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Synthesis and Properties of Alkyl β -D-Galactopyranoside

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Abstract A series of alkyl β -D-galactopyranosides were prepared by the trichloroacetimidate method with Dgalactose and alcohols with different chain lengths as raw materials. Their solubility, surface tension, emulsification, foaming, wettability, thermotropic liquid crystalline properties, and thermal stability were investigated. Alkyl β -Dgalactopyranosides are soluble in water and ethanol, and the solubility decreases with increasing alkyl chain length. Decyl β -D-galactopyranoside was insoluble in water, but soluble in ethanol. Dissolution of alkyl β -D-galactopyranoside in water is an endothermic process with dissolution enthalpies greater than zero. Nonyl β -D-galactopyranoside had an excellent emulsifying property, better foaming ability and the best foam stability. The CMC values of alkyl β -D-galactopyranosides decrease with increasing of alkyl chain length. Alkyl β -D-galactopyranosides are thermally stable up to 270 °C. Alkyl β -D-galactopyranosides show the distinctive optical texture of a thermotropic liquid crystal smectic A type phase. Decyl β -D-galactopyranoside showed the strongest wettability.

Keywords Non-ionic surfactants · Synthesis · Interfacial science · Surface activity

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Introduction

With increasing concerns regarding environmental protection, much attention has been paid to environmentally friendly surfactants. The research and development of various green surfactants has become a hot topic [1–3]. Consequently, environmentally friendly surfactants are an attractive alternative to those that can potentially damage our environment. Among the various types of surfactants, alkyl glycosides or/and alkyl polyglycosides are becoming more and more attractive for commercial use because of their excellent properties such as high surface activity, excellent biodegradability, as well as antimicrobial activity [4, 5]. Moreover, they are low toxicity and readily obtained from renewable resources including sugars and alcohols [6].

surfactants contain two parts: the Sugar-based hydrophobic part, which can be an alcohol and the hydrophilic glycosyl moiety, which can be a monosaccharide, disaccharide, oligosaccharide, or polysaccharide [4, 7, 8]. They have a very wide application field, not only as the surfactants for detergents and emulsifiers, but also in food applications [4, 9-15]. In addition, they can also be used as drug carriers due to their peculiar physicochemical behavior including insensitivity to variations in temperature and salinity, which is very important in drug development. Alkyl galactosides as sugar-based surfactants possesses potential benefits in pharmaceutical development, and can be used to formulate conventional and advanced drug delivery systems, often being used as a substitute for conventional surfactants [16]. It is noteworthy that galactoside has special pharmaceutical value because of its high affinity towards the liver, specifically in the binding of hepatocytes [17]. Large scale industrial manufacture of glycoside surfactants has only recently become possible using different alcohols and a large

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number of carbohydrates such as glucose, galactose, maltose, dextrose, starch, cellulose and so on.

We believe that well-defined alkyl glycosides are necessary for basic scientific research in surface activity, thermal stability, molecular biology thermotropic liquid crystalline properties, and for practical and broader application in food, cosmetic products and pharmaceuticals [6, 18, 19]. Therefore, additional research is required to explore the stereoselective synthesis and physico-chemical properties of alkyl glycosides due to the potential polyfunctionality.

Alkyl glycoside surfactant molecules in aqueous or oil media are affected by two forces. One is the intermolecular repulsion forces between the hydrophobic alkyl chain and water or between their hydrophilic glycosyl components and oil. Another is the intermolecular attraction forces between their hydrophilic glycosyl components and water or between their hydrophobic alkyl chain and oil. The competition between the opposite intermolecular forces regulates the properties involving solubility, surface tension, emulsification, foaming, wettability, and so on.

Many scientists have carried out a variety of investigations since the first alkyl glucoside was synthesized and identified by Emil Fischer. As a kind of nonionic surfactant, alkyl glucosides are electrolyte tolerant to the various levels of naturally occurring hard water. The alkyl chain length has a far stronger influence on the critical micelle concentration (CMC) than the number of glycosyl units in the head group. The CMC values of octyl, decyl and dodecyl β -D-glucoside were found to be 25, 2.2 and 0.19 mmol L⁻¹ at 25 °C, respectively [4]. However, Castro reported that the CMC values of octyl and dodecyl β -Dglucoside were 10 and 2.3 mmol L⁻¹ at 25 °C [12]. Yakimchuk reported that the initial foam height of hexyl and octyl glucoside were 2 and 4 mm at 0.5 g L⁻¹ and 20 °C by the Ross-Miles method, respectively [13].

Hashim studied sugar stereochemistry (epimers and anomers), for example β -glucosides and α -galactosides, and collected the data for thermotropic phases and transition temperatures of α Gal-C₈ (Cr ~ 40 °C, S_A95 ± 4 °C Iso), αGlc-C₈ (Cr69 °C, S_A116 °C Iso), βGal-C₈ (Cr96 °C, S_A127 °C Iso) and *β*Glc-C₈ (Cr69 °C, S_A107 °C Iso), and pointed out that thermotropic (dry state) phase was perhaps the smectic A (S_A) for the glycosides composed of simple sugar and single alkyl chain [20]. Thermotropic mesophase of octyl β -D-glucopyranoside was found as a texture of Smectic A* phase, and the thermotropic data of octyl β -Dglucopyranoside, octyl α -D-glucopyranoside, octyl β -Dgalactofuranoside, decyl β -D-galactofuranoside, and decyl α-D-galactofuranoside were Cryst 67.1 °C SmecticA* 106.4 °C Iso Liq, Cryst 72.3 °C SmecticA* 116.3 °C Iso Liq, Cryst 96.0 °C SmecticA* 128.5 °C Iso Liq, Cryst 98.0 °C SmecticA* 155.0 °C Iso Liq, and Cryst 62.4 °C SmecticA* 107.0 °C Iso Liq, in respective [21]. In fact, researchers had studied transition temperature which was affected by factors such as variation of sugar ring, alkyl chain length, H-bond, polymorphism of crystal phases and/ or thermotropic liquid crystals, miscibility of different glycosides.

Xu researched the chemical synthesis, thermostability, and cytotoxicity of hydrocarbon ($-C_6H_{13}$ to $-C_{16}H_{33}$) and fluorocarbon ($-(CH_2)_2C_6F_{13}$) alkyl β -D-xylopyranoside surfactants [22]. The structure–property relationships for the alkyl β -D-glycosides such as solubility, CMC value, emulsifying, foaming, wettability, thermotropic liquid crystalline property, and thermal stability are generally affected by various factors such as sugar ring (furanoside or pyranoside, anomeric configuration), type (normal, branched, complex, substituted) and size of aliphatic chain, temperature, and so on. Some influences are regular, but others are relatively optional owing to complexity of influence of various factors.

A variety of methods for synthesis of alkyl glycosides have been reported [23, 24], such as the Koenigs-Knorr method and modification thereof, the Fischer glycosylation method and the trichloroacetimidate method. The Koenigs-Knorr method is a kind of mature method involving an S_N2 substitution at the anomeric carbon and proceeds stereoselectively with inversion of configuration. The method has been widely employed to prepare 1,2-*trans*-glycoside. In general, the catalysts or/and promoters are very expensive or highly poisonous heavy metal salts, for example the former is silver salt and the latter is mercury salt, and the poisonous heavy metal salts would inevitably cause serious environment pollution [25, 26].

The greatest disadvantage of the Fischer glycosylation method is that the reaction products contain a complex mixture of α - and β -anomers dominated by pyranoside via kinetically favored furanoside, since the glycosylation is an equilibrium reaction. Another is the formation of randomly linked glycoside oligomers owing to the polyfunctionality of the carbohydrate. Therefore, individual glycoside component is often difficult to isolate from the mixture of the Fischer glycosylation [4, 27].

The transglycosidation method (also called two-stage transacetalization method) may have the shortcoming since the composition and quality of the product are severely affected by catalyst, residual lower alcohol and the raw material carbohydrate, overreaction, degradation of glycoside, polymerization, and exact control of reaction time [28]. The trichloroacetimidate method can as well be used to synthesize a single configuration of 1,2-*trans*-glycosides with high selectivities, mainly β -anomers for glucose and galactose [27, 29].

The aim of this paper was to prepare a series of alkyl β -D-galactopyranosides with different alkyl chain lengths

and investigate their properties as surfactants. We first synthesized alkyl β -D-galactopyranosides by the trichloroacetimidate method involving five steps: acetylation, deacetylation at the position of C1, conversion to trichloroacetimidate, coupling with alcohol and deprotection (Fig. 1). Next, we investigated their properties in order to obtain the data of their solubility, surface activity, thermotropic liquid crystalline property, and thermal stability based previous literature on [20, 28–38].

Experimental Section

General Methods and Synthesis of Alkyl β -D-galactopyranosides

¹H-NMR spectra were recorded using an Avance 400 spectrometer (Bruker) for solutions in CDCl₃ or D₂O. Melting points were determined with a X-4 digital melting point apparatus (Dura Labs). Thermal stability was determined with a TGA Q50 thermogravimetric analyzer (TA Instruments). The liquid crystal properties were determined with a DM-LM-P polarization microscope (Leica). Surface tension was determined with DP-A precision digital pressure thermometer (Nanjing Sangli electronic equipment factory). Thin-layer chromatography (TLC) was performed on silica gel HF₂₅₄ with detection by charring with a mixture of 30 % (ν/ν) sulfuric acid and methanol. The purity of all raw materials are analytical pure or chemical pure.

The detailed synthesis and characterization of alkyl β -Dgalactopyranosides are shown in Supplementary Information.

Solubility Properties

Methods for determining the solubility of the prepared alkyl β -D-galactopyranosides in water, ethyl acetate and ethanol at room temperature (25 °C) were described by Li [30]. A certain amount of the glycoside was accurately weighed. Then the glycoside and a certain amount of solvent that was accurately measured and put into a test cup that was put on a shaking table. According to the situation of dissolution after 1 h, a small amount of solvent was added and the test cup was shaken further until the glycoside had dissolved completely. The solubility of the glycosides at 15, 20 and 30 °C was determined using the same method as described above.

Dissolution Enthalpy and Entropy

Using the same method described by Li [31], the solubility of the glycosides (**6a–6d**) was measured at temperatures of 15–30 °C, the solubility (x_A) and the temperature (T) were correlated using the Eq. 1:

$$\ln x_A = A + \frac{B}{T} \tag{1}$$

where *A* and *B* represent fitting parameters obtained from least squares fitting of the experimental data and *T* is the temperature in Kelvin. x_A represents the saturated solubility of glycoside in mole fraction units obtained from Eq. 2 where m_A and m_B represent the mass of solute and solvent, respectively.

$$x_A = \frac{m_A/M_A}{m_A/M_A + m_B/M_B} \tag{2}$$

The Dissolution Enthalpy $(\Delta_{sol}H)$ and Dissolution Entropy $(\Delta_{sol}S)$ Can Be Calculated as Follows



Fig. 1 Synthetic scheme for alkyl β -D-galactopyranoside

$$\Delta_{\rm sol}H = RT^2 \left(\frac{\mathrm{d}\ln x_{\rm A}}{\mathrm{d}T}\right)_p \tag{3}$$

$$\Delta_{\rm sol}S = RT \left(\frac{\mathrm{d}\ln x_{\rm A}}{\mathrm{d}T}\right)_p \tag{4}$$

The Eqs. 3 and 4 are deduced by the Gibbs–Duhem equation. The following Eqs. 5 and 6 are the simplified form from Eqs. 3 and 4.

$$\Delta_{\rm sol}H = -RB \tag{5}$$

 $\Delta_{sol}S = -RB/T \tag{6}$

where
$$B = -T^2 \left(\frac{\mathrm{d}\ln x_A}{\mathrm{d}T}\right)_p$$
.

Emulsifying Properties

Using the same method described by Liu [38], a 0.1 % aqueous solution of the glycoside was first prepared. At 25 °C, 20 mL of the solution and 20 mL of rapeseed oil or toluene were added to a measuring cylinder with a plug and vigorously shaken to mix. The emulsifying property was determined by the volume of emulsion ($V_{\rm ER}$ or $V_{\rm ET}$) or the clear aqueous phase ($V_{\rm wr}$ or $V_{\rm wt}$) separating from the emulsion after 1 h.

Foaming Properties

Using the same method described by Patist [32] and Liu [38], a 0.1 % aqueous solution of the glycoside was first prepared. At 25 °C, 10 mL of the solution was added into a 100 mL measuring cylinder with a plug. The foamability was evaluated by the initial foam height (H_0) after the solution was vigorously shaken for 1 min. After 5 min, the foam height (H_5) of the solution was also recorded. The foam stability was evaluated by the disappearance rate (υ) of bubble as Eq. 7.

$$v = (H_0 - H_5)/t \;(\text{mm/s})$$
 (7)

Interfacial Properties

The maximum bubble pressure method (MBPM) was used to study the surface tension of the glycoside in water at 25 and 35 °C [33, 34]. A series of different concentrations of the glycoside were prepared. The excess pressure value (Δ P) of the different solutions at 25 and 35 °C was measured, and the equilibrium surface tension (γ) of the glycosides in water was calculated at different concentration using the Laplace Eq. 8. *K* is a constant obtained using the bidistilled water as reference solution. The isotherm curve of the γ versus the concentration (C) of the solution was drawn, thus obtaining the critical micelle concentration (CMC) and the surface tension (γ_{CMC}). According to the linear fitting of the front section below CMC value in the isotherm surface tension curve, the slope $(d\gamma/dlnC)$ was estimated. The surface excess concentration (Γ_{max}) of single layer saturated adsorption, i.e., the maximum surface excess, could be calculated by the Gibbs Eq. 9, where *R* is the universal gas constant $(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$, *T* is the temperature (K) and n = 1 since the glycosides are nonionic surfactants. Thus the minimum cross-sectional area (packing area, A_{\min} , in Å²) per glycoside could be calculated by the Eq. 10, where N_0 is the Avogadro number.

$$\gamma = K\Delta P \tag{8}$$

$$\Gamma_{\max} = -\frac{1}{nRT} \cdot \frac{d\gamma}{d\ln C}$$
(9)

$$A_{\min} = \frac{1}{N_0 \Gamma_{\max}} \tag{10}$$

The effectiveness (π_{CMC}) represents the surface pressure at the CMC and is calculated by the difference between the surface tension of bidistilled water (γ_0) and that of the glycoside solution (γ_{CMC}) at the CMC as dscribed in by Eq. 11 [35].

$$\pi_{\rm CMC} = \gamma_0 - \gamma_{\rm CMC} \tag{11}$$

The standard free energy of micellization (ΔG_{mic}) and adsorption (ΔG_{ads}) of individual glycoside could be calculated using Eq. 12 [35] and Eq. 13 [36], respectively.

$$\Delta G \operatorname{mic} = RT \ln(\mathrm{CMC}) \tag{12}$$

$$\Delta G_{\rm ads} = \Delta G_{\rm mic} - \frac{\pi_{\rm CMC}}{\Gamma_{\rm max}}.$$
 (13)

Thermal Stability

The thermograms were obtained for the glycosides (3-5 mg) by a TGA (thermal gravity analysis) at a heating rate of 20 °C per min, using nitrogen as the shielding gas.

Thermotropic Phase Behavior

Using the same method described by Hashim [20], the thermotropic liquid crystalline phases of the galactopyranosides were observed by a OPM (optical polarizing microscope) at a heating rate of 3 °C per min. The phase transition temperatures were recorded during the course of heating, the changes were subsequently investigated at a cooling rate of 3 °C per min.

Wettability

Using the same method described by Li [37], a 0.1 % aqueous solution of the galactopyranoside was first

prepared. Then the sinking time of a canvas disc (Φ 35 mm, HG/T2575-94) in the solution was measured at 35, 45 and 55 °C.

Results and Discussion

Solubility Properties

The solubilities of alkyl β -D-galactopyranoside (**6a–6e**) in water, ethanol and ethyl acetate at 25 °C are shown in Fig. 2. The solubilities in water and ethanol all decrease with increasing alkyl chain length. The solubility in ethyl acetate first increased with increasing alkyl chain length for $6 \le n \le 8$ until a maximum value [1.05/100 g for **6c** (n = 8)] was reached, and subsequently, decreased with increasing alkyl chain length for $8 < n \le 10$. The solubility in ethanol is obviously higher than that in water or ethyl acetate for n = 6-10. The solubility in water is very low, 0.11/100 g for **6d**, and 0.05/100 g for **6e**. The latter is considered to be insoluble as its solubility was less than 0.1 g per 100 g of water. The solubility of decyl β -Dgalactopyranoside (**6e**, n = 10) in ethyl acetate was also very small, 0.14/100 g.

Dissolution Enthalpy and Entropy

The dissolution enthalpy $(\Delta_{sol}H)$ and dissolution entropy $(\Delta_{sol}S)$ were only investigated for **6a–6d** (n = 6–9) in water at 15, 20, 25 and 30 °C since **6e** (n = 10) is insoluble in water.

The relationship between the solubility $(\ln x_A)$ in water and temperature of alkyl β -D-galactopyranosides (**6a–6d**) is shown in Fig. 3. The solubility $(\ln x_A)$ decreases with the increase in the reciprocal of temperature (1/T) for each galactopyranoside (**6a–6d**) over the temperature range of



Fig. 2 Solubility of alkyl β -D-galactopyranoside in water, ethanol and ethyl acetate



Fig. 3 Solubility of alkyl β -D-galactopyranoside in water at different temperature

15–30 °C. The solubilities of hexyl galactoside (**6a**) and heptyl galactoside (**6b**) were rather large and the difference of their solubility (ln*x_A*) was small, but the solubilities (ln*x_A*) of octyl galactopyranoside (**6c**) and nonyl galactopyranoside (**6d**) were obviously decreasing with increase of alkyl chain length. The parameters *A* and *B* in Eq. (1) obtained from Fig. 3 are shown in Table 1. The dissolution enthalpy ($\Delta_{sol}H$) calculated from Eq. 5 is shown in Table 1. Since $\Delta_{sol}H > 0$, the dissolution process of alkyl β -D-galactopyranoside (**6a–6d**) in water is an endothermic process and the solubility became larger with increasing temperature.

The dissolution entropy $(\Delta_{sol}S)$ obtained from Eq. (6) decreased linearly with increases in temperature as shown in Fig. 4. The $\Delta_{sol}S$ value of hexyl β -D-galactopyranoside (**6a**) was the lowest. The $\Delta_{sol}S$ values of heptyl galactopyranoside (**6b**) and octyl galactopyranoside (**6c**) were increasing in turn. The $\Delta_{sol}S$ value of nonyl β -D-galactopyranoside (**6d**) reached the highest. As described by Kocherbitov [35], the phase transition is driven by enthalpy and entropy changes. Since $\Delta_{sol}H$ and $\Delta_{sol}S$ were both positive, the dissolution process is driven by entropy.

Emulsification and Foaming Properties

The emulsification and foaming properties were only investigated for alkyl β -D-galactopyranoside (**6a–6d**) (n = 6-9) since the solubility of **6e** (n = 10) in water was quite low. The emulsification properties are shown in Fig. 5. Hexyl β -D-galactopyranoside (**6a**) showed poor emulsification properties for both toluene and rapeseed oil as the aqueous phase and the organic phase returned to their original volumes ($V_{wt} = V_{wr} = 20$ mL) after 1 h. For toluene, alkyl β -D-galactopyranosides (**6b–6d**) exhibited improved emulsification properties as the alkyl chain length increases. Nonyl β -D-galactopyranoside (**6d**)

Table 1 Parameters of Eq. 1 and dissolution enthalpies $\Delta_{sol}H$ for different solutions

Glycoside	Α	В	$\Delta_{\rm sol} H ({\rm KJ} \cdot {\rm mol}^{-1})$
6a	6.78	-3826.05	31.81
6b	16.41	-6701.61	55.72
6c	26.37	-10217.18	84.95
6d	28.87	-11581.63	96.29



Fig. 4 Dissolution entropy of alkyl β -D-galactopyranoside (**6a–6d**) at different temperature



Fig. 5 Emulsifiability of alkyl β -D-galactopyranoside

reached the lowest value ($V_{\rm wt} = 13.5$ mL). For rapeseed oil, the alkyl β -D-galactopyranosides (**6b–6d**) exhibited a similar trend with emulsification properties improving with increase in alkyl chain length. Nonyl β -D-galactopyranoside (**6d**) again reached the lowest value ($V_{\rm wr} = 15.0$ - mL). These results suggest that nonyl β -D-galactopyranoside (**6d**, n = 9) interacts stronger with rapeseed oil through the longer alkyl chain of the glycoside itself.



Fig. 6 Foaming ability of alkyl β -D-galactopyranoside

The foam properties are shown in Fig. 6. Hexyl β -Dgalactopyranoside (6a) showed the weakest foaming ability $(H_0 = 4.0 \text{ mm})$. Heptyl β -D-galactopyranoside (**6b**) was slightly stronger than **6a.** Octyl β -D-galactopyranoside (**6c**) had the strongest foaming ability ($H_0 = 33.0$ mm). Nonyl β -D-galactopyranoside (6d) was down slightly to $H_0 = 25.0$ mm. The foam height (H_5) of the alkyl β -Dgalactopyranoside (6a-6d) after 5 min increased with alkyl chain length. For nonyl β -D-galactopyranoside (6d), its $H_5 = 22.0$ mm, rather near the foaming height $(H_0 = 25.0 \text{ mm})$. The foaming ability of octyl β -D-galactopyranoside (**6c**, n = 8) was the strongest $(H_0 = 33.0 \text{ mm})$, but the disappearance rate of the bubble was maximum, v = 0.05 mm/s, suggesting that the foam stability was the worst. The foaming ability of nonyl β -Dgalactopyranoside (6d, n = 9) was the stronger $(H_0 = 25.0 \text{ mm})$, but the disappearance rate of the bubble was the smallest, $v = 0.01 \text{ mm s}^{-1}$, suggesting that the foam stability was the best. Overall, nonyl β -D-galactopyranoside (**6d**, n = 9) was considered as excellent emulsifying property, better foaming ability and the finest foam stability.

Interfacial Properties

At low concentrations in water, alkyl glycoside molecules adsorb at the air/water interface and reduce the surface tension by the hydrophobic effect. The hydrophobic alkyl chains orientate towards air with the glycosyl head group in the water phase. In general, the lower the surface tension, the higher the surface activity. Because hexyl β -D-galactopyranoside (**6a**) displayed the worst emulsification and foaming properties, we did not measure its surface activity. Surface tension isotherms for the alkyl β -D- galactopyranosides (**6b–6e**) by the maximum bubble pressure method at 25 and 35 °C are shown in Fig. 7.

Figure 7 shows that alkyl β -D-galactopyranosides (**6b**-**6e**) could efficiently decrease the surface tension at 25 and 35 °C. The critical micelle concentration (CMC) of the galactopyranosides (**6b**-**6e**) decreases with increasing alkyl chain length. Meanwhile, the CMC values are higher at 25 °C than at 35 °C for same glycoside.

The $\gamma_{\rm CMC}$ values are roughly the same at 25 and 35 °C for the same glycoside. Linear fitting of the pre-micellar data was performed, and the $-d\gamma/d\ln C$ at 25 °C was calculated (11.72–10.57 mol m⁻²), which was smaller than the slope at 35 °C (13.04–12.21 mol m⁻²). The slope was substituted into the Gibbs equation to obtain the surface excess concentration values ($\Gamma_{\rm max}$) given in Table 2. The $\Gamma_{\rm max}$ values at 25 °C are smaller than the value at 35 °C for same glycoside, and decreases with increasing alkyl chain length.

The minimum cross-sectional area (A_{\min}) per surfactant molecule, i.e., the minimum surface area per alkyl glycoside (**6b–6e**) at the air/water interface at 25 °C was larger than the area at 35 °C for same glycoside. The A_{\min}



Fig. 7 Relationship between surface tension vs concentration of alkyl β -D-galactopyranoside (**6b–6e**) at 25 °C (*up*) and 35 °C (*down*)

values increase with alkyl chain length at both temperatures.

The higher the effectiveness of surface tension reduction at the CMC (π_{CMC}), the stronger the surface activity. The π_{CMC} values at 25 °C are larger than the values at 35 °C for the same glycoside, but the values first increased rapidly and then decreased slightly with increasing alkyl chain length. The effectiveness of decyl galactopyranoside (**6e**) was the highest at 25 and 35 °C suggesting it had the maximum surface activity.

The efficiency of surface tension reduction (pC_{20}) is given by the $-\log C$ required to reduce the surface tension of the solvent by 20 mN/m [35]. The larger the pC_{20} value, the stronger the ability to decrease surface tension. The pC_{20} value at 25 °C are larger than that at 35 °C for same glycoside, and increase with increasing alkyl chain length of the glycoside.

The negative value of the standard free energy of micellization (ΔG_{mic}) and adsorption (ΔG_{ads}) of individual glycoside at 25 and 35 °C imply that micelle (perhaps including vesicle formation) and surface excess formation are thermodynamically favored for alkyl glycosides (**6b**-**6e**). The absolute values of ΔG_{mic} and ΔG_{ads} at 25 °C are larger than the values at 35 °C for same glycoside, and increase with increasing alkyl chain length. Since the alkyl chain of the glycoside is hydrophobic, both adsorption and aggregation are entropy driven process. As a result, the longer the alkyl chain, the greater the entropic gain. Comparing ΔG_{mic} and ΔG_{ads} , the ΔG_{ads} values are larger than that of ΔG_{mic} and the tendency is stronger for the glycoside being adsorbed to the air–water interface rather than forming micelles.

Thermal Stability

The thermal decompistion of alkyl galactopyranosides was measured by thermogravmetric analysis. Figure 8 and Table 3 show the weight loss as a function of temperature. The temperature ranges of decomposition of alkyl β -D-galactopyranosides (**6a–6e**) were 274.3–360.1 °C, 300.6–340.5 °C, 284.1–320.1 °C, 303.0–344.7 °C and 294.2–326.4 °C in sequence. The rate of weight loss reached their maximum at 316.3, 327.7, 314.4, 333.4 and 321.1 °C. These results suggest that the maximum thermal temperature is below 270 °C.

Thermotropic Liquid Crystalline Properties

The cell membranes of living systems contain vast resources of liquid crystals which are often related to normal physiological function, plant defense, microbial infection and the occurrence of disease [21]. Alkyl β -D-galactopyranosides are monoalkylated galactosides. Sakya

<u>Classes</u> 1	- -	CMC			1/11C	Г	4	C	A.C.	10
Glycoside	°C	mmol L^{-1}	$\gamma_{\rm CMC}$ mN m ⁻¹	m_{CMC} mN m ⁻¹	dγ/dinC	$1 \text{ max} \times 10^{-6} \text{ mol m}^{-2}$	${\rm \AA}^{\rm A_{\rm min}}{\rm \AA}^2$	pC_{20}	$\Delta G_{\rm mic}$ KJ mol ⁻¹	ΔG_{ads} KJ mol ⁻¹
6b	25	17.54	39.0	32.97	-11.72	4.73	35.12	2.22	-10.02	-16.99
	35	28.72	39.2	31.18	-13.04	5.26	31.58	1.90	-8.80	-14.73
6с	25	16.23	31.0	40.97	-11.26	4.54	36.59	2.62	-10.21	-19.23
	35	21.11	32.0	38.38	-12.92	5.21	31.87	2.31	-9.56	-16.93
6d	25	3.21	32.0	39.97	-10.69	4.31	38.54	3.30	-14.23	-23.50
	35	5.34	34.4	35.98	-12.76	5.12	32.27	2.79	-12.97	-19.99
6e	25	1.00	30.0	41.97	-10.57	4.26	38.99	3.85	-17.12	-26.97
	35	2.10	31.2	39.18	-12.21	4.93	33.71	3.26	-15.28	-23.23

Table 2 Adsorption parameter at 25 and 35 °C



Fig. 8 TG curve of alkyl β -D-galactopyranoside (6a–6e)

reported that thermotropic phase behavior of seven monoalkyl glycosides. The data for *n*-octyl β -D-galactopyranoside was 96 °C S_{Ad} 127 °C [39]. Monoalkylated glycosides can exhibit different thermotropic phase behavior from branched chain glycosides. Hashim mentioned that monoalkylated glycosides could only exhibit a S_A (L_{α}) phase when heated, however, Guerbet glycosides could exhibit a variety of phases (L_{α}, H_{II} and Q_{II}) [40].

The thermotropic phase behavior of alkyl β -D-galactopyranoside (**6a–6e**) in the heating process was observed by using the polarization microscope and results are shown

Table 3 TG Parameters of alkyl β -D-galactopyranosides (6a–6e)

in Figs. 9, 10 and Table 4. Alkyl β -D-galactopyranosides (**6a–6e**) show thermotropic liquid crystallinity upon heating. β -D-Galactopyranosides (**6b–6e**) has a distinctively optical texture (a smectic A type phase) [21]. Alkyl β -Dgalactopyranosides (**6a–6e**) possessed sharp melting points (mp, a transition from a solid state to a liquid crystal phase) and sharp clearing points (C_p , a change from the liquid crystal phase into a liquid state), and the mesophase temperature ranges ($\Delta T = C_p$ –mp) rose gradually with increasing alkyl chain length [22].

Wettability

The wettability of alkyl β -D-galactopyranosides (**6a–6e**) solution was investigated at 35, 45 and 55 °C, and the results are shown in Table 5. Hexyl β -D-galactopyranoside (**6a**) and heptyl β -D-galactopyranoside (**6b**) did not wet the canvas disc after 12 h indicating that their wetting properties are the worst. The wettability of alkyl β -D-galactopyranoside (**6c–6e**) solution increased with increasing alkyl chain length. Decyl β -D-galactopyranoside (**6e**) showed the strongest wettability, and the sinking time (also called wetting time) of canvas disc in the solution fell within a very short range (52.7–94.3 s) at 35–55 °C. The wettability was affected by temperature, the higher the temperature, the shorter the sinking time and the better the wetting ability.

Glycoside	Temperature of initial decomposition/°C	Temperature of terminal decomposition/°C	Temperature of maximum decomposition rate/°C	Percent of weight loss/%
6a	274.3	360.1	316.3	93.6
6b	300.6	340.5	327.7	93.6
6c	284.1	320.1	314.4	93.2
6d	303.0	344.7	333.4	96.7
6e	294.2	326.4	321.1	69.7



Fig. 9 Texture of alkyl β -D-galactopyranoside characterized by OPM upon heating (a) and cooling (b)



Fig. 10 Phase transition temperature of alkyl β -D-galactopyranoside (6a-6e)

Table 4 Phase transition temperature of alkyl β -D-galactopyranosides

R	mp/°C	$C_{\rm p}/^{\circ}{\rm C}$	$\Delta T/^{\circ}C$
<i>n</i> -C ₆ H ₁₃	113.6	116.7	3.1
n-C ₇ H ₁₅	96.9	113.6	16.7
$n-C_8H_{17}$	98.9	131.6	32.7
<i>n</i> -C ₉ H ₁₉	94.3	146.2	51.9
$n-C_{10}H_{21}$	93.3	153.9	60.6
	R n-C ₆ H ₁₃ n-C ₇ H ₁₅ n-C ₈ H ₁₇ n-C ₉ H ₁₉ n-C ₁₀ H ₂₁	R mp/°C n-C ₆ H ₁₃ 113.6 n-C ₇ H ₁₅ 96.9 n-C ₈ H ₁₇ 98.9 n-C ₉ H ₁₉ 94.3 n-C ₁₀ H ₂₁ 93.3	Rmp/°C C_p /°C n -C ₆ H ₁₃ 113.6116.7 n -C ₇ H ₁₅ 96.9113.6 n -C ₈ H ₁₇ 98.9131.6 n -C ₉ H ₁₉ 94.3146.2 n -C ₁₀ H ₂₁ 93.3153.9

Conclusion

This paper reports on the synthesis and properties of a series of *n*-alkyl β -D-galactopyranosides. With D-galactose as raw material, a series of n-alkyl β -D-galactopyranosides

Table 5 Wettability of alkyl β -D-galactopyranoside (6a–6e) solution

	• • • •		
Glycoside	35 °C	45 °C	55 °C
6a	_	-	-
6b	-	_	_
6c	9.30 h	6.56 h	3.50 h
6d	32.4 min	26.3 min	16.5 min
6e	94.3 s	74.3 s	52.7 s

(**6a–6e**) were prepared by successive five steps including acetylation, selective deacetylation at the C1 position, conversion to glycosyl trichloroacetimidate, coupling with alcohols, and deprotection.

Their structure-property relationships including solubility, surface tension, emulsification, foaming, wettability, thermotropic phase behavior, and thermal stability were investigated. The solubility of alkyl β -D-galactopyranosides (6a-6e) in water is lower than in ethanol at 25 °C and solubilities decreased with increasing alkyl chain length in both solvents. Alkyl β -D-galactopyranosides (**6a–6d**) were soluble in water, but decyl β -D-galactopyranosides (6e) was insoluble in water. The solubility of alkyl β -D-galactopyranosides (6a-6e) in ethyl acetate shows a downward parabola with nonyl β -D-galactopyranosides (6d) being the most soluble. The dissolution enthalpy and entropy values of alkyl β -D-galactopyranoside (**6a–6d**) (n = 6-9) in water at 15-30 °C are larger than zero and increase with increasing alkyl chain length. Dissolution is an endothermic process and the solubility became larger with increasing solution temperature. In addition, the dissolution entropy values decrease linearly with increasing temperature. The alkyl β -D-

galactopyranoside (**6b–6d**, n = 7-9) showed moderate emulsifying and foaming properties, and the volume of the aqueous phase separated from the emulsion decreased with increasing alkyl chain length. Nonyl β -D-galactopyranoside (6d) showed the emulsifying property, foaming ability and foam stability. Alkyl β -D-galactopyranosides (**6b–6e**, n = 7-10) were able to decrease the surface tension of aqueous solution at 25 and 35 °C. The CMC decreases with increasing alkyl chain length, and is higher at 25 °C than at 35 °C for the same glycoside. The glycosides (6b-6e) could migrate more favorably to the interface than remain in the solution. Alkyl β -D-galactopyranosides (**6a–6e**, n = 6-10) were stability below 270 °C. Alkyl β -D-galactopyranoside (**6a–6e**, n = 6-10) possess melting points and sharp clearing points, and their mesophase temperature ranges rose gradually with increasing alkyl chain length. The β -D-galactopyranosides (6b-6e) had distinctively optical texture of a thermotropic liquid crystal smectic A type phase. The wettability of aqueous solution was affected by alkyl β -Dgalactopyranoside and temperature. Alkyl β -D-galactopyranoside (**6c–6e**, n = 8-10) show moderate wetting times. Decyl β -D-galactopyranoside (**6e**) shows the strongest wettability with a wetting time of 52.7 s at 55 °C.

Overall, the alkyl chain length was found to affect the property of galactoside significantly. Alkyl β -D-galactopyranosides (6a-6e) with different chain length showed different solubility in different solvents and their solubilities in water and ethanol both decrease with increasing alkyl chain length. The longer the alkyl chain, the stronger emulsifying ability for toluene and rapeseed oil. However, their foaming property exhibited different trend with increasing alkyl chain length. Octyl β -D-galactopyranosides (6c) exhibited the best foaming ability, but its foaming stability was the worst. Generally, nonvl β -Dgalactopyranosides (6d) exhibited the best foaming properties. The minimum cross-sectional area (A_{\min}) and CMC value increased with increasing alkyl chain length. The absolute values of ΔG_{ads} increased with increasing alkyl chain length, suggesting that the longer the alkyl chain length, the stronger the adsorption at the air-water interface. Their mesophase temperature ranges rose gradually and their wettability increased with increasing alkyl chain length.

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