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Selective Syntheses and Properties of Anionic Surfactants Derived from Isosorbide

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Abstract Two series of anionic surfactants (endo-5-Oalkyl isosorbide-2-O-propyl sulfonic acid sodium salt and exo-2-O-alkyl isosorbide-5-O-propyl sulfonic acid sodium salt) with straight alkyl chains (hexyl, octyl, decyl, and dodecyl) were synthesized from isosorbide derived from biomass, through steps of allylation, alkylation, and sulfonation. The selectivity and efficiency of the reactions were optimized by adjusting the solvent, catalyst, reactant molar ratio, and temperature. The product 2-O-allyl isosorbide was obtained with a yield of 81% and selectivity of 23:1 (endo: exo), and 2-O-alkyl isosorbide was obtained with a vield of 72% and selectivity of 24:1 (exo:endo). The synthesized anionic surfactants were characterized using the critical micelle concentration (CMC), surface activity, emulsion stability, foaming height, and the Turbiscan Stability Index. The CMC decreased with increasing alkyl chain length. The properties of endo form and exo form were compared.

Keywords Isosorbide · Surfactants · Surface tension · Critical micelle concentration · Foam stability

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Introduction

A major focus of bioenergy is using plant-derived biomass from crops such as corn, rapeseed, cassava, and sweet potatoes (Seo et al., 2009; Studer et al., 2009). Carbohydrates obtained from the biomass can be used to create surfaceactive compounds (i.e., surfactants) by linking an alkyl chain (hydrophobic tail group) to a hydrophilic head group (Stubenrauch, 2001). Generally, surfactants can be divided into three types: cationic, nonionic, and anionic. Cationic surfactants are adaptable for many applications, including antibacterials, antielectrostatics, bentonite inhibitors in oil fields, corrosion inhibitors for metals, and as structural and mesoporous templates. Nonionic surfactants such as alcohol ethoxylate (AE) and nonylphenol ethoxylate have useful properties such as low foam, high temperature sensitivity, high tolerance to water hardness, and good oily soil detergency. Meanwhile, anionic surfactants such as linear alkylbenzene sulfonate and alkyl ethoxylate sulfates (AES) have high foam, low temperature sensitivity, low tolerance to water hardness, and good particulate soil detergency (Raney, 1991). Anionic surfactants account for more than 60% of the total surfactant production globally.

Despite the effectiveness of traditional surfactants derived from petrochemicals, their possible toxicity is an environmental concern (Geng et al., 2017; Laudet-Hesbert, 2005). Alkylbenzene sulfonates, AES, and alkyl sulfates are anionic surfactants that are commonly used in detergents (Miller and Neogi, 2007), home and industrial cleaning agents, and in cosmetics and medicines. However, they also negatively impact the environment and have toxicity issues (Cserháti et al., 2002). In contrast, sugar-based surfactants, such as alkyl polyglucoside (APG, developed by Henkel Corp., Düsseldorf, Germany), sucrose esters, and sorbitan esters are eco-friendly, renewable, nontoxic, and

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biodegradable. As a result, the demand for them is growing despite their currently small scale of industrial production (Nickel et al., 2007). APG is derived using plant-based food resources (such as maize and coconuts) and compounded using fatty alcohols and glucose. It is also known to have a synergistic effect when used with anionic surfactants. However, because APG is currently priced higher than alkylphenolethoxylates, it is only used for specialized purposes such as cosmetics, medicines, and food (Roussel et al., 2005; Rybinski and Hill, 1998). Another example of sustainable, eco-friendly surfactant is fatty-acid methyl ester sulfonate, which can be easily synthesized using biological oils as raw material, and is widely used in the chemical industry on account of its great surface activity and selfassembly behavior (Jin et al., 2016).

Biomass is used to synthesize sorbitan esters such as the nonionic surfactants Tween and Span (through the single dehydration of sorbitol) and to produce isosorbide. Thus, research has been conducted on synthesizing related ionic surfactants. Isosorbide, or dianhydrohexitol, is a primary product of the starch industry: thousands of tons of it are produced by Roquette Frères (Zhu et al., 2008). Scheme 1 shows the different reactivity based on the geometry of the two hydroxy groups. The hydroxy group of C2 appears to be in the exo orientation, whereas that of C5 appears to be in the endo orientation, because of the fused tetrahydrofuran (THF) cycles (Abenhaïm et al., 1994; Claffey et al., 2004; Kumar and Ramachandran, 2005; Zhu et al., 2009). The reaction shown in Scheme 1 is used to prepare many compounds such as isosorbide nitrates (used to treat cardiac or vascular disease) and alkyl derivatives (used as solvents in pharmaceutical and cosmetic compositions) (Durand et al., 2009; Fenouillot et al., 2010; Lavergne et al., 2011).

In this study, a new method is proposed for the synthesis of isosorbide-based sulfonate anionic surfactants with hexyl, octyl, decyl, and dodecyl side chains. Compared with the traditional synthesis routes, the new reactions are more efficient, simpler, highly selective, and provide higher yield and comparable purity. The two series of synthesis products are endo-5-O-alkyl isosorbide-2-O-propyl sulfonic acid sodium salt (ENISS-*n*) and exo-2-O-alkyl isosorbide-5-O-propyl sulfonic acid sodium salt (EXISS-*n*) with n = 6, 8, 10, and 12. Their critical micelle concentration (CMC) value, surface tension,



foaming power, emulsifying capacity, and dispersion stability

were measured and compared with two commercial surfac-

Experimental Procedures

Materials

(SLES-3).

All the following chemicals were used as received: isosorbide (TCI, [Tokyo, Japan] 98%), 1-bromohexane (TCI, 98%), 1-bromooctane (TCI, 98%), 1-bromodecane (TCI, 98%), 1-bromodecane (TCI, 98%), potassium hydroxide (KOH; Samchun, [Pyeongtaek, Korea] 95%), sodium chloride (Samchun, 98%), toluene (Samchun, 99.5%), hexane (Samchun, 99.5%), ethyl alcohol (Samchun, 99.5%), methanol (Samchun, 99%), ethyl acetate (Samchun, 98%), sodium sulfite anhydrous (Samchun, 95%), tetrabutylammonium bromide (TBAB; Samchun, 99%), allyl bromide (Junsei, [Tokyo, Japan] 98%), and sodium bisulfite (Duksan, [Ansan, Korea] 95%).

Instruments

The purity of the synthesized compounds was ascertained by gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectroscopy. GC analyses were performed on an Agilent apparatus equipped with a DB-1HT column (J & W Scientific, Folsom, CA) (length: 30 m, ID: 0.32 mm), with nitrogen as gas vector and a FID (Flame Ionization Detector) detector. The GC conditions were: column pressure of 55 kPa, carrier gas flow rate of 2.2 mL min⁻¹, split ratio of 20:1, initial oven temperature of 60 °C, initial time of 3 min, ramp of 12 °C min⁻¹, final temperature of 360 °C, and final time of 30 min. The NMR spectra were recorded on Brucker AC spectrometers at 300.13 MHz for ¹H and 75.47 MHz for ¹³C.

The surface tension was measured using a DuNuoy platinum ring tensiometer (K100; Kruss, Hamburg, Germany) at room temperature (El-Shahawi et al., 2016; Kang et al., 2000; Zhou et al., 2013). The foaming power was tested at 25 °C with 25 mL of 0.1% aqueous surfactant solution in a 100-mL measuring cylinder. After shaking 20 times, the initial height of the foam was measured for foam height. After 5 min, it was used to assess the foaming power (Mohamed et al., 2005). For emulsion stability measurement, 20 mL of 0.1% aqueous solution of the surfactant and 10 mL of toluene were used. The emulsifying property at 25 °C was determined by the time it took for 80% of the aqueous volume to separate from the emulsion layer, starting immediately after the mixture was shaken 20 times (El Dib et al., 1988).

The stability of the emulsions was monitored by measuring the transmittance and backscattering of a pulsed

Scheme 1 The conversion of biomass to isosorbide

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Biomass Sorbitol HOHH

near infrared light ($\lambda = 880$ nm) using a Turbiscan Lab Expert system (Formulaction, Toulouse, France). The transmittance detector received the light passing through the dispersion in a Turbiscan tube at an angle of 180° with respect to the source, while the backscattering detector received that scattered backward by the dispersion at an angle of 45° . The stability of emulsions can be evaluated by the Turbiscan Stability Index (TSI) using Turbiscan EasySoft: the higher the TSI value, the less stable the emulsion (Chanamai et al., 2000; Kang et al., 2011; Mengual et al., 1999; Pu et al., 2016).

Synthesis and Purification of the Compounds

Synthesis of Endo-5-O-Hexyl Isosorbide-2-O-Propyl Sulfonic Acid Sodium Salt

Sodium salts of endo-5-*O*-alkyl isosorbide-2-*O*-propyl sulfonate and exo-2-*O*-alkyl isosorbide-5-*O*-propyl sulfonate are denoted as ENISS-*n* and EXISS-*n*, respectively. Here, n = 6, 8, 10, and 12 correspond to the hexyl, octyl, decyl, and dodecyl alkyl groups, respectively (Scheme 2). As all the ENISS-*n* and EXISS-*n* were prepared similarly, here we only give the procedure for one compound (endo-5-*O*-hexyl isosorbide-2-*O*-propyl sulfonic acid sodium salt [ENISS-6]) as a representative.

Isosorbide (7.3 g, 0.05 mol), KOH (2.8 g, 0.05 mol), and allyl bromide (6.05 g, 0.05 mol) were dissolved in toluene (20 mL). The solution was stirred at 65 °C. After 3 h, the residue was extracted with toluene and 5% NaCl solution. 5-*O*-Monoallyl isosorbide and 2-*O*-monoallyl isosorbide were observed in the extract by GC. This crude mixture was separated chromatographically on silica under pressure with ethyl acetate/hexane (10/90–90/10 v/v) as the eluent. The diallyl derivative was eluted first ($R_f = 0.21$ in 10/90 mixture), followed by isolating 2-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture), and then 5-*O*-monoallyl isosorbide ($R_f = 0.1$ in 10/90 mixture) ($R_f = 0.1$ in 10/90 mix

monoallyl isosorbide ($R_f = 0.04$ in 50/50 mixture). The purity of the compounds was checked by ¹H NMR spectra and GC. The synthesis and purification procedures were identical for 2-*O*-monoallyl isosorbide and 5-*O*-monoallyl isosorbide.

The purified 2-*O*-monoallyl isosorbide (9.31 g, 0.05 mol) was dissolved in hexane (30 mL) and heated to 65 °C under stirring. KOH (5.6 g, 0.1 mol), alkyl bromide (9.9 g, 0.06 mol), and TBAB (0.81 g, 0.05 mol) were then added, and the mixture was refluxed for 3 h. Afterward, the crude residue was extracted with hexane and 5% NaCl solution twice. The product was purified by distillation and obtained in the pure form after column chromatography on silica with elution by hexane/methanol (100:0 and 0;100 v/v). The purity of the compounds was identified using the ¹H NMR spectra and GC. The synthesis and purification procedures were identical for the other compound endo-5-*O*-alkyl-2-*O*-allyl isosorbide.

The sulfonation reaction of endo-5-*O*-alkyl-2-*O*-allyl isosorbide was as follows. Na₂SO₃ (2.16 g, 0.02 mol) and NaHSO₃ (2.03 g, 0.02 mol) were dissolved in distilled water (100 mL), and then ethyl alcohol (100 mL) was added under stirring. Endo-5-*O*-alkyl-2-*O*-allyl isosorbide (9 g, 0.04 mol) was added to the mixture and heated at 70 °C for 24 h. After evaporating the water and ethyl alcohol, the product was extracted with hexane and deionized water. The extracted product was dried in an oven overnight, and then washed with EtOH and filtered. The purity of the compounds was ascertained by ¹H NMR spectroscopy. The NMR spectra of ENISS-*n* and EXISS-*n* are given below.

The synthesized compounds ENISS-6 and exo-2-*O*-hexyl isosorbide-5-*O*-propyl sulfonic acid sodium salt (EXISS-6) were examined by the nuclear Overhauser effect for signal assignment. Irradiation of ENISS-6 at δ 3.49 (CH_{2a}) enhanced the intensity of the signal at δ 3.91 (H₆) by 4.45% and that at δ 3.64 (H_{1a}) by 2.05%, while



Scheme 2 The synthesis of anionic surfactants from isosorbide

irradiation of EXISS-6 at δ 3.54 (CH_{2a}) enhanced the intensity of the signal at δ 3.90 (H_{1b}) by only 3.86%.

ENISS-6 (yield: 99%) ¹H NMR (300 MHz, D_2O): δ 0.87 (3H, m, CH₃), 1.29–1.34 (6H, m, CH₂), 1.54–1.61 (2H, m, CH_{2b}), 1.96–2.03 (2H, m, CH_{2B}), 2.94–2.98 (2H, m, CH_{2C}), 3.49–3.59 (2H, m, CH_{2a}), 3.64–3.72 (3H, m, H_{1a}, CH_{2A}), 3.86–3.92 (1H, m, H_{1b}), 3.98–4.04 (2H, m, H₆), 4.11 (1H, m, H₂), 4.19–4.24 (1H, m, H₅), 4.64 (1H, m, H₃), and 4.73 (1H, m, H₄).

EXISS-6 (yield: 98%) ¹H NMR (300 MHz, D_2O): δ 0.87 (3H, m, CH₃), 1.29–1.31 (6H, m, CH₂), 1.55–1.58 (2H, m, CH_{2b}), 1.99–2.06 (2H, m, CH_{2B}), 2.96–2.99 (2H, t, CH_{2C}), 3.54–3.66 (3H, m, CH_{2a}, H_{1a}), 3.66–3.71 (1H, m, CH_{2A1}), 3.75–3.79 (1H, m, CH_{2A2}), 3.90–3.93 (1H, m, H_{1b}), 4.00–4.03 (2H, m, H₆), 4.06–4.10 (1H, m, H₂), 4.21–4.26 (1H, m, H₅), 4.62–4.63 (1H, m, H₃), and 4.75 (1H, m, H₄).

Synthesis of Endo-5-O-Octyl Isosorbide-2-O-Propyl Sulfonic Acid Sodium Salt

Endo-5-*O*-octyl isosorbide-2-*O*-propyl sulfonic acid sodium salt (ENISS-8) was synthesized using a method similar to that of ENISS-6, except that reaction step 2 used octyl bromide as a reagent and the reaction time of step 3 was 24 h under stirring. The final product was confirmed by NMR. Exo-2-*O*-octyl isosorbide-5-*O*-propyl sulfonic acid sodium salt (EXISS-8) also was synthesized in the same way with high purity and a yield of 98%.

ENISS-8 (yield: 98%) ¹H NMR (300 MHz, D_2O): δ 0.83 (3H, m, CH₃), 1.26–1.28 (10H, m, CH₂), 1.54–1.55 (2H, m, CH_{2b}), 1.94–2.01 (2H, m, CH_{2B}), 2.91–2.95 (2H, m, CH_{2C}), 3.40–3.45 (2H, m, CH_{2a}), 3.49–3.53 (3H, m, H_{1a}, CH_{2A}), 3.62–3.68 (1H, m, H_{1b}), 3.84–3.97 (3H, m, H₆, H₂), 4.03–4.06 (1H, m, H₅), 4.57–4.58 (1H, m, H₃), and 4.66 (1H, m, H₄).

EXISS-8 (yield: 97%) ¹H NMR (300 MHz, D_2O): δ 0.86–0.89 (3H, m, CH₃), 1.28–1.30 (10H, m, CH₂), 1.54–1.56 (2H, m, CH_{2b}), 1.99–2.06 (2H, m, CH_{2B}), 2.94–2.98 (2H, m, CH_{2c}), 3.48–3.57 (3H, m, CH_{2a}, H_{1a}), 3.62–3.68 (1H, m, CH_{2A1}), 3.74–3.79 (1H, m, CH_{2A2}), 3.91–3.93 (2H, m, H_{1b}, H₂), 3.95–3.97 (2H, m, H₆), 4.16–4.21 (1H, m, H₅), 4.52–4.53 (1H, m, H₃), and 4.67 (1H, m, H₄).

Synthesis of Endo-5-O-Decyl Isosorbide-2-O-Propyl Sulfonic Acid Sodium Salt

The synthesis of endo-5-*O*-decyl isosorbide-2-*O*-propyl sulfonic acid sodium salt (ENISS-10) was similar to that of ENISS-8, except that in step 2 decyl bromide was used as a reagent. The final product was confirmed by NMR. Synthesis of Exo-2-*O*-decyl isosorbide-5-*O*-propyl sulfonic acid

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sodium salt (EXISS-10) was conducted using the same method, with high product purity and a yield of 97%.

ENISS-10 (yield: 98%) ¹H NMR (300 MHz, D_2O): δ 0.84 (3H, m, CH₃), 1.18–1.25 (14H, m, CH₂), 1.54 (2H, m, CH_{2b}), 1.93–2.00 (2H, m, CH_{2B}), 2.89–2.93 (2H, m, CH_{2C}), 3.36–3.42 (1H, m, CH_{2a1}), 3.48–3.52 (1H, m, CH_{2a2}), 3.60–3.66 (3H, m, H_{1a}, CH_{2A}), 3.83–3.89 (2H, m, H₆), 3.92–3.95 (1H, m, H_{1b}), 3.99–4.04 (2H, m, H₂, H₅), 4.55–4.59 (1H, m, H₃), and 4.64–4.70 (1H, m, H₄).

EXISS-10 (yield: 97%) ¹H NMR (300 MHz, D₂O): δ 0.82–0.84 (3H, m, CH₃), 1.25–1.30 (14H, m, CH₂), 1.53 (2H, m, CH_{2b}), 1.95–2.03 (2H, m, CH_{2B}), 2.90–2.94 (2H, m, CH_{2C}), 3.45–3.53 (3H, m, CH_{2a}, H_{1a}), 3.55–3.67 (1H, m, CH_{2A1}), 3.70–3.76 (1H, m, CH_{2A2}), 3.91 (1H, m, H_{1b}), 3.94–3.96 (2H, m, H₆), 3.97–3.98 (1H, m, H₂), 4.10–4.17 (1H, m, H₅), 4.47–4.48 (1H, m, H₃), and 4.63–4.65 (1H, m, H₄).

Synthesis of endo-5-O-dodecyl Isosorbide-2-O-Propyl Sulfonic Acid Sodium Salt

Endo-5-*O*-dodecyl isosorbide-2-*O*-propyl sulfonic acid sodium salt (ENISS-12) was prepared using the same 2-step reaction as for ENISS-8, using dodecyl bromide as a reagent. The final product was confirmed by NMR. The synthesis of exo-2-*O*-dodecyl isosorbide-5-*O*-propyl sulfonic acid sodium salt (EXISS-12) was also conducted using this method with high product purity, and the yield was 97%.

ENISS-12 (yield: 97%) ¹H NMR (300 MHz, D₂O): δ 0.81 (3H, m, CH₃), 1.24–1.28 (18H, m, CH₂), 1.54 (2H, m, CH_{2b}), 1.95–1.98 (2H, m, CH_{2B}), 2.89–2.92 (2H, m, CH_{2C}), 3.37–3.41 (1H, m, CH_{2a1}), 3.48–3.51 (1H, m, CH_{2a2}), 3.62–3.63 (3H, m, H_{1a}, CH_{2A}), 3.86–3.88 (2H, m, H₆), 3.92–3.94 (1H, m, H_{1b}), 3.98–4.01 (2H, m, H₂, H₅), 4.54–4.55 (1H, m, H₃), and 4.64 (1H, m, H₄).

EXISS-12 (yield: 96%) ¹H NMR (300 MHz, D₂O): δ 0.82–0.84 (3H, m, CH₃), 1.25–1.28 (18H, m, CH₂), 1.53 (2H, m, CH_{2b}), 1.97–2.01 (2H, m, CH_{2B}), 2.90–2.94 (2H, m, CH_{2C}), 3.44–3.52 (3H, m, CH_{2a}, H_{1a}), 3.57–3.63 (1H, m, CH_{2A1}), 3.70–3.74 (1H, m, CH_{2A2}), 3.88–3.90 (1H, m, H_{1b}), 3.93–3.96 (2H, m, H₆), 3.98 (1H, m, H₂), 4.09–4.14 (1H, m, H₅), 4.46–4.47 (1H, m, H₃), and 4.63–4.71 (1H, m, H₄).

Results and Discussion

Synthesis of Endo-5-*O*-Alkyl Isosorbide-2-*O*-Propyl Sulfonic Acid Sodium Salt

Allylation of isosorbide was carried out at 65 °C by mixing isosorbide, allyl bromide, and a base in a 1/1/1 M ratio in a

suitable solvent, resulting in a product mixture of monomer 2-O-allyl isosorbide (A), monomer 5-O-allyl isosorbide (B), and dimer 2,5-O-diallyl isosorbide (C) (Scheme 3). The reaction solvent was dimethylsulfoxide (DMSO), toluene, cyclohexane, THF, or distilled water; and the base was sodium hydroxide, KOH, or lithium hydroxide (Table 1). The goal was to find the reaction conditions that selectively formed A and avoided the formation of C. The reaction employing KOH and DMSO was carried out at a reaction temperature of 25 °C and completed after 5 h, yielding 20.8% A, 14.6% B, and 4.8% C. The same reaction at 65 °C did not progress after 3 h, yielding 33.7% A, 13% B, and 8% C; and that at 90 °C did not proceed further after 5 h, resulting in 2.6% A, 2.5% B, and 6.7% C. The products were analyzed using NMR and GC. A fast reaction rate was observed in the initial neat reaction. However, the reaction did not proceed further due to solid product formation. A low yield of A (2-33%) was obtained when using lithium hydroxide or sodium hydroxide as the base in various solvents, while it was 15-81% when using KOH. The highest selectivity and efficiency were observed when using KOH in toluene (81% A, 3.5% B, and 5% C). The salt affected the reactivity and selectivity after 3 h of reaction at 65 °C. These data were compared with the results obtained by Abenhaïm's group. They performed the reaction in DMSO at 90 °C for 18 h, resulting in 3% A, 69% B, and 6% C. In comparison, our new method is faster, uses milder conditions, and has higher selectivity for the desired product. The regioselectivity of the base was in the order of $K^+ > Li^+ > Na^+$ regardless of the solvent. As a result, the regioselective reaction of monoallyl isosorbide could yield a maximum ratio of A:B = -23:1 when using allyl bromide and KOH in toluene.

Next, 5-*O*-hexyl-2-*O*-allyl isosorbide was synthesized with various alkyl groups using the previously synthesized 2-*O*-allyl isosorbide. The reaction was performed in DMSO, toluene, or hexane, with respective yields of 34%, 68%, and 98%.

Endo-5-*O*-alkyl-2-*O*-allyl isosorbide from the previous step was converted into the sodium salt of endo-5-*O*alkyl isosorbide-2-*O*-propyl sulfonate, by adjusting the pH to 7 at 50 °C using Na_2SO_3 and $NaHSO_3$. The reaction was carried out for 5–24 h (depending on the length

Table 1 Effects of solvent and base on the allylation of isosorbide

Solvent	Base	A (%)	B (%)	C (%)	Isosorbide (%)
Dimethyl sulfoxide	KOH	15	16	8	61
	LiOH	3	16	1	70
	NaOH	2	7	0	91
Toluene	KOH	81	3.5	5	10.5
	LiOH	33	29	2	36
	NaOH	22	10	0	68
Cyclohexane	KOH	47	15	16	22
	LiOH	31	19	8	42
	NaOH	7	2	0	91
THF	KOH	29	17	34	20
	LiOH	20	10	12	58
	NaOH	10	7	0	83
Neat	KOH	32	15	23	27
	LiOH	38	27	5	30
	NaOH	43	14	9	34
Distilled water	KOH	27	10	12	51
	LiOH	24	17	1	58
	NaOH	10	8	2	80

Isosorbide/AllylBr/base = 1:1:1, 3 h, 65 °C, 10 mL of solvent.

of alkyl chains), and a yield of 99% was obtained in all cases.

Synthesis of Exo-2-O-Alkyl Isosorbide-5-O-Propyl Sulfonic Acid Sodium Salt

An experiment was carried out to synthesize monoalkyl isosorbide selectively. The reaction was performed at 90 °C using isosorbide, 1-bromoalkane, a base, and TBAB in a molar ratio of 1:2:4:0.05. A product mixture of monomers D and E and dimer F was obtained (Scheme 4). DMSO, toluene, or hexane was used as the solvent, while sodium hydroxide, KOH, and lithium hydroxide were used as the base (Table 2). The reaction using lithium hydroxide in hexane at reflux temperature occurred slowly, yielding 16% D, 30% E, and 0% F. The reaction did not proceed further after 3 h. Reaction in toluene showed no apparent selectivity (20% D, 26% E, and 10% F). However, selective synthesis could be carried out in DMSO for 3 h at



Scheme 3 Allylation of isosorbide

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Scheme 4 Alkylation of isosorbide

reflux temperature, resulting in 72% D, 3% E, and 6% F. The products were analyzed using GC and NMR. Although a fast reaction rate was observed initially in the neat reaction, the reaction did not proceed further due to solid product formation. Thus, a solvent was used. The reaction using sodium hydroxide proceeded more slowly than those using KOH or lithium hydroxide. In terms of selectivity and reaction rate, the effect of lithium hydroxide was more significant than KOH ($Li^+ > K^+ > Na^+$). The reaction between alkyl bromide and lithium hydroxide in DMSO at 90 °C produced 72% D, 3% E, and 6% F (D:E ratio of 24:1) after 3 h, showing the highest selectivity. Zhu et al. performed an alkylation of isosorbide using lithium hydroxide in DMSO, and obtained 5% D and 32% E after separation and purification (Jin et al., 2016). Abenhaïm's group performed this reaction with lithium hydride in Dimethylformamide (DMF) with ultrasound, and the reaction yielded 5% D, 60% E, and 15% F. Owing to the effects from the solvent, the bases showed a selectivity order of $Li^+ > Na^+ > K^+$ (Abenhaïm et al., 1994). Accordingly, we concluded that lithium hydroxide had the highest selectivity.

In the second step, the previously synthesized 2-O-alkyl isosorbide was reacted with allyl bromide and KOH through a neat reaction at 65 °C to synthesize 2-O-alkyl-5-O-allyl isosorbide. A high-purity product was obtained after filtration. The final product was obtained by sulfonation.

Surface Activity

One important feature of surfactant solutions is the formation of micelles above a specific concentration. The CMC of ENISS-*n* and EXISS-*n* was determined by measuring the surface tension at 25 °C. Plots of surface tension against the logarithm of concentration are shown in Figs. 1 and 2 for ENISS-*n* and EXISS-*n*, respectively. For ENISS*n* with n = 6, 8, 10, and 12, the CMC was 1.62×10^{-2} , 4.46×10^{-3} , 7.76×10^{-4} , and 1.12×10^{-4} mol L⁻¹, and the surface tension was 29.78, 25.81, 27.24, and 29.95 mN m⁻¹, respectively. For EXISS-6, EXISS-8, EXISS-10, and EXISS-12, the CMC was 7.24×10^{-3} , 1.99×10^{-3} , 7.94×10^{-4} , and 4.17×10^{-4} mol L⁻¹, and the surface tension was 27.99, 26.91, 28.53, and 31.61 mN m⁻¹,

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respectively. For both the ENISS-n and EXISS-n series, the CMC decreased as the chain length of the alkyl group increased. There is a known linear relationship between the CMC and the carbon number, n, of the alkyl group within a series of the surfactants:

$$\log CMC = A - Bn \tag{1}$$

where A is an empirical constant dependent on the temperature and hydrophilicity, B is a constant with saturated alkyl chains and a single ionic head group, and n is the number of carbon atoms of the alkyl chain. The values of A and B for ENISS-n were determined to be -1.52 and 0.36, and those for EXISS-n were -2.07 and 0.20, respectively (Fig. 3).

The maximum surface excess (Γ_{max}) and the minimum area per molecule (A_{min}) of the surfactant at the interface are calculated using Eq. (2) (El-Shahawi et al., 2016; Kang et al., 2000; Zhou et al., 2013):

$$d\gamma/d\mu = \partial\gamma/\partial lnC = -2\Gamma RT$$
(2a)

$$\Gamma_{\max} = (1/2RT)(-d\gamma/dlnC)_T = (4.606RT)^{-1}(-\partial\gamma/\partial logC)_T$$

$$A_{\min} = 10^{14} / (N\Gamma_{\max}) \tag{2c}$$

where *R* is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), T is the temperature in Kelvin, $(-\partial \gamma / \partial \log C)_T$ is the gradient of the surface tension *versus* log *C*, and *N* is Avogadro's number (6.023 × 10²³). According to Table 3, the A_{\min} values were 1.21, 1.10, 1.02, and 0.81 nm² for ENISS-*n* and 1.23, 1.16, 1.06, and 0.92 nm² for EXISS-*n* with n = 6, 8, 10, and 12, respectively. It was observed that Γ_{\max} gradually decreased and A_{\min} was noticeably reduced, as the hydrophobic alkyl chain became longer. The difference in A_{\min} between the endo and the exo forms may be attributed to their different molecular structures (planar and bent).

It is well known that the Krafft temperature depends on the alkyl chain length, the type of polar head, the nature of counterions, and the head group interaction including hydrogen bonding. The determined Krafft temperatures (1% aqueous surfactant solution) for n = 6 and 8 are below freezing temperature; whereas those of ENISS-12 and EXISS-12 are 10 and 35 °C, respectively. These observations show that the Krafft temperature depends on the alkyl

Solvent and base effect					
Solvent	Base	D (%)	E (%)	F (%)	Isosorbide (%)
Dimethyl sulfoxide	КОН	18	19	30	33
	LiOH	72	3	6	19
	NaOH	0	0	0	100
Toluene	KOH	0	0	5	95
	LiOH	20	26	10	43
	NaOH	3	4	0	93
Hexane	KOH	0	0	9	91
	LiOH	16	30	0	54
	NaOH	1	0	9	90

Table 2 Effects of solvent and base on the alkylation of isosorbide

Isosorbide/1-bromoalkane/base/TBAB = 1:2:4:0.05, 3 h, 90 °C, 10 mL of solvent.

chain length due to the isomeric effects on the molecular properties and on the isosorbide synthon in aqueous solutions. In this case, the structural effect imposed by the V-shaped isosorbide moiety should be considered. EXISS-*n* has more efficient packing in the solid state, leading to a strong tendency for crystallization. It is not compensated by an increase in hydrophilicity, and thus leads to a higher Krafft temperature.

Foaming Test

A simple test was performed to assess the foaming power. Five minutes after shaking the 0.1% surfactant solution, the height of the foam was measured (Mohamed et al., 2005) to be 13, 46, 48, and 49 mL for ENISS-6, ENISS-8, ENISS-10, and ENISS-12 and 9, 42, 45, and 47 mL for EXISS-6, EXISS-8, EXISS-10, and EXISS-12, respectively (Table 4). Overall, the foam height in EXISS-*n* was



Fig. 1 Surface tension *versus* concentration for the four isosorbide derivatives ENISS-6 ■, ENISS-8 □, ENISS-10 ●, and ENISS-12 ○



Fig. 2 Surface tension *versus* concentration for the four isosorbide derivatives EXISS-6 ■, EXISS-8 □, EXISS-10 ●, and EXISS-12 ○

2–4 mL lower than in the corresponding ENISS-*n*. Except ENISS-6 and EXISS-6, all other synthesized surfactants had a foam height above 40 mL. For reference, the foam height of the general surfactant LAE-9 was reduced from 39 to 36 mL after 5 min, while that of SLES-3 remained at 21 mL. From the comparison with LAE-9 and SLES-3, the foam heights of the newly synthesized surfactants (except ENISS-6 and EXISS-6) after 5 min were significantly higher (by 21–27 mL).

Emulsion Stability

The emulsion stability was assessed by the time it takes for a mixture containing 0.1% surfactant, toluene, and water to recover 80% of the aqueous layer at 25 °C (El Dib et al., 1988). The measured time for ENISS-n increased with the carbon length, with the respective times of ENISS-6, ENISS-8, ENISS-10, and ENISS-12 being 140, 244, 380, and 478 s. As the alkyl chain length increased from 6 to 12, the emulsion stability increased from 140 to 478 s. The emulsion stability time for EXISS-6, EXISS-8, EXISS-10, and EXISS-12 was 75, 208, 282, and 383 s, respectively. Notably, EXISS-6 showed much lower emulsion stability compared with other surfactants. As the carbon chain length increased, the time taken to recover 80% of the aqueous layer increased from 75 to 383 s. Therefore, the emulsion stability is twice as high for ENISS-6 (140 s versus 75 s) than that for EXISS-6. The stereostructural differences between the endo and exo forms of the molecule have an effect: excluding ENISS-6 and EXISS-6, the emulsion stability of ENISS-n is 40–100 s better than EXISS-n. The common surfactant LAE-9 took 125 s and SLES-3 took 181 s for the emulsion to stabilize. In comparison, the surfactants prepared in this study with eight or more carbon atoms showed >100 s difference compared with



Fig. 3 Cologarithm of the CMC *versus* carbon chain for the surfactants ENISS- $n \blacksquare$ and EXISS- $n \spadesuit (n = 6, 8, 10, \text{ and } 12)$

LAE-9 and SLES-3, indicating better emulsion stability (Table 4).

Finally, detailed Turbiscan device measurements were carried out to assess the emulsion stability. In Turbiscan measurements, the particles in a sample at a high concentration produce backscattered light from a light source. When the sample has a low concentration, the emulsion stability is analyzed by measuring the transmitted light intensity as a function of time (Chanamai et al., 2000; Kang et al., 2011; Mengual et al., 1999; Pu et al., 2016). Figures 4 and 5 show the graphs of light backscattering and transmission measured in 25 s intervals for 30 min. After 15 min of stirring, a clear bottom layer was observed in the sample tube, and the transmission became stronger with time. The sample was divided into three layers: the bottom, middle, and top. The TSI was calculated every hour for 6 h. The backscattering data changed according to the height of ENISS-6, indicating that the backscattering decreased because of the lower concentration in the bottom layer during 0-30 min of the measurement, leading to a clearer layer. In the middle layer of the sample, coagulation occurred due to the overall decrease in stability. In the top

Table 4 Foaming and emulsion tests for the isosorbide derivatives ENISS-*n*, EXISS-*n*, LAE-9, and SLES-3 at 25 $^{\circ}$ C

	Surfactant	Foaming power (vol, mL)		Emulsion life time (80% destroyed) (s)
		Initial	After 5 min	
ENISS-n	ENISS-6	18	13	140
	ENISS-8	49	46	244
	ENISS-10	52	48	380
	ENISS-12	53	49	478
EXISS-n	EXISS-6	12	9	75
	EXISS-8	45	42	208
	EXISS-10	49	45	282
	EXISS-12	51	47	383
	LAE-9	39	36	125
	SLES-3	21	21	181

layer, backscattering decreased because when the concentration surpasses the saturation point, light does not distinguish between individual particles and "sees" the sample as one large particle, and the resultant packed creaming decreases the backscattering. In some parts of the top layer, the backscattering first decreased and then increased. This is known as the wall effect, in which light is reflected by the walls of the tube and re-enters as backscattered light even when there is a clear separation of the sample (Fig. 4). As the carbon chain length of ENISS-n increased, backscattering decreased in the bottom layer, and the TSI gradually decreased with time and n.

Figure 5 shows that the concentration in the bottom layer decreased with time. Thus, in the case of EXISS-6, this layer became clear. As the bottom layer became clear, a small decrease in the middle layer indicated coagulation. In the top layer, backscattering decreased due to packed creaming, although such coagulation effect did not occur as much as in ENISS-6. For EXISS-*n*, the backscattering decreased as the carbon chain length increased, and the TSI values decreased with time. At 6 h, the TSI values of ENISS-*n* were 107.5, 42.1, 30.1, and 27.6, and those of

	Surfactant	T Krafft (°C)	$\gamma_{cmc} \ (mN \ m^{-1})$	CMC (mol L^{-1})	$\Gamma_{\rm max} \ ({\rm mol} \ {\rm cm}^{-3})$	$A_{\min} (\mathrm{nm}^2)$
ENISS-n	ENISS-6	<0	29.78	1.62×10^{-2}	1.37	1.21
	ENISS-8	<0	25.81	4.46×10^{-3}	1.51	1.10
	ENISS-10	4	27.24	7.76×10^{-4}	1.63	1.02
	ENISS-12	10	30.63	1.12×10^{-4}	2.06	0.81
EXISS-n	EXISS-6	<0	27.99	7.24×10^{-3}	1.35	1.23
	EXISS-8	<0	26.91	1.99×10^{-3}	1.44	1.16
	EXISS-10	5	28.53	7.94×10^{-4}	1.57	1.06
	EXISS-12	35	31.61	4.17×10^{-4}	1.81	0.92

Table 3 Surface properties of ENISS-*n* and EXISS-*n* measured at 25 $^{\circ}$ C (*n* = 6, 8, 10, and 12)



Fig. 4 Changing of delta transmission and backscattering light with time for surfactant formulation ENISS-6



Fig. 5 Changing of delta transmission and backscattering light with time for surfactant formulation EXISS-6

EXISS-*n* were 118.6, 82.3, 61.2, and 43.1. The smaller TSI values of ENISS-*n* indicate their better emulsion stability compared with EXISS-*n*. The TSI values of LAE-9 from 1 to 6 h were 5.7, 11, 17, 22.5, 26.3, and 28.2; while those of SLES-3 were 8.8, 16.2, 22.3, 26.8, 29.7, and 31.4, respectively. At 6 h, the values of LAE-9 and SLES-3 (31.4 and 28.2) were higher than that of ENISS-12 (27.6). Moreover, the emulsion stability improved (lower TSI value) as the carbon chain length increased, which was also shown in terms of the emulsion separation timescale after shaking. ENISS-*n* also displayed better stability than EXISS-*n* in both the emulsion separation experiment and the measured TSI data.

Conclusion

In this study, we synthesized isosorbide-based anionic surfactants ENISS-*n* and EXISS-*n* with sulfonic acid groups and different carbon chain lengths (hexyl, octyl, decyl, and dodecyl).

1. These reactions occurred in a highly regioselective and effective manner under phase transfer catalytic conditions. ENISS-*n* was synthesized as a mixture of 81% endo and 3.5% exo orientations using KOH in toluene as the solvent, and EXISS-*n* was synthesized as a mixture of 72% exo and 3% endo using lithium hydroxide and alkyl bromide in DMSO.

- 2. The CMC values of ENISS-*n* were 1.62×10^{-2} to 1.12×10^{-4} mol L⁻¹, and those of EXISS-*n* were 7.24×10^{-3} to 4.17×10^{-4} mol L⁻¹. The CMC decreased with increasing length of the carbon chain, and the minimum area per molecule also decreased. The steric difference between ENISS-*n* and EXISS-*n* affected the characteristics of the surfactants.
- 3. ENISS-*n* had better foaming power than EXISS-*n*. The foaming power increased as the carbon chain length increased. This indicated that a longer carbon chain length led to a lower TSI and thus better stability.

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Conflict of Interest The authors declare that they have no conflict of interest.

References

- Abenhaïm, D., Loupy, A., Munnier, L., Tamion, R., Marsais, F., & Quéguine, G. (1994) Selective alkylations of 1,4:3,6-dianhydrod-glucitol (isosorbide). *Carbohydrate Research*, **261**:255–266.
- Chanamai, R., Herrmann, N., & McClements, D. J. (2000) Probing floc structure by ultrasonic spectroscopy, viscometry, and creaming measurements. *Langmuir*, 16:5884–5891.
- Claffey, D. J., Casey, M. F., & Finan, P. A. (2004) Glycosylation of 1,4:3,6-dianhydro-d-glucitol(isosorbide). *Carbohydrate Research*, **339**:2433–2440.

- Cserháti, T., Forgács, E., & Oros, G. (2002) Biological activity and environmental impact of anionic surfactants. *Environment International*, 28:337–348.
- Durand, M., Zhu, Y., Molinier, V., Feron, T., & Aubry, J. M. (2009) Solubilizing and hydrotropic properties of isosorbide monoalkyl and dimethyl ethers. *Journal of Surfactants and Detergents*, **12**: 371–378.
- El Dib, F., El Sawy, A. A., El Ashry, S. H., & El Sukkary, M. A. M. (1988) Surface active properties of some alkylsulphosuccinates. *Journal of the Serbian Chemical Society*, **53**:93–96.
- El-Shahawi, M. M., Shalaby, A. A. S., Gabre, A. M. E. D., & Ghonim, A. E. H. M. (2016) Surface active properties and biological activities of novel anionic surfactant based on oxapyridazinone derivatives. *Journal of Surfactants and Detergents*, 19:137–144.
- Fenouillot, F., Rousseau, A., Colomines, G., Saint-Loup, R., & Pascault, J. P. (2010) Polymers from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review. *Progress in Polymer Science*, 35:578–622.
- Geng, T., Zhang, C., Jiang, Y., Ju, H., & Wang, Y. (2017) Synergistic effect of binary mixtures contained newly cationic surfactant: Interaction, aggregation behaviors and application properties. *Journal of Molecular Liquids*, 232:36–44.
- Jin, Y., Tian, S., Guo, J., Ren, X., Li, X., & Gao, S. (2016) Synthesis, characterization and exploratory application of anionic surfactant fatty acid methyl ester sulfonate from waste cooking oil. *Journal of Surfactants and Detergents*, 19:467–475.
- Kang, H. C., Lee, B. M., Yoon, J. H., & Yoon, M. J. (2000) Synthesis and surface-active properties of new photosensitive surfactants containing the azobenzene group. *Journal of Colloid and Interface Science*, 231:255–264.
- Kang, W., Xu, B., Wang, Y., Li, Y., Shan, X., An, F., & Liu, J. (2011) Stability mechanism of W/O crude oil emulsion stabilized by polymer and surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **384**:555–560.
- Kumar, S., & Ramachandran, U. (2005) The synthesis and applications of asymmetric phase-transfer catalysts derived from isomannide and isosorbide. *Tetrahedron*, **61**:4141–4148.
- Laudet-Hesbert, A. (2005) The activities of INRS in the classification and labeling of glycol ethers. *Toxicology Letters*, **156**:51–58.
- Lavergne, A., Zhu, Y., Pizzino, A., Molinier, V., & Aubry, J. M. (2011) Synthesis and foaming properties of new anionic surfactants based on a renewable building block: Sodium dodecyl isosorbide sulfates. *Journal of Colloid and Interface Science*, **360**:645–653.
- Mengual, O., Meunier, G., Cayre, I., Puech, K., & Snabre, P. (1999) TURBISCAN MA 2000: Multiple light scattering measurement for concentrated emulsion and suspension instability analysis. *Talanta*, 50:445–456.

- Miller, C. A., & Neogi, P. (2007) Interfacial phenomena: Equilibrium and dynamic effects (2nd ed., pp. 40–42). New York, NY: CRC Press.
- Mohamed, M. Z., Ismail, D. A., & Mohamed, A. S. (2005) Synthesis and evaluation of new amphiphilic polyethylene glycol-based triblock copolymer surfactants. *Journal of Surfactants and Detergents*, 8:175–180.
- Nickel, D., Nitsch, C., Kurzendorfer, P., & Rybinski, W. (2007) Interfacial properties of surfactant mixtures with alkyl polyglycosides. *Progress in Colloid and Polymer Science*, 89:249–252.
- Pu, W., Yuan, C., Hu, W., Tan, T., Hui, J., Zhao, S., ... Tang, Y. (2016) Effects of interfacial tension and emulsification on displacement efficiency in dilute surfactant flooding. *RSC Advances*, 6: 50640–50649.
- Raney, K. H. (1991) Optimization of nonionic/anionic surfactant blends for enhanced oily soil removal. *Journal of the American Oil Chemists' Society*, 68:525–531.
- Roussel, M., Benvegnu, T., Lognone, V., Le Deit, H., Soutrel, I., Laurent, I., & Plusquellec, D. (2005) Synthesis and physico-chemical properties of novel biocompatible alkyl D-mannopyranosiduronate surfactants derived from alginate. *European Journal of Organic Chemistry*, 2005:3085–3094.
- Rybinski, W., & Hill, K. (1998) Alkyl polyglycosides—Properties and applications of a new class of surfactants. *Angewandte Chemie*, *International Edition*, **37**:1328–1345.
- Seo, S. G., Lee, J. E., Jeon, S. B., Lee, B. H., Koo, B. C., Suh, S. J., & Kim, S. H. (2009) Current status on miscanthus for biomass. *Journal of Plant Biotechnology*, 36:320–326.
- Stubenrauch, C. (2001) Sugar surfactants aggregation, interfacial, and adsorption phenomena. *Current Opinion in Colloid and Interface Science*, 6:160–170.
- Studer, M. H., DeMartini, J. D., Brethauer, S., McKenzie, H. L., & Wyman, C. E. (2009) Engineering of a high-throughput screening system to identify cellulosic biomass, pretreatments, and enzyme formulations that enhance sugar release. *Biotechnology and Bioengineering*, **105**:231–238.
- Zhou, M., Zhao, J., Wang, X., Jing, J., & Zhou, L. (2013) Synthesis and characterization of novel surfactants 1,2,3-tri(2-oxypropylsulfonate-3-alkylether-propoxy) propanes. *Journal of Surfactants and Detergents*, 16:665–672.
- Zhu, Y., Durand, M., Molinier, V., & Aubry, J. M. (2008) Isosorbide as a novel polar head derived from renewable resources. Application to the design of short-chain amphiphiles with hydrotropic properties. *Green Chemistry*, 10:532–540.
- Zhu, Y., Molinier, V., Durand, M., Lavergne, A., & Aubry, J. M. (2009) Amphiphilic properties of hydrotropes derived from isosorbide: Endo/exo isomeric effects and temperature dependence. *Langmuir*, 25:13419–13425.

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