reducing the surface tension showed an increasing trend with increasing the alkyl chain length. The effectiveness (π_{CMC}) of reducing surface tension first increased rapidly, and then increased slowly to the maximum with increasing the alkyl chain length. Both π_{CMC} of octyl *β-D*-thioglucopyranoside (**4c**) and nonyl *β-D*-thioglucopyranoside (**4d**) solutions reached the highest (42.34 mN·m^{-1}). Therefore, octyl *β-D*-thioglucopyranoside (**4c**) and nonyl *β-D*-thioglucopyranoside (**4d**) had the greatest surface activity. Herein, such excellent amphiphilic molecules should self-aggregate readily at the air/solution interface and reduce effectively the corresponding *CMC* values.

The result of the standard micellization free energy (ΔG_{mic}) and surface adsorption free energy (ΔG_{ads}) was also shown in **Table 2**. All values were negative, which indicated that alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) with amphiphilicity had a tendency to form micelles in the solution, and also possessed an adsorption capacity at the air/water interface. Both ΔG_{mic} and ΔG_{ads} values were observed to change more negative with increasing the alkyl chain length and such phenomenon indicated that the longer alkyl chain should have more chance to form micelles in the solution and migrate to air/solution interface. In addition, ΔG_{ads} value was more negative than ΔG_{mic} value. It was inevitable that all amphiphilic molecules were easy to adsorb at the air/water interface rather than forming micelles in water when the

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concentration of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) was below *CMC*.

3.4 Foaming property and emulsifying property

The foam properties of any surfactants can be readily measured. The bigger the foaming volume, the better the foaming performance; the slower the rate of foam disappearing, the better the stability of the foam. In this paper, the volume of foam and the rate of foam disappearance of a certain concentration of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) were measured by the above-described method.

In **Fig. 3**, the results showed that the initial foam volume (V_0) increased first and then decreased with increasing the alkyl chain length. Hexyl *β-D*-thioglucopyranoside (**4a**) showed the weakest foaming ability (V_0 = 20 cm^3), and octyl *β-D*-thioglucopyranoside (**4c**) showed the strongest foaming ability (V_0 = 88 cm^3). When n ≥ 8, the rate of foam disappearance rapidly decreased, showing good stability. In general, the foam stability should be determined by the strength of the foaming performance, and there should be a reasonable illustration that the surfactants would be adsorbed on the air/solution interface to form a rather sturdy adsorption film to stabilize the foam.

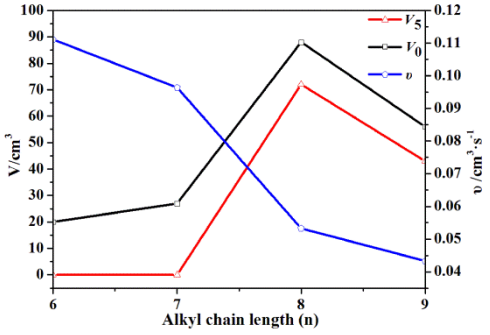

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Fig. 3 Foam property of alkyl *β-D*-thioglucopyranoside (**4a** ~ **4d**)

From **Fig. 4**, the results showed that alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) had some emulsifying ability for both octane/water and toluene/water immiscible phase systems, and the emulsification capacity increased with increasing the alkyl chain length. Nonyl *β-D*-thioglucopyranoside (**4d**) had the best emulsifying ability in both systems. In the process of emulsification, alkyl *β-D*-thioglucopyranoside with the longer alkyl chain separated itself more easily away from the bulk solution and was adsorbed onto the interface to form readily a stronger interfacial film, preventing the discontinuous liquid particles of disperse phase in the emulsion from reaggregation, so as to maintain the stability of the emulsion. However, when $n \geq 10$ and $\log P \geq 2.45$, alkyl *β-D*-thioglucopyranosides did not have emulsifying property since the related hydrophilicity was rather weak due to the double function from the hydrophobicity of alkyl chain and the amphiphilicity of sulfur atom, and the related hydrophobicity was special strong. In the process of oil/water emulsification, the reasonable alternative range of the log*P* value should be carefully considered, such as a choice of $1.50 \leq \log P \leq 2.04$ maybe is laudable or even perfect. The higher log*P* value would destroy the dynamic balance partly due to violating the Bancroft rule [47, 48].

In addition, the selected oil phase was different, the emulsified effect was different each other. Herein, toluene was used as the oil phase, the obtained result was the emulsion layer and oil layer. In the comparison, n-octane was used as an oil phase, the obtained result was the emulsion layer and excess water.

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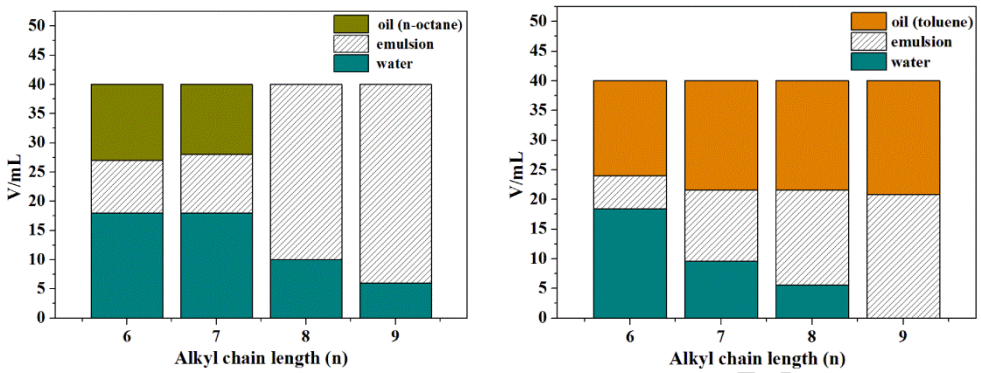

Fig. 4 Emulsifying property of alkyl *β-D*-thioglucopyranoside

(1) n-octane/water system, (2) toluene/water system

3.5 Thermotropic liquid crystal property

Polarizing optical microscopy (POM) and differential scanning calorimeter (DSC) were used to study the phase behavior of the related thermotropic liquid crystals. **Table 3** showed that the phase transition temperature of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) and the related enthalpy value during the second heating process obtained by DSC. **Fig. 5** showed the DSC patterns for the second heating of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**). Some thioglucopyranosides (**4c** ~ **4f**) showed a double melting phase transition temperatures at heating process: (1) the liquid crystal temperature (T_{lc}) from the crystallized solid turned into a translucent liquid crystal, (2) the liquid crystal disappearing temperature (T_{iso}) from a translucent liquid crystal into an isotropic liquid, also called as the clear point temperature.

Table 3 Thermotropic transition temperature of alkyl *β-D*-glucopyranoside [44] and alkyl *β-D*-thioglucopyranoside under the second heating process with DSC scan

Alkyl *β-D*-gluco-	Alkyl *β-D*-thiogluco-	ΔH_{iso}

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pyranoside (n)	T_{lc}(°C)	T_{iso}(°C)	ΔT(°C)	pyranoside (n)	T_{lc}(°C)	T_{iso}(°C)	ΔT(°C)	(kJ·mol^{-1})
6	90.6	-	-	6	—	70.2	—	2.7
7	73.2	80.5	7.3	7	—	101.9	—	5.8
8	67.4	105.4	38.0	8	57.4	124.5	67.1	5.2
9	73.3	119.9	46.6	9	61.8	139.7	77.9	7.4
10	76.6	127.1	50.5	10	64.8	147.1	82.3	6.1
12	78.2	141.6	63.4	12	62.5	160.6	98.1	5.7

As shown in **Table 3**, the melting points of alkyl *β-D*-thioglucopyranosides (**4c** ~ **4e**) increased with increasing the alkyl chain length during heating process, but the melting point of dodecyl *β-D*-thioglucopyranoside (**4f**) turned to decrease since its hydrogen bonding network would be weaken as glucopyranosyl part became small to some content in solid crystal state despite that its Van der Waals interactions should slightly increase [49, 50]. Relatively, the related T_{iso} still increased monotonously with increasing the alkyl chain length, and the T_{iso} vulue of dodecyl *β-D*-thioglucopyranoside (**4f**) reached as high as 160.6 °C. The gap (ΔT) between phase transition temperatures also increased with increasing the alkyl chain length. Besides, there was no obvious relationship between the enthalpy change and the alkyl chain length each other.

Liu [44] also showed the similar phase transition process of alkyl *β-D*-glucopyranosides (**Table 3**). In the *O*-glycosides and the *S*-glycosides due to the difference between sulfur atom and oxygen atom, there were the same and different points as follows: (1) both of hexyl *β-D*-glucopyranoside and hexyl *β-D*-thioglucopyranoside (**4a**) had only one phase transition temperature; (2) heptyl *β-D*-thioglucopyranoside (**4b**) had only one phase transition temperature although

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heptyl *β-D*-glucopyranoside had two phase transition temperatures; (3) for both of other *β-D*-glucopyranosides and *β-D*-thioglucopyranosides with n = 8, 9, 10, 12), there were two phase transition temperatures; (4) the *S*-glycosidic linkage had lower T_{lc} value and higher T_{iso} value than the related *O*-glycosidic linkage with the same alkyl chain length, therefore the corresponding difference (ΔT) of *β-D*-thioglucopyranoside was broader than that of the related *β-D*-glucopyranoside. Compared with small atomic radius and strong hydrophilicity of oxygen and fine intermolecular hydrogen bonding network of the *O*-glycosides, sulfur atom had amphipathicity to some extent and made the intermolecular hydrogen bond network of the *S*-glycosides weaken although there probably were small improvement/promotion for the intermolecular interactions between nonopolar alkyl chain and sulfur atom. In addition, sulfur atom had big atomic radius and perhaps obstructed intermolecular close alignment and high orientation in the related ordered crystal structure. Such issue would further result in the reduction of the corresponding T_{lc} and somewhat enhancement of liquid crystalline phase temperature range, and the polarizability/deformability of sulfur atom should also take part in the synergistic action. The homologous *S*-glycosides with wide mesomorphic temperature range (ΔT) and other characters would probably have their potential and unexpected values in many cases such as life sciences and material sciences.

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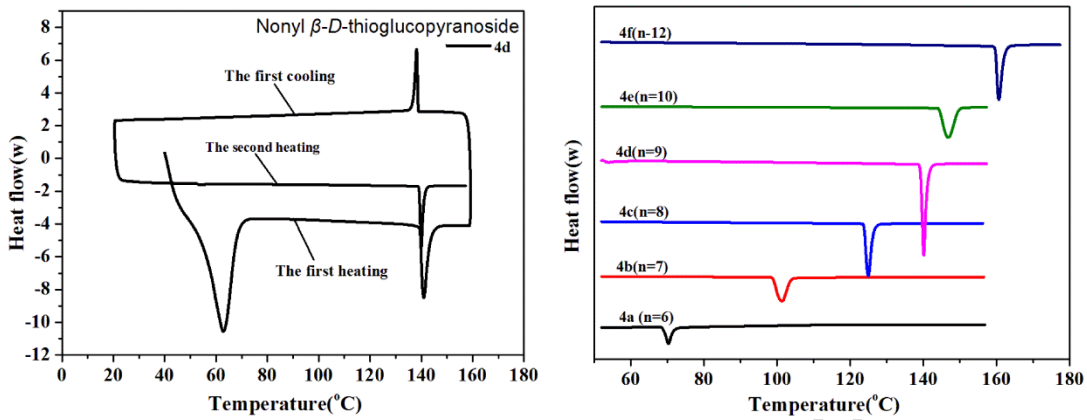

Fig. 5 DSC curve of alkyl *β-D*-thioglucopyranoside

Nonyl *β-D*-thioglucopyranoside (**4d**) was investigated as shown on the left side of **Fig. 5**. At first, the related two endothermic peaks at heating process were successively observed and considered as melting point peak and clear point temperature peak. Seconding, an exothermic peak was observed since the isotropic liquid was transformed into a liquid crystalline phase at cooling process and the process was exothermic. Thirdly, the second heating process caused another endothermic peak. And the characteristic peak and the exothermic peak were really similar each other in appearance and size apart from the opposite direction [1].

POM was used to observe the thermotropic liquid crystalline behavior of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) during heating process, so as to disclose the relationships between their alkyl chain length and thermotropic liquid crystalline properties, and the results were showed in **Fig. 6**. Alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) were observed to have birefringence. Their thermotropic liquid crystal texture was examined during the process of heating under a polarizing microscope. Octyl *β-D*-thioglucopyranoside (**4c**) only appeared a clear Maltese cross pattern texture.

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However, other alkyl *β-D*-thioglucopyranosides (**4a**, **4b**, **4d**, **4e**, **4f**) appeared vague or even unformed Maltese cross pattern texture. During cooling, all thioglucopyransides (**4a** ~ **4f**) showed clear focal-conic fan textures, and such textures of several samples (**4c** ~ **4f**) were more stylish. These fan structures should be the common characteristics of the smectic A phase [50, 51]. The focal-conic fan textures still maintained unchanged even if the temperature was reduced to room temperature. And the observed thermotropic liquid crystal characteries of such nonionic sugar-based thio-containing amphiprotic surfactants would be expected to have certain scientific significance and applicable prospects.

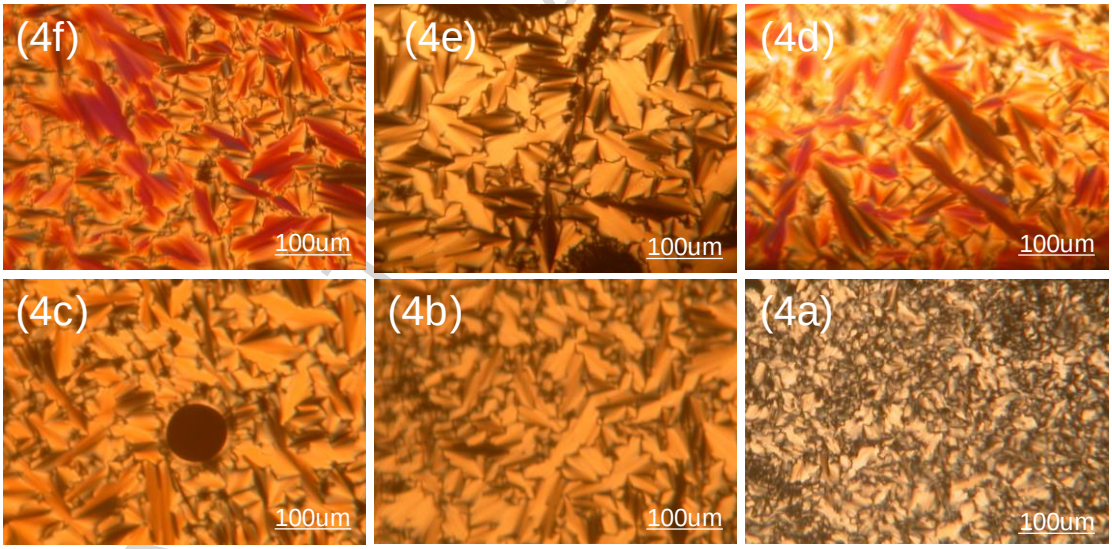

Fig. 6 Liquid crystal texture of alkyl *β-D*-thioglucopyranoside (**4a** ~ **4f**)

4. Conclusions

In the paper, peracetylglucose (**2**) was coupled with mercaptans under the catalysis of Lewis acid $BF_3 \cdot Et_2O$, followed by deprotection to obtain alkyl

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β-D-thioglucopyranosides (**4a** ~ **4f**). The 1,2-trans *β-D*-thioglucopyranosides were characterized by ^{1}H NMR technology, the coupling constants ($J_{1,2}$) of alkyl *S*-glucopyranosides were at the range of 9.7–9.9 Hz, the values were obviously higher than that of alkyl *O*-glucopyranosides [44].

With the prepared sugar-based sulfur-containing amphiphiles in hands, their *HLB* number, log*P* value, water solubility, surface tension, foam property, emulsifying property, focal-conic fan texture and so on were investigated. The results indicated as follows: (1) A new method was introduced to calculate reasonably the related *HLB* number (11.7 (**4**a, n = 6) → 9.0 (**4f**, n = 12)) since sulfur atom had special electronegativity and weaker hydrophilicity. (2) The *HLB* number of alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) decreased gradually as the related log*P* value increased with increasing the alkyl chain length. (3) The related solubility in water and ethanol gradually decreased with increasing the alkyl chain length, and alkyl *β-D*-thioglucopyranosides were not soluble in water while the alkyl chain length n ≥ 10. (4) Octyl *β-D*-thioglucopyranoside (**4c**) and nonyl *β-D*-thioglucopyranoside (**4d**) had excellent foaming ability and foam stability. (5) Alkyl *β-D*-thioglucopyranosides (**4a** ~ **4d**) reduced the surface tension of their aqueous solution, octyl *β-D*-thioglucopyranoside (**4c**) and nonyl *β-D*-thioglucopyranoside (**4d**) had relative strong surface activity. (6) Octyl *β-D*-thioglucopyranoside (**4c**) had the strongest foaming ability and better foaming stability; nonyl *β-D*-thioglucopyranoside (**4d**) had the strongest emulsifying properties for both n-octane/water system and toluene/water system. (7) Alkyl *β-D*-thioglucopyranosides (**4a** ~ **4f**) were observed to have the

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thermotropic liquid crystalline behavior.

Indeed, sulfur, as a functional heteroatom, linked hydrophilic glucopyranosyl group and hydrophobic alkyl group so as to construct the *S*-glucopyranoside and endue a lot of interesting structure-property relationships, which is of course different from *O*-glucopyranoside involving in preparation [52], structure modification, characterization, amphilicity [53, 54], theoretical simulation [55], water solubility, surface activity [10, 56, 57], thermotropic and/or lyotropic liquid crystalline [1, 58], phase diagram [59, 60], functional materials, chemical technology and engineering optimization, bioactivity [61], protein-glycoside interaction [62], biodegradation [63], biotoxicity [11, 13], eco-environmental concerns [64] and so on. Although there have been a number of progressive investigations, it is particularly for the necessity that more efforts should be made on their scientific research, practical advanced application and potential commercial value as well.

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Elemenary Supporting Information (ESI) to this article can be found online at ….

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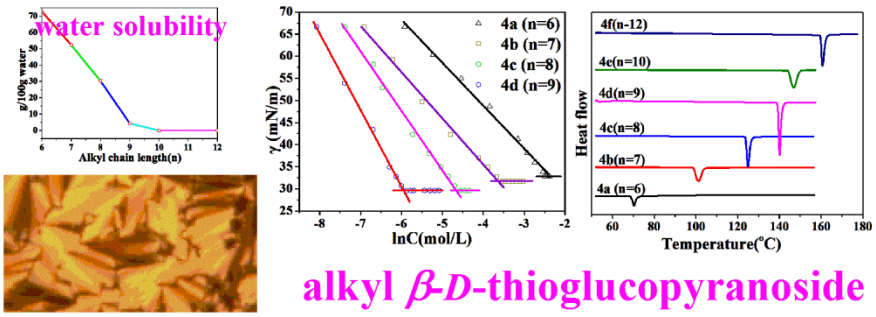
Graphical abstract



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Research Highlights

1. Alkyl *β-D*-thioglucopyranosides in anomerically pure form were prepared.

2. A new equation was introduced to calculate their HLB number.

3. Their surface properties changed regularly with increasing the alkyl chain length.

4. Their thermotropic liquid crystalline property was observed.

5. They should be used as sugar-based sulfur-containing surfactants and bioreagents.

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