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Synthesis and property of alkyl dioxyethyl α-D-xyloside

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Due to the inherent defects of the long alkyl chain in the related hydrophilicity and water solubility, alkyl α-D-xylosides (7) had hardly the practical application as sugar-based surfactants and should be reconstructed to obtain alkyl dioxyethyl α-D-xylosides (5) with dioxyethylene fragment (–(OCH2CH2)n–) as the hydrophilic spacer to increase the related CMC value. With D-xylose as the raw material, 1,2-cis alkyl dioxyethyl α-D-xylosides (5a–5f, n = 6–12) were stereoselectively synthesized. Their physicochemical properties including water solubility, surface tension, foamability, emulsification, thermotropic liquid crystal, and hygroscopicity had been investigated. Their water solubility was found to decrease gradually whereas their calculated HLB numbers were 14.72 → 11.67 (n = 6 → 12) with increasing alkyl chain length (n). Dodecyl dioxyethyl α-D-xyloside (5f) had not water solubility because the HLB number was low. Furthermore, their CMC values decreased with increasing the alkyl chain length, and the CMC value of decyl dioxyethyl α-D-xyloside (5e) was as low as 9.21 × 10−5 mol·L−1. Octyl dioxyethyl α-D-xyloside (5c) had the lowest surface tension (27.25 mN·m−1) at the CMC. Both of nonyl and decyl dioxyethyl α-D-xylosides (5d & 5e) possessed good foaming power and foam stability. Decyl dioxyethyl α-D-xyloside (5e) had the strongest emulsifying property either in the toluene/water system or in the octane/water system. Nonyl dioxyethyl α-D-xylosides (5d) had the most stylish S5 texture. Hexyl dioxyethyl α-D-xyloside (5a) possessed the strongest hygroscopicity. Therefore, the alkyl dioxyethyl α-D-xylosides as a class of novel sugar-based surfactants will be widely considered as promising candidates for various practical applications.

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1. Introduction

For the fatty alcohol polyoxyethylene ethers (AEO) and the related derivatives, such as fatty alcohol polyoxyethylene ether carboxylate (AEC), sulfonate and sulfate, these surfactants have good biodegradability, water-solubility, salt tolerance, resistance to hard water, wetting ability, emulsifying capacity, foaming ability, detergency performance, lubrication properties, and flow behavior, and in addition, they should have application value to a certain extent [1–4]. For example, AEO with a relatively flexible hydrophilic part, as the conventional poly(ethylene oxide) (PEO)-based surfactants, can adsorb strongly on silica/water and air/water interfaces with the hydrogen bonding as the main driving force for the adsorption [3,4]. However, one may perceive an issue that the raw material ethylene oxide (EO) and its derivatives could be prepared from petroleum oil [5]. Due to a lot of unexpected events including the subprime mortgage crisis in 2007 and the current COVID-19 (the Corona Virus Disease 2019) pandemic, the relevant global economy should be seriously dragged down, resulting in a short-term downward tendency on oil prices [6,7]. Nevertheless, the petroleum oil, as a scarce fuel and non-renewable chemical raw material, should be replaced to afford other valuable surfactants by some renewable resources to relieve/delay the energy crisis/depletion to certain content. Therefore, to avoid such an obstacle, much attention should be paid to the efficient synthesis of the related surfactants rather than petroleum-based surfactants.

On the contrary, carbohydrates should be attractive bioorganic materials on the earth because they are natural sources, environmentally friendly, and highly functionalized, thus promoting green and sustainable development in chemistry, life science, and functional materials [3,8]. Besides, sugar-based surfactants would indeed be available for various potential applications such as the chemical cleaning [9], the flotation [10], the oil recovery [11,12], the oil spill treatment [13], the textile printing and dyeing [14], the pesticides [15], the liquid crystal materials [16–19], the nanotechnology [20], the emulsion [21], the membrane protein research [22–25], the chemical catalysis [26], the pharmacology [27–31], the bacteriology [32], the toxicology [33], the antibacterial activity [34,35], the cosmetics [36], and biotechnology [37] due to their excellent surface activity, fine and stable foam, good biocompatibility, low/non-toxic, seldom irritation, easy biodegradation, and strong detergent. Also, such sugar-based surfactants would rather stay in the aqueous phase than adsorb on silica [3,4].

Besides polyethylene glycol monooalkyl ether (CnEo) [38], alkyl glycosides such as alkyl xylosides [32], alkyl polyglucosides (APG) [39], alkyl β-D-maltoside [38], and NBD-alkyl lactosides [40], are classic nonionic...
surfactants. Because of the unique function of hydrophilic glycosyl group, the aqueous solutions of the sugar-based surfactants are less temperature-sensitive than those of alkyl polyoxyethylene ether solutions although the relevant water solubility decreases continuously with the extension of hydrophobic chain length, and such results should hint that the corresponding glycosides would be more advantageous than the corresponding non-ionic alkyl polyoxyethylene ethers in certain fields of application. Unlike alkyl polyoxyethylene ethers and polyglycerol surfactants, alkyl glycosides surfactants such as dodecyl maltoside can be prepared as pure single-chemical species, so that it should be escaped from the serious issue of the mixtures with the various activity and more or less side products and even residual starting material. Furthermore, alkyl glycosides should be difficult to subject to oxidative degradation so that the related harmful immune response would be not elicited. Therefore, they can offer a potential alternative in the related therapeutic formulations, whether oral, nasal, anal and external use or injection [41].

However, for both complex APG and anomerically pure alkyl glycosides with long hydrophobic chains, their water solubility should be poor since their hydrophilicity should be low [42,43]. In this context, their applications would also be restricted to some content because of their low or no water solubility. Therefore, it would be eager to develop new surfactants with proper water solubility and excellent surface activity with long hydrophobic chains.

To the best of our knowledge, D-xylose should be the second most abundant monosaccharide with a reasonable low price after glucose because its natural polymer xylan is a renewable heterogeneous polysaccharide existing in the plant cell wall, accounting for about 15–35% of the dry weight of plant cells. As a major component of plant hemicellulose and a complex pentancarbose, D-xylose can be easily obtained from the agricultural wastes and other biomass such as corn, bagasse, wheat bran, and straw [37,43–45]. Thereof, we should make full of xylan, xylooligosaccharides and xylose to convert various value-added materials, functional food (for the growth of probiotic bacteria) [46,47], fuel [48,49], and other products [32,43,46–50].

However, compared with other alkyl monoglycosides, alkyl xylosides should not be suitable for hydrophilic surfactants since they were not water solubility with longer alkyl chain (n) due to their small hydrophilic sugar portion. For the hexoses such as glucose and galactose, they have a strong hydrophilic hydroxymethyl group, but xylose lacks such group so that xylose’s derivatives alkyl xylosides had poor since their hydrophilicity should be low [42,43]. In this context, their low or no water solubility. Therefore, it would be eager to develop new surfactants with proper water solubility and excellent surface activity with long hydrophobic chains.

As shown in Fig. 1, alkyl dioxymethyl α-D-xylosides (5a–5f) were readily prepared by the Helferich method through three-step reactions. First of all, with D-xylose (1) as raw material, acetylation was taken to afford 1,2,3,4-tetra-O-acetyl-D-xylopyranose (2) at the catalysis of anhydrous NaOAc. Next, alkyl dioxymethyl 2,3,4-tri-O-acetyl-α-D-xylosides (4a–4f) were readily synthesized by the coupling reaction of 2 and diethylene glycol monoether (3a–3f) with SnCl4 as the Lewis acid catalyst. Finally, alkyl dioxymethyl α-D-xyloside (5a–5f) was prepared through the deacylated process of 4a–4f. The detailed preparation and structural characterization were documented in the Supporting Information (SI).

3. Property

3.1. Hydrophilic-lipophilic balance (HLB) number and octanol-water partition coefficients (LogP) value

The HLB numbers of alkyl dioxymethyl α-D-xylosides (5a–5f) were calculated from Eq. (1) by the Griffin method [53–55].

\[
\text{HLB} = \frac{20X}{W} \quad (1)
\]

where X and W were the molecular mass of the hydrophilic portion and the whole molecular mass, respectively.

**Fig. 1.** Synthesis of alkyl dioxymethyl α-D-xylosides (5a–5f).
The LogP value of the synthetic alkyl dioxyethyl α-D-xyloside (5a-5f) was calculated by using ChemBioDraw (Ultra 14.0) to estimate their lipophilic character [53].

3.2. Solubility

The solubility of alkyl dioxyethyl α-D-xyloside (5a-5f) in water or ethanol was determined at room temperature (25 °C) with the described methods [52].

3.3. Surface tension

The surface tensions were measured at room temperature (25 °C) by using the BZY-2 full-automatic surface/interfacial tensiometer that was calibrated by double-distilled water. The aqueous solutions of alkyl dioxyethyl α-D-xylosides (5a-5e) were freshly prepared as a stock solution and then diluted to the desired concentration for each measurement. The Wilhelmy plate was rinsed with water, then the glassware was rinsed with water and washed once with the sample solution to be tested before testing. The surface tension was measured three times for each concentration to reduce the measurement error.

The critical micelle concentration (CMC) and the surface tension at the CMC were determined from the breakpoint of the plot of the surface tension concerning the logarithm of the concentration. The relevant surfactant surface excess concentration at the air-solution interface (Γmax) was calculated out by using the Gibbs adsorption isotherm equation (Eq. (2)) [52,56].

\[
\Gamma_{\text{max}} = - \frac{1}{2} \frac{303}{nRT} \frac{d\gamma}{d \log C}
\]

where \(\gamma\) was the surface tension, \(C\) was the surfactant concentration, \(T\) was the thermodynamic temperature (K), \(R\) represents the gas constant \((8.314 \text{ J·mol}^{-1}·\text{K}^{-1})\), herein, \(n = 1\) because alkyl dioxyethyl α-D-xylosides should be classified as a nonionic surfactant, and \(d\gamma/d\log C\) was the slope below CMC in the surface tension plots. The area occupied by the surfactant molecule at the air-solution interface \(A_{\text{min}}\) was calculated according to Eq. (3).

\[
A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}}
\]

where \(N_A\) is Avogadro's number \((6.02 \times 10^{23})\). Besides, the effectiveness of reducing surface tension \((\pi_{\text{mic}})\) was obtained by Eq. (4). The adsorption efficiency of reducing surface tension \((p_{C_{20}})\) was calculated by Eq. (5) [52].

\[
\pi_{\text{mic}} = \gamma_0 - \gamma_{\text{CMC}}
\]

\[
p_{C_{20}} = - \lg C_{20}
\]

Herein, \(\gamma_0\) represented the surface tension of the distilled water, \(\gamma_{\text{CMC}}\) was the surface tension of the aqueous solution at the CMC. \(C_{20}\) was the surfactant concentration required to reduce the surface tension by 20 mN·m⁻¹.

The standard free energy of micellization (\(\Delta G_{\text{mic}}\)) and surface adsorption free energy (\(\Delta G_{\text{ads}}\)) for the nonionic surfactants were calculated using the relevant equations (Eqs. (6) and (7)) [52,57].

\[
\Delta G_{\text{mic}} = RT \ln(C_{\text{MIC}})
\]

\[
\Delta G_{\text{ads}} = \Delta G_{\text{mic}} - \pi_{\text{CMC}} / \Gamma_{\text{max}}
\]

3.4. Foaming property

According to the literature [52,53], the foaming property of the aqueous solution of alkyl dioxyethyl α-D-xylosides (5a-5f) was determined at 25 °C. An aqueous solution of alkyl dioxyethyl α-D-xylosides (0.25% (w/w)) 10 mL was obtained and transferred to a 100-mL graduated cylinder with a plug. The initial volume of foam \((V_0)\) was recorded just after 60 s of intense shock, which evaluating the foaming performance according to the initial volume of foam. Just after the solution kept in a static state for 5 min, the foam volume \((V_5)\) was recorded, the foam stability was evaluated by Eq. (8) according to the foam disappearance rate (\(\nu\)).

\[
\nu = \frac{V_0 - V_5}{t} \text{ (cm}^3 \text{ s}^{-1})
\]

3.5. Emulsifying property

According to the literature [58], the emulsifying property of alkyl dioxyethyl α-D-xylosides (5a-5e) was measured at 25 °C. A series of aqueous surfactant solutions (0.25% (w/w)) were prepared. At first, a 20 mL aqueous solution of alkyl dioxyethyl α-D-xyloside was put into a 100-mL cylinder with a plug, and n-octane of 20 mL as the oil phase was added. The related mixture was strongly shocked for 60 s and kept in a static state for 1 h, and the volumes of the water layer, the emulsion layer, and the oil layer were recorded respectively. The emulsifying ability was determined according to the volume of the emulsion layer.

3.6. Thermotropic phase behavior

The thermal phase transition behavior of alkyl dioxyethyl α-D-xylosides was measured by polarizing optical microscopy (POM) during the heating and cooling process, and the rate of temperature change was controlled at 5 °C·min⁻¹. The phase transition temperature of alkyl dioxyethyl α-D-xylosides was observed by DSC [53].

3.7. Hygroscopicity

Approximately 1.00 g of each dried sample was placed in hermetic pots in the surround of the relative humidity \((RH = 81\% \text{ or } 43\%)\), the sample was weighed again after 2 h, 4 h, 6 h, 8 h, 12 h, 24 h, 48 h, 72 h, respectively. The hermetic pots were kept in an incubator with controlled temperature (25 °C). The hygroscopicity \((M)\) of alkyl dioxyethyl α-D-xylosides was expressed by Eq. (9) [55].

\[
M = \frac{M_t - M_0}{M_0} \times 100\%
\]

where \(M_0\) was the initial quality of samples, and \(M_t\) was the quality of samples after the test time.

4. Results and discussion

4.1. Preparation and structural characterization

In Fig. 1, with D-xylose (1) was used as the starting material, alkyl dioxyethyl α-D-xylosides (5a-5f) were readily prepared by a three-step reaction involving acetylation, stereoselective coupling with diethylene glycol monooether (3a-3f) and deacetylation. Herein, the Helfrich procedure was concisely used to get stereoselectively a series of protected α-D-xylosides (4a-4f). The corresponding chemical shift (\(\delta\)) (coupling constant) of the anomeric hydrogen (H-1) in CDCl₃ was 5.06 ppm \((J_{1,2} = 3.6 \text{ Hz})\) (4a). The data disclosed that the coupled compound was 1,2-cis α-anomer [51,53]. The protected α-D-xylosides (4a-4f) were deacetylated to obtain alkyl dioxyethyl α-D-xylosides (5a-5f) which were 1,2-cis α-anomers by the NMR spectroscopy [51,59].
4.2. Hydrophobic characteristics

The HLB number is introduced to be convenient for the explanation of the functional properties of various surfactants. The high HLB number should be ascribed to the hydrophilic surfactants, which would be handily used to construct spontaneously the oil-in-water (O/W) micellar microstructure by supramolecular self-assembly. Whereas the lipophilic surfactants would be considered to possess low HLB number, they would be applied to stabilize spontaneously water-in-oil (W/O) emulsions. In this paper, the related HLB numbers of alkyl dioxyethylenedioxyethyl α-D-xyllosides (5a-5f) were calculated by the Griffin method, and the results were listed in Table 2 [53-55].

From Table 2, the HLB numbers of alkyl dioxyethylenedioxyethyl α-D-xyllosides (5) were from 14.72 (n = 6) to 11.67 (n = 12) with increasing alkyl chain length (n). By making a sharp contrast with alkyl α-D-xyllosides (7), the HLB number of alkyl dioxyethyl α-D-xylloside (5a-5f) was bigger than the HLB number of alkyl α-D-xylloside (7a-7f) with the same alkyl chain length [53].

The logarithm of the partition coefficient between octanol-water (LogP) is often used to represent the molecular lipophilicity, which is an important parameter in many areas, including modeling pharmacological and toxicological properties, metabolism of molecules, the environmental fate of chemicals, aggregation of surfactants, detergency and biological and toxicological properties, metabolism of molecules, the environmental fate of chemicals, aggregation of surfactants, detergency and other functionality.

Table 1

| Glycoside (n) | a (6) | b (7) | c (8) | d (9) | e (10) | f (12) |
|-------------|------|------|------|------|-------|------|
| Glycoside shift (δ, ppm) (J1,2, Hz) of alkyl dioxyethyl β-D-xylloside (5a-5f) in solvent. | | | | | | |
| Chemical shift (J1,2) | 4.85 | 4.88 | 4.86 | 4.85 | 4.61 | 4.61 |
| solvent | D2O | D2O | D2O | D2O | DMSO-d6 | DMSO-d6/D2O |

(Table 1 continued)

Table 2

| Alkyl α-D-xylloside (n) | LogP | HLB | Water solubility | Alkyl dioxyethyl α-D-xylloside (n) | LogP | HLB | Water solubility |
|-------------------------|------|-----|-----------------|---------------------------------|------|-----|-----------------|
| 7a (6) | 0.60 | 12.73 | Soluble | 5a (6) | 0.29 | 14.72 | High |
| 7b (7) | 1.02 | 12.01 | Soluble | 5b (7) | 0.70 | 14.10 | High |
| 7c (8) | 1.43 | 11.37 | Low | 5c (8) | 1.12 | 13.54 | High |
| 7d (9) | 1.85 | 10.79 | Low | 5d (9) | 1.54 | 13.02 | Soluble |
| 7e (10) | 2.27 | 10.27 | Insoluble | 5e (10) | 1.96 | 12.54 | Soluble |
| 7f (12) | 3.10 | 9.37 | Insoluble | 5f (12) | 2.79 | 11.67 | Insoluble |

(The related coupling constants) of H-1 for the prepared 1,2-cis α-D-xyllosides (5a-5f) were 4.61–4.88 ppm (J1,2 = 3.6–3.7 Hz).

4.3. Interfacial property

The surface tension of different concentration of aqueous alkyl dioxyethylenedioxyethyl α-D-xyllosides (5a-5e) solution was measured by the BZY-2 full-automatic surface/interfacial tensiometer. However, the surface tension of dodecyl dioxyethylenedioxyethyl α-D-xylloside (5f) was not investigated because of its insolubility in water.

Fig. 4 presented the relationship between the surface tension (γ) and the concentration (C). Increasing the alkyl chain length resulted in decreasing the critical micelle concentration (CMC). The surface tension value (γCMC) firstly decreased and then increased with increasing the alkyl chain length at the CMC although their difference was not very obvious, and octyl dioxyethylenedioxyethyl α-D-xylloside (5c) possessed the lowest surface tension (27.26 mN m⁻¹) at its CMC. Compared with some fundamental interfacial adsorption parameters of the traditional alkyl β-D-xyllosides, the CMC values and γCMC values of the synthesized alkyl dioxyethylenedioxyethyl α-D-xyllosides were found to be less than that of alkyl D-xyllosides [43]. The results indicated that introducing the molecules involving the molecular transport properties, particularly intestinal absorption, and blood-brain barrier (BBB) penetration. However, in the virtual sugar-based surfactant library, they should also be helpful in the respect of fast and effective screening of water solubility, surface activity, bioavailability, and other functionality.
dioxoyethylene fragment indeed improved the surface-active properties of glycosides to some extent.

Table 3 listed the CMC, $I_{\text{max}}$, and $A_{\text{min}}$ values. First of all, the CMC values decreased gradually from $8.31 \times 10^{-4}$ mol·L$^{-1}$ (5a, n = 6) to $9.21 \times 10^{-5}$ mol·L$^{-1}$ (5e, n = 10). However, the $\gamma_{\text{mic}}$ values first decreased to the lowest, then increased with increasing the alkyl chain length, i.e. from 28.06 mN·m$^{-1}$ (5a, n = 6) to 27.25 mN·m$^{-1}$ (5c, n = 8) → 28.86 mN·m$^{-1}$ (5e, n = 10). For the short alkyl chain, for example, hexyl dioxoyethyl $\alpha$-D-xyloside (5a), more free energy was required to form micelles and thereby resulting in a higher CMC value ($8.31 \times 10^{-4}$ mol·L$^{-1}$) due to its small hydrophobic group which would stretch out and had in contact with water to some content. Furthermore, the $I_{\text{max}}$ values tended to increase from $4.93 \times 10^{-6}$ mol·m$^{-2}$ (5a, n = 6) to $6.64 \times 10^{-6}$ mol·m$^{-2}$ (5e, n = 10) with increasing the alkyl chain length. On the contrast with the $I_{\text{max}}$ values, there can be no doubt that the $A_{\text{min}}$ value showed a decreasing trend from $33.67 \AA^2$ (5a, n = 6) to $25.01 \AA^2$ (5e, n = 10) with increasing the alkyl chain length, which was just similar to the changing trend of the CMC value. Both of the $I_{\text{max}}$ and the $A_{\text{min}}$ values were a sign of the packing densities of the absorbed molecules at the air-solution interface. The larger $I_{\text{max}}$ value and the smaller $A_{\text{min}}$ value should correspond to the denser arrangement at the air-solution interface. It was disclosed that the molecular arrangement in longer alkyl chain $\alpha$-D-xyloside was much denser than that in shorter alkyl chain $\alpha$-D-xyloside. Because there should be the repulsive force between hydrophobic alkyl chain and water, the longer alkyl chain $\alpha$-D-xyloside would readily adsorb onto the air-solution interface, such surfactant molecule would have the better ability to maintain less contact with water via the strong hydrophobic interaction between the long hydrocarbon chains [60,61].

The obtained $p_{\text{C50}}$ values showed an increasing trend with increasing the alkyl chain length, which indicated that decyl dioxoyethyl $\alpha$-D-xyloside (5e) had the highest adsorption efficiency, and the related tendency to adsorb at the air-water interface was the greatest. But, the obtained $p_{\text{mic}}$ values revealed that first increased rapidly, then decreased with increasing the alkyl chain length, i.e. from $43.91$ mN·m$^{-1}$ (5a, n = 6) → $44.72$ mN·m$^{-1}$ (5e, n = 8) → $43.11$ mN·m$^{-1}$ (5e, n = 10). The standard free energy of micellization ($\Delta G_{\text{mic}}$) was negative for the prepared sugar-based nonionic surfactants (5a-5e), suggesting that the micellization process was spontaneous. Whereas surface adsorption free energy ($\Delta G_{\text{ads}}$) implied that the surfactants 5a-5e had a great ability to adsorb at the air-water interface. With the same alkyl chain length, their negative $\Delta G_{\text{mic}}$ values were deduced to be smaller than their negative $\Delta G_{\text{ads}}$ values, indicating that the adsorption was promoted more than the micellization. Besides, both of negative $\Delta G_{\text{mic}}$ values and negative $\Delta G_{\text{ads}}$ values increased with increasing alkyl chain length.
length, suggesting that the driving force of the micellization and/or the adsorption was derived from the hydrophobic alkyl moieties due to the hydrophobic interaction between alkyl chains, those results were powerfully supported by the pC<sub>10</sub> values, HLB numbers, and LogP values as described above [62].

4.4. Foaming property and emulsifying property

Generally speaking, the bigger the foaming volume (V<sub>f</sub>), the better the foaming performance; the slower the foam disappearing rate (v'), the better the foam stability. In addition, the foaming ability and the foam stability probably were closely related to each other since the surfactant molecules would adsorb on the liquid film to form strong or weak adsorption film to stabilize the various foam.

Fig. 5 plotted the foaming property of alkyl dioxyethyl α-D-xylosides (5a-5e). The results showed that their foam volume (V<sub>f</sub>) first increased significantly from the bottom to a high platform (62 mL, 5d (n = 9)), and then decreased slightly with increasing the alkyl chain length. Among these glycosides, 5d had the strongest foaming performance. Their foam disappearing rate (v') gradually decreased from the high point to almost zero (5a → 5d and 5e) with increasing the alkyl chain length. Although the foam of 5a vanished the fastest, 5d, and 5e were observed to have the minimum disappearance rate (v' = 0.01 mL·s<sup>-1</sup>). Therefore, both of 5d and 5e were considered to have good foaming property and foam stability in such homologous series.

For an emulsion system, the hydrophilicity and hydrophobicity of an emulsifier would have an important impact on the type of the emulsified layer. In general, when the HLB number of a used emulsifier is 3.5–6, the related emulsified layer should be the W/O type; however, the related emulsified layer should be the O/W type when the HLB number of a used emulsifier is 8–18. For alkyl dioxyethyl α-D-xylosides (5a-5e), their calculated HLB numbers were 14.72 → 12.54 and their LogP values were 0.29 → 1.96 with increasing the alkyl chain length (n = 6 → 10). Therefore, their emulsified layer should reasonably be oil-in-water (O/W) either in the toluene/water system or in the n-octane/water system with the related concentration of 0.25%.

As shown in Fig. 6, the emulsifying ability in the n-octane/water system was, on the whole, stronger than that in the toluene/water system although both systems had rather near emulsion layer for 5a (n = 6) with the short hydrophobic alkyl chain length. Their emulsion layers thickened monotonously with increasing the alkyl chain length, 5e (n = 10) had the best emulsifying ability in both systems. A shorter hydrophobic chain in such sugar-based surfactants would severely hinder the hydrophobic interactions between the surfactant and the oil phase at the interface at all, which further weakened the adsorption at the interface. On the contrary, a longer hydrophobic chain made the α-D-xyloside itself migrated more easily away from the bulk solution and went onto the interface to form readily a stronger interfacial film, preventing the discontinuous liquid particles of the dispersed phase in the emulsion layer from reaggregation [63]. However, the emulsifying ability would not keep strengthening with increasing the alkyl chain length because not only the appropriate HLB number, and LogP value but also the rational TPAS value, and water solubility should be demanded to certain extent. Excessive long hydrophobic alkyl chain made the related HLB number too small and LogP value too big with the same TPAS value, which would destroy the hydrophilic and hydrophobic balance in the O/W emulsion due to violating of the Bancroft rule [64–66].

4.5. Thermotropic liquid crystal property

The thermotropic liquid crystalline properties of the homologous series of alkyl dioxyethyl α-D-xylosides (5a-5f) with different alkyl chain lengths were investigated by the DSC and the POM, respectively.

Fig. 7 showed the DSC thermograms of decyl dioxyethyl α-D-xyloside (5e). Through the first cooling and the second heating processes at 5 °C·min<sup>-1</sup>, there were two-phase transition peaks, the first phase transition was the melting point (solid → liquid crystalline), the second phase transition was the clearing point (liquid crystalline → liquid). Also, the peak area of the melting point was much larger than that of the clearing point, so the enthalpy required from anisotropic liquid crystal phase to the isotropic liquid phase was rather low. The DSC thermograms of dodecyl dioxyethyl α-D-xylosides (5f) were similar to decyl dioxyethyl α-D-xyloside (5e). For nonyl dioxyethyl α-D-xylosides (5d), its peak of the melting point did not appear, and the peak of the clearing point was not obvious, but its liquid crystalline property was observed by the POM and the clear point temperature was measured as 38.9 °C. The specific data were listed in Table 4.

In Table 4, for decyl dioxyethyl α-D-xyloside (5e), its melt point (Mp) and clearing point (Cc) were —19.2 °C and 30.5 °C, respectively. The length of the hydrophobic tail should directly have an impact on the phase transition of both of Mp and Cc [67]. Nevertheless, the phase transition temperature of alkyl dioxyethyl α-D-xyloside (5f) was found to have its data. Indeed, the stronger the intermolecular hydrogen bonds network and the weaker the van der Waals interactions, in general. Therefore, both interactions would just probably jointly determine the related phase transition temperature. Finally, nonyl dioxyethyl α-D-xyloside (5d) had only one transition peak due to its shorter hydrophobic alkyl chain [67,68].

The POM was used to investigate the thermotropic liquid crystal behavior. For alkyl dioxyethyl α-D-xylosides (5a-5f), their liquid crystalline properties began to appear in the heating process as its alkyl chain length n ≥ 9. From Fig. 8, alkyl dioxyethyl α-D-xylosides (5d-5f) were observed to have birefringent structures that were considered as the characteristic focal-conic fan schlieren textures below T<sub>c</sub> during the cooling process [52,58]. Although 5f had overall ambiguous foci-conic domains, whereas the foci-conic domains of 5e were not big and their edges seemed very indistinct and even slight blurring to some content. In comparison, 5d displayed the biggest and rather sharp focal-conic and fan-shaped schlieren domains, suggesting that such texture might be attributed as the lamellar phase and/or smectic phase which was similar to the stated texture in the previous studies [68,69]. The formed focal-conic and fan-shaped schlieren texture was characterized by hyperbolic and elliptical lines of optical discontinuity. Such ordered liquid crystal structures could perhaps be arranged in sequence by self-assembly and self-organizing formations due to the driving forces involving strong intermolecular hydrogen bonding network and weak intermolecular dispersion force. The phenomenon would perhaps lead to open a new channel for the research and development of liquid crystal light valve and light-addressable sugar-based material with favorable biodegradability and biocompatibility.
4.6. Hygroscopicity

The hygroscopicity of alkyl dioxyethyl α-D-xylosides (5a-5f) was determined with the relative humidity (RH) of 43% and 81%. The experimental results were shown in Fig. 9.

As seen in Fig. 9, their hygroscopicity weakened gradually with the extension of alkyl chain length. On the whole, the moisture absorption capacity of the samples was close to the highest level after 48 h. The hygroscopic ability of 5a (n = 6) was the strongest. On the comparison, the hygroscopic ability of 5f (n = 12) was the weakest.

Compared with the different RH, it could also be seen that the absorption rate of alkyl dioxyethyl α-D-xylosides for RH = 81% was greater than that for RH = 43%. Such α-D-xylosides had the hygroscopic properties, the main reason was that both of glycosyl group and dioxyethylene fragment interacted with water by the intermolecular hydrogen bond network, so they could absorb efficiently the water from the environment. However, longer alkyl chain α-D-xylosides should have a low moisture absorption rate because of their smaller HLB number and bigger LogP value.

5. Conclusions

With D-xylose as the raw material, a series of 1,2-cis alkyl dioxyethyl α-D-xylosides (5a-5f) were stereoselectively synthesized via three-step reactions including the acetylation, the coupling reaction, and the deacetylation.

With the same TPSA value, their HLB number and water solubility decreased gradually with increasing alkyl chain length. Dodecyl dioxyethyl α-D-xyloside (5f) had not water solubility at all whereas hexyl dioxyethyl α-D-xyloside (5a) had strong water solubility. Also, compared with alkyl α-D-xyloside with the same alkyl chain length, alkyl dioxyethyl α-D-xylosides indeed improved the related water solubility due to the introduction of dioxyethylene fragment as the hydrophilic spacer to increase their TPSA value from 79.15 Å² (7) to 97.61 Å² (5). Their CMC values decreased with increasing the alkyl chain length. The CMC value of decyl dioxyethyl α-D-xyloside (5e) was as low as 9.21 × 10⁻³ mol·L⁻¹. Among them (5a-5e), octyl dioxyethyl α-D-xyloside (5e) had the lowest surface tension (27.25 mN·m⁻¹) at the CMC. Nonyl and decyl dioxyethyl α-D-xyloside (5d & 5e) had good foaming power and foam stability. Decyl dioxyethyl α-D-xyloside (5e) had the strongest emulsifying property either in the toluene/water system or in the octane/water system. Moreover, glycosides (5d) had the most stylish focal-conic fan schlieren texture. The hygroscopicity of alkyl dioxyethyl α-D-xylosides (5a-5f) decreased gradually with increasing alkyl chain length although hexyl dioxyethyl α-D-xyloside (5a) possessed the strongest hygroscopicity.

In a word, such interesting and charming alkyl dioxyethyl α-D-xylosides indeed improved the water solubility and surface activity with the hygroscopicity and the thermotropic liquid crystalline behavior. In order to make full of the renewable and sustainable sugar resources and activate their practical application as novel sugar-based surfactants, it is suggested that a lot of the related technology [37], surfactant activity [70,71], synergistic effect, phase behavior [72], functional property [16,17,73], tolerance performance, toxicity [36], biodegradability, biocompatibility [29,33], structural modification [26,68], and
application [74, 75] should be effectively investigated in the future in detail.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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