

Nonionic lactose and lactitol based surfactants: comparison of some physico-chemical properties

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Abstract

The octyl (C8), dodecyl (C12) and hexadecyl (C16) mono-esters of lactose and lactitol have been synthesized. The lactose derivatives are a mixture of both anomers of two mono-esters while the lactitol derivatives are a mixture of both anomers of three monoesters. Generally, lactose and lactitol surfactants of equivalent chain length exhibited very similar physico-chemical properties. All six surfactants displayed thermotropic transitions of solid to smectic (A_d) to isotropic liquid as the temperature was raised. Concentration gradient experiments indicated that for the C8 and C12 surfactants the lyotropic transitions were micellar (L_1) to hexagonal (H_1) to lamellar (L_2) as the surfactant concentration increased relative to water. For the C16 surfactants the lyotropic transitions were micellar (L_1) to lamellar (L_2). Air–water surface tension curves have been employed to determine the critical micelle concentration (cmc), free energy of micellization, minimum area per surfactant molecule at the air–water interface, surface tension at the cmc and minimum surface tension for each surfactant. Interfacial tensions for aqueous surfactant solutions in contact with hexadecane and triolein have been measured. The interfacial tensions suggested that, above the cmc, the lactose and lactitol mono-esters would be good emulsifiers. Ross–Miles foam heights have shown that the C8 and C12 lactose and lactitol surfactants form foams with good height and stability above the cmc. All six surfactants have been found to be relatively poor cotton wetting agents. © 1998 Elsevier Science B.V.

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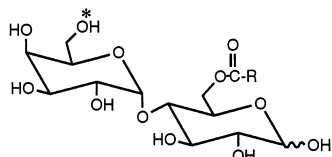
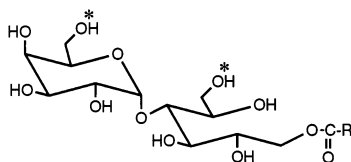
1. Introduction

The surfactant industry relies heavily on petrochemical feedstocks. With the inevitable growth in the cost and the forecast shortages of petroleum-based products, the need for surfactants derived solely from renewable raw materials is obvious. The surfactant hydrophobe can be renewably sourced from oleochemicals such as palm oil, palm kernel oil and coconut oil. Renewable carbohy-

drates, such as glucose from corn starch, sucrose from sugar cane and lactose from whey (a by-product of cheese manufacture) are options for the surfactant hydrophile.

To date, both industry and academia have focused primarily on sucrose and glucose based surfactants as alternatives to those derived from petroleum [1–15]. Comparatively, there has been little attention given to surfactants based on lactose and lactose-derivatives like lactitol [16–19]. In this work we present some physico-chemical data for the C8, C12 and C16 fatty acid mono-esters of lactose and lactitol. The general surfactant struc-

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**Lactose Esters****Lactitol Esters**

Scheme 1. General lactose and lactitol mono-ester surfactant structures. The asterisks denote alternative locations for the fatty acid substitution.

tures are given in Scheme 1. The method of preparation for these surfactants leads to final products that are a mixture of the mono-ester isomers. The physico-chemical data that we have determined include thermotropic and lyotropic liquid crystalline phase transitions, air–water surface tension curves that allow the determination of the critical micelle concentrations and minimum molecular packing areas at the air–water surface, some oil (hexadecane and triolein)/water interfacial tensions, Ross–Miles foam heights and rates of cotton tape wetting.

2. Experimental section

2.1. Syntheses

All the starting materials were purchased from Aldrich except where otherwise noted. α -lactose monohydrate was a 97% ACS reagent. β -lactose was supplied by Prof. Jim Hourigan of the University of Western Sydney. The fatty acids were of the highest grade available; either 98% or 99%. All column chromatography was conducted with Merck silica gel 60 (230–400 mesh).

Thin layer chromatography (TLC) analyses were performed using plates of Merck silica gel 60 F₂₅₄ on aluminium. The sheets were cut to 67 mm long since this gave adequate separation with a fast development time. The solvent mixture used for the analysis was chloroform–methanol–water in the ratio 60:39:1. All the mono-esters of both lactose and lactitol have an R_f in the vicinity of 0.45. To separate lactitol di- and tri-esters a mixture of the same solvents in the ratio 81:18:1 was used. The chromatogram was developed by spraying with a solution of 10% ammonium molybdate in 10% sulphuric acid and heating in an oven at 100°C.

Nuclear magnetic resonance (NMR) spectra were run on a Bruker AC200. The spectra were reprocessed for analysis and presentation by Swan-MR written by Giuseppe Balacco © 1994 Menarini Ricerche s.p.a.

2.1.1. General lactose ester syntheses

The synthesis basically followed the method of Scholnick et al. [16]. However, it was found that the reaction would not proceed using α -lactose monohydrate, as described, even when the method of water removal was changed to molecular sieve, or the solvent changed to dimethyl formamide. The method proceeded readily using anhydrous β -lactose, and molecular sieve was added before the acid chloride to remove any last traces of water from the solvent. These syntheses gave the di-ester as well as the mono-ester. They separated cleanly from each other upon column chromatography. The ratio of lactose to acid was chosen so that a high proportion of the mono-ester was produced. In the separation, the higher esters were completely eluted before the polarity of the eluant was increased and the mono-esters obtained.

2.1.2. Lactose mono-dodecanoate (C12-lactose) synthesis

β -lactose (30 g) was stirred overnight with type 4A molecular sieve (15 g) in pyridine (7 ml) and 1-methyl-2-pyrrolidinone (750 ml). It was then heated and stirred at 70°C and, after most of the lactose dissolved, redistilled dodecanoyl chloride (6.75 g) was added. This was maintained at 70°C and stirred for 24 h. The solution was filtered to

remove the molecular sieve and was washed three times with petroleum spirit b.p. 60–80°C (50–100 ml). The solvent was evaporated at 90°C on a rotary evaporator connected to a high vacuum pump, and the product partitioned between 1-butanol and 10% aqueous NaCl. The aqueous phase was washed with butanol three times and the combined butanol extracts were extracted three times with more 10% aqueous NaCl. The butanol extract was evaporated to give 15.5 g of mixed esters containing no lactose. This was deposited from methanol on silica gel (15 g), slurried with chloroform and placed on the top of a column of silica gel (150 g). Development with chloroform removed the last of the butanol and any trace of dodecanoic acid. Ten per cent methanol–chloroform gave the lactose di-ester (3 g). When the polarity was increased to 15% methanol–chloroform, the first 500 ml had a small amount of both di- and mono-esters, after which the product showed one spot on TLC analysis. 9 g of pure mono-ester eluted with this solvent. Further elution with 20–25% methanol–chloroform gave more material (1.5 g) which was of much lower solubility than the previous mono-ester, but had an NMR spectrum integration which was consistent with that of a mono-ester. No attempt has been made to identify this extra product. The 9 g mono-ester batch was recrystallized four times from ethyl acetate–methanol to give 5.3 g of product.

¹H NMR spectrum (DMSO): triplet 0.85, splitting 6.4 Hz (chain CH₃); broad singlet 1.25, (8 chain CH₂s); broad singlet 1.51, (chain β-CH₂); triplet 2.29, splitting 7.1 Hz (~0.5 chain α-CH₂); triplet 2.30, splitting 7.1 Hz (~0.5 chain α-CH₂); multiplet 2.80–5.50, (14 lactose CH and CH₂ + ~6 OH); broad singlet 6.13, (0.25 OH); broad singlet 6.50, (0.2 OH); broad singlet 6.70, (0.3 OH). The multiplet section at 3.85–5.50 reduced to 4H and the resonances below that disappeared on treatment with D₂O. We have found that the triplets at 2.29 and 2.30 have slightly different ratios in different preparations of this compound. The ¹H NMR spectrum showed an integration consistent with mono-ester assignment.

¹³C NMR spectrum (CDCl₃): 13.72 (CH₃); 22.08, 24.23, 28.55, 28.73, 28.91, 29.01, 31.29,

33.34, 33.58, 38.23, 38.64, 39.06, 39.48, 39.90, 40.31, 40.77 (alkyl CH₂s); 60.68, 61.08, 61.30, 62.79, 63.0 (CH₂O); 67.09, 67.98, 69.38, 70.33, 71.40, 71.65, 71.90, 71.90, 72.52, 73.01, 73.27, 74.05, 74.23, 74.50, 75.21, 80.35, 80.65, 81.2391.86, 96.52, 103.74 (lactose CHO_Hs); 172.93 (C=O). It is apparent from the number of carbons (some of which are quite small) that a number of different isomers and anomers are present. The assignment given to the carbons is based on the expected positions for carbons of that type and a ¹H–¹³C heteronuclear *J* modulation (JMODO) spectrum (from the Bruker Pulse sequence library) which gives the multiplicities of the protons on each carbon. The JMODO spectrum indicates that there are many different primary carbons, so this is probably a mixture of both the α and β forms of the esters of each primary alcohol group.

2.1.3. Lactose mono-hexadecanoate (C16-lactose) synthesis

The previous method was followed using β-lactose (40 g), 1-methyl-2-pyrrolidinone (1 l), pyridine (10 ml), molecular sieve (20 g) and distilled hexadecanoyl chloride (11.5 g). The chromatography gave 4.3 g of di-esters and 9.9 g of mono-esters. The product was recrystallized once from ethyl acetate/methanol and once from butanone to give 6.3 g of white crystals. It was dried by pumping at 0.3 mm for 24 h.

¹H NMR spectrum (DMSO): triplet 0.85, splitting 6.4 Hz (chain CH₃); broad singlet 1.25, (12 chain CH₂s); broad singlet 1.50, (chain β-CH₂); triplet 2.27, splitting 7.1 Hz (~0.45 chain α-CH₂); triplet 2.29, splitting 7.1 Hz (~0.55 chain α-CH₂); multiplet 2.80–5.50, (14 lactose CH and CH₂s + ~6 OH); broad doublet 6.13, splitting 4.5 Hz (0.25 OH); doublet 6.50, splitting 4.7 Hz (0.2 OH); doublet 6.68, splitting 6.7 Hz (0.2 OH); doublet 6.68, splitting 6.7 Hz (0.08 OH). The multiplet at 3.85–5.50 reduced to 4H and the resonances below that disappeared on treatment with D₂O. The ¹H NMR spectrum showed an integration consistent with mono-ester assignment.

2.1.4. Lactose mono-octanoate (C8-lactose) synthesis

The previous method was followed using β-lactose (40 g), 1-methyl-2-pyrrolidinone (1 l), pyr-

idine (10 ml), molecular sieve (20 g) and distilled octanoyl chloride (9.2 g). The chromatography gave 3.3 g of di-esters and 9.6 g of mono-esters. The product was recrystallized three times from ethyl acetate–methanol, the second time had 0.5 g activated charcoal added. It was found that if the temperature of the solution was too high when the mono-ester began to precipitate, an oily gel formed. The mother liquors even at -10°C had much material still in solution. Therefore, each time, the liquor was concentrated and a second crop harvested which was added to the first one. The final product was 6.2 g of white crystals. It was dried by pumping at 0.3 mm for 24 h.

^1H NMR spectrum (DMSO): triplet 0.85, splitting 6.4 Hz (chain CH_3); broad singlet 1.25, (4 chain CH_2s); broad singlet 1.51, (chain $\beta\text{-CH}_2$); triplet 2.29, splitting 7.1 Hz (~ 0.45 chain $\alpha\text{-CH}_2$); triplet 2.30, splitting 7.1 Hz (~ 0.55 chain $\alpha\text{-CH}_2$); multiplet 2.80–5.50, (14 lactose CH and $\text{CH}_2\text{s} + \sim 6$ OH's); broad singlet 6.36, (0.25 OH); broad singlet 6.50, (0.15 OH); broad singlet 6.71, (0.45 OH). On treatment with D_2O the multiplet section at 3.85–5.50 reduced to 4H and the resonances below that disappeared. The ^1H NMR spectrum showed an integration consistent with mono-ester assignment.

2.1.5. General lactitol ester syntheses

α -lactose monohydrate was reduced to lactitol by following the procedure of Scholnick et al. [17]. The transesterification method of Scholnick et al. [17] was then followed with some modifications. The method could not be made to work using the methyl esters of the acids, but it did so with the much more reactive vinyl esters. The vinyl esters of octanoic, dodecanoic and hexadecanoic acids were prepared using the standard method [20], and had boiling points consistent with the literature. It was also found that the solvent had to be completely dry before it was used, otherwise the reaction produced either very little or none of the desired product. In view of the sensitivity to water, as an extra precaution, molecular sieve was added to the reaction before the addition of potassium *t*-butoxide. The lactitol synthesis produced a glass and any methanol trapped in it was removed with the water. Chromatography of the product followed the same course as that of the lactose esters.

From lactitol it is possible to obtain a tri-ester as well as the mono- and di-esters. All three ester fractions, mono-, di- and tri- can be cleanly separated if desired.

2.1.6. Lactitol mono-octanoate (C8-lactitol) synthesis

Lactitol (34 g) in dried dimethylformamide (200 ml) was heated at near reflux at 90° under vacuum (≈ 90 mm) overnight. Type 4A molecular sieve (15 g) was added and heating continued for a further 3 h. Vinyl octanoate (16.7 g) and potassium *t*-butoxide (.5 g) were added and the mixture heated for about 20 h. The product was worked up in a way that was similar to that of the lactose esters. The product (36 g) was deposited from methanol onto silica gel (35 g) and this was placed on a dry silica gel column (350 g, 55 mm diam.) in a chloroform slurry. Initial elution with chloroform gave material (30 mg) which showed octanoic acid and nondescript paraffinic type protons in the ^1H NMR spectrum. 3–5% methanol/chloroform gave tri-ester (8 g). Five to ten per cent methanol–chloroform gave di-ester (9.9 g) which showed one spot on TLC analysis. Fifteen to twenty-five per cent methanol–chloroform gave mono-ester (15.5 g) which also showed one spot on a TLC. The mono-ester could not be crystallized. After trying a number of different solvent combinations and conditions, it was eventually precipitated as an oil from ethyl acetate–methanol. This oil was pumped at 21°C at 1 mm for 24 h to give a glass-like solid material.

^1H NMR spectrum (DMSO): triplet 0.83, splitting 6.4 Hz (chain CH_3); broad singlet 1.22, (4 chain CH_2s); broad singlet 1.50, (chain $\beta\text{-CH}_2$); triplet 2.26, splitting 7.1 Hz (~ 0.47 chain $\alpha\text{-CH}_2$); triplet 2.28, splitting 7.1 Hz (~ 0.53 chain $\alpha\text{-CH}_2$); multiplet 3.2–5.5, (15 lactitol CH and $\text{CH}_2\text{s} + \sim 6$ OHs). On treatment with D_2O , the section of the multiplet at 4.0–5.50 reduced from 10.7H to 4H terminating at 5.3. The ^1H NMR spectrum showed an integration consistent with mono-ester assignment.

2.1.7. Lactitol mono-dodecanoate (C12-lactitol) synthesis

The previous procedure was repeated using lactitol (55 g), dried dimethylformamide (375 ml), type

4A molecular sieve (12 g), vinyl dodecanoate (13.1 g) and potassium *t*-butoxide (1 g). Work up was similar to before. Chromatography was on silica gel (300 g). Elution with chloroform gave 1 g of paraffinic materials. Ten to twelve percent methanol–chloroform gave higher esters (6.1 g). Fifteen to twenty per cent methanol–chloroform gave mono-ester (17.2 g). The mono-ester was recrystallized from ethyl acetate–methanol. The crystals appeared to be hygroscopic so they were filtered under a blanket of nitrogen. They were dried in a vacuum desiccator.

^1H NMR spectrum (DMSO): triplet 0.83, splitting 6.4 Hz (chain CH_3); broad singlet 1.24, (4 chain CH_2s); broad singlet 1.50, (chain $\beta\text{-CH}_2$); triplet 2.26, splitting 7.1 Hz (~ 0.5 chain $\alpha\text{-CH}_2$); triplet 2.29, splitting 7.1 Hz (~ 0.5 chain $\alpha\text{-CH}_2$); multiplet 3.2–5.5, (15 lactitol CH and $\text{CH}_2\text{s} + \sim 6$ OH). On treatment with D_2O , the section of the multiplet at 4.0–5.50 reduced from 10.8H to 4.8H terminating at 5.3. The ^1H NMR spectrum showed an integration consistent with mono-ester assignment.

^{13}C NMR spectrum (DMSO): 13.86 (CH_3); 22.03, 24.35, 28.44, 28.66, 28.85, 28.94, 31.23, 33.21, 33.44, 38.05, 38.47, 38.88, 29.30, 39.72, 40.14, 40.55 (chain CH_2s); 59.83, 60.28, 62.01, 62.51, 63.27, 65.04, 65.41 (lactitol $\text{-CH}_2\text{O-}$); 67.64, 67.91, 68.25, 69.20, 69.68, 70.82, 71.10, 71.41, 72.13, 72.91, 73.25, 75.18, 75.45, 82.14, 82.96, 104.28, 104.61 (lactitol -CHOH-); 172.82 (C=O). It is apparent from the number of carbons (some of which are small) that a number of different isomers and anomers are present. The assignment given to the carbons is based on the expected positions for carbons of that type and a JMOD spectrum which gives the multiplicities of the protons on each carbon. The JMOD spectrum indicated that there were six different primary carbons, so the product is a mixture of the mono-esters of each primary alcohol group.

2.1.8. Lactitol mono-hexadecanoate (C16-lactitol) synthesis

The previous procedure was repeated using lactitol (55 g), dried dimethylformamide (375 ml), type 4A molecular sieve (12 g), vinyl hexadecanoate (16.5 g) and potassium *t*-butoxide (1 g). Work up

and chromatography was identical to that of the dodecanoate ester, except that the higher esters (6.7 g) eluted with 5–10% methanol/chloroform and the mono-ester (19.5 g) with 10–20%. The product was recrystallized from ethyl acetate–*i*-propanol and pumped at 0.8 mm overnight.

^1H NMR spectrum (DMSO): triplet 0.85, splitting 6.4 Hz (chain CH_3); broad singlet 1.25, (4 chain CH_2s); broad singlet 1.50, (chain $\beta\text{-CH}_2$); triplet 2.26, splitting 7.1 Hz (~ 0.45 chain $\alpha\text{-CH}_2$); triplet 2.30, splitting 7.1 Hz (~ 0.55 chain $\alpha\text{-CH}_2$); multiplet 3.2–5.5, (15 lactitol CH and $\text{CH}_2\text{s} + \sim 6$ OH's). On treatment with D_2O , the section of the multiplet at 4.0–5.50 reduced from 10.2H to 4H terminating at 5.3. The ^1H NMR spectrum showed an integration consistent with mono-ester assignment.

2.2. Differential scanning calorimetry

This was performed on a Mettler TA3000 at a rate of 2°C min^{-1} . Most of the samples initially gave a broad endotherm between 30° and 100° , but after the samples were pumped at <0.3 mm vacuum for several hours (after being made up in the sample crucibles and pumped immediately before being tested) this disappeared to give reasonably flat baselines. The Mettler software was used to calculate the energy represented by any transition which was observed.

2.3. Thermotropic phase behaviour

Solid material was placed on a clean microscope slide and covered with a coverslip. Thermotropic transitions were measured by using a Mettler FP90 hot stage, programmed at a 3°C min^{-1} heating rate, and an Olympus IMT-2 microscope equipped with crossed polarizing filters.

2.4. Lyotropic liquid crystalline phase behaviour

Concentrated isotropic (micellar) aqueous solutions of each surfactant were prepared and a small drop placed on a clean microscope slide and covered by a coverslip. The size of the drop was chosen so that after placing the cover slip, it had very little remaining uncovered. The slides were

left in an oven adjusted to the temperature of interest. The oven temperature was stable to $\pm 0.5^\circ\text{C}$. The solutions were examined periodically over several days using an Olympus IMT-2 microscope equipped with crossed polarizing filters. Phases were identified from the optical textures [21–24].

2.5. Air–water surface tensions

Surface tensions, $\gamma_{a/w}$, were measured by the du Noüy ring method with the ring being formed from platinum wire. The ring was suspended under a balance. The aqueous surfactant solutions were contained in a large Petrie dish which rested on the top of a hydraulically driven platform. The ring was brought into contact with the surface of an aqueous solution, which was then lowered. The entire ring and platform set-up was enclosed in a cabinet, with the temperature controlled to $25 \pm 0.5^\circ\text{C}$, and an atmosphere which was near saturated with water vapour. The solutions were allowed to thermally equilibrate in the cabinet prior to measurement. The ring was cleaned by flaming in a bunsen burner flame immediately before measurement. The Petrie dish and solution flasks were boiled in concentrated nitric acid for at least 2 h and then steamed for at least 15 min. Most of the surfactant solutions exhibited a time dependant surface tension, with the value decreasing on standing. Consequently, each solution was swirled vigorously immediately prior to a measurement, which was then performed as fast as possible. In order to accomplish this, the surface was rapidly lowered until the force on the ring was about 90% of the maximum and then a relatively slow speed was resumed. It was found that the surface equilibrium was restored long before the maximum was reached. Surface tensions were calculated from the maximum force on the ring [25]. Immediately after the first measurement on a solution, a repeat was performed. The solution was swirled before the repeat, but the ring was not flamed. Generally, if the measured surface tension did not agree within 0.2 mN m^{-1} of the first, then it was repeated until three concordant values were obtained. However, in the case of solutions with surfactant concentrations below $5 \times 10^{-5} \text{ M}$, the values often had a

spread of about $\pm 1 \text{ mN m}^{-1}$, and reported values were the average of four to six readings.

2.6. Oil–water interfacial tensions

Interfacial tensions, $\gamma_{o/w}$, were measured by using a Krüss spinning drop tensiometer model SITE 04/02. For each surfactant solution, $\gamma_{o/w}$ was measured at four different speeds and the results averaged over all four. The first speed measurement was repeated after the others and the $\gamma_{o/w}$ was generally identical to the first. When it did differ, the cycle was repeated until it did not. The speed range incorporated the minimum speed necessary to give adequate clearance from the wall of the measurement tube, and ended at about 1500 rpm higher. The measurements were done in an irregular order of speed. Some surfactants showed a small, bordering on insignificant, trend to lower surface tension at lower measurement rpm. Where possible (see below) measurements were made with 0.01%, 0.1%, and 1.0% wt/wt aqueous surfactant solutions. At each concentration, $\gamma_{o/w}$ was measured against both hexadecane and triolein. Due to low solubility, lactose mono-hexadecanoate was measured at only one concentration, at saturation (very close to 0.01%) at 21°C . There appeared to be a change of $\gamma_{o/w}$ with time over a period of 15–30 min, so the measurements on each sample were completed as fast as possible, and were generally done within 10 min. The equipment was equilibrated to 25°C for at least 1/2 h before commencing. It was dismantled and washed out thoroughly with ethanol and chloroform between surfactants.

2.7. Ross–Miles foam heights

All measurements were performed with a custom built all glass apparatus made following the design given in ASTM D 1173, which mirrors the method published by Ross and Miles [26]. The apparatus was filled with concentrated nitric acid for 48 h and after rinsing with Milli-Q water, it was allowed to stand with Milli-Q water for a further 24 h before being used with each surfactant. It was found that the solutions did not change their behaviour with time and so the time of measure-

ment after making the solution was not relevant. A 1% solution was made up by weighing about 6.5 g of surfactant and adding distilled water to make up the requisite weight, 0.1% and 0.01% solutions were made by successive dilutions by weight of the first solution. The solutions were equilibrated at 21°C prior to the measurement being performed. Foam heights were repeated until two readings were within 5% of each other, and the reported heights are the average of these. The results were very reproducible and usually only two or three measurements were necessary. The average foam height was measured immediately and after 30 min.

2.8. Modified Shapiro tape wetting

Tape wetting was performed according to the modified Shapiro test method [27]. The tape was tape cotton heavy (TCH) BS1626 natural uncalendered 0.75 in from Bole Hall Mill Co., Tolson's Hill, Fazeley, Tamworth, Staffs, UK. The aqueous surfactant solutions were the same as those used for the Ross–Miles foam heights. Measurements were repeated until two values were within 5% of each other. Reported values are the average of these two values.

3. Results and discussion

3.1. Thermotropic phase transitions

DSC curves are presented in Fig. 1. Thermotropic transitions were also observed with a cross-polarizing optical microscope. All the neat lactose and lactitol mono-esters transformed from solid to anisotropic liquid crystalline to isotropic liquid as the temperature was raised. Due to the samples being a mixture of the mono-ester isomers, the transitions can occur over broad temperature ranges.

Many carbohydrate-based surfactants exhibit thermotropic behaviour [28,29]. For surfactants that have a disaccharide headgroup and an alkyl chain of medium length (C8–C16), it has been shown that the anisotropic liquid crystalline phase is a smectic (A_d) mesophase [28]. This phase is

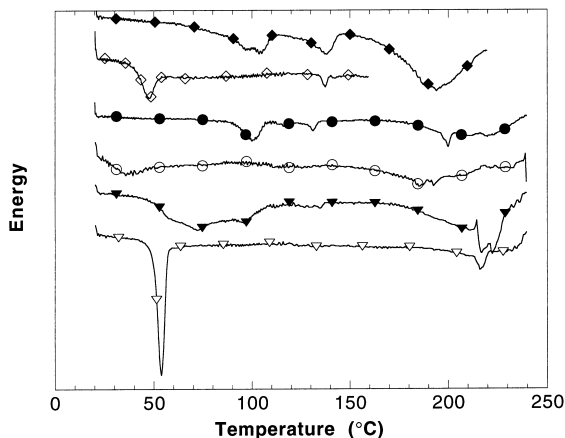


Fig. 1. DSC plots for lactose mono-octanoate (◆), lactitol mono-octanoate (◇), lactose mono-dodecanoate (●), lactitol mono-dodecanoate (○), lactose mono-hexadecanoate (▼), and lactitol mono-hexadecanoate (▽).

very similar to the lyotropic lamellar (L_d) phase. In the present study, the optical texture for the lactose and lactitol surfactants' anisotropic liquid crystalline phase was consistent with smectic (A_d) phase assignment.

The DSC curve for C8-lactose shows two broad endotherms from 70–108°C (maximum ca. 102°C) and 110–145°C (maximum ca. 138°C). The first corresponds to approximately 8.2 kJ mol⁻¹, while the second 5.5 kJ mol⁻¹. Based on optical microscopy, the C8-lactose crystals appeared to have two forms. The first form transformed at 114–120°C and the second at 137–141°C, both to give an anisotropic liquid crystalline phase. The entire sample visually melted at 146–149°C to give an isotropic liquid.

Two endotherms are evident for C8-lactitol at 38–55° and 133–140°, with enthalpies of approximately 3.5 kJ mol⁻¹ and 0.6 kJ mol⁻¹. From optical microscopy, the glass-like material appeared to transform to an anisotropic liquid crystalline phase at 105–135°C and this melted to an isotropic liquid at 138–140°C.

There were three endotherms in the DSC scan for C12-lactose. The first and largest one is at 86–107°C (maximum ca. 100°C), the second and smallest is at 111–117°C (maximum ca. 116°C) and the third is at 125–135°C (maximum at 131°C). There may be further endotherms in the

area of 195–225°C, but this is the decomposition area which makes identification difficult. The enthalpy of the first endotherm is approximately 9.0 kJ mol⁻¹, and the third is 2.2 kJ mol⁻¹. From optical microscopy, it began to change texture at 108°C, with the major amount transforming at 148–152°C to give an anisotropic liquid crystalline phase which melted to an isotropic liquid at 206–208°C.

C12-lactitol shows no sharp peaks in the DSC curve. There is a broad band at 25–50°C with possibly a second small, very broad one at 40–90°C. A third band is at 150–220°C (with a double maximum at 187°C and 193°C). There are more small endotherms above 220°C, but there is a lot of noise in this scan and consequently these are of uncertain significance. From optical microscopy, the crystals transformed to an anisotropic liquid crystalline phase at 182–187°C which in turn melted at 226–228°C to an isotropic liquid.

C16-lactose has a broad endotherm in the area of 45–110°C which did not change with extra vacuum pumping. There may be further endotherms in the area of 214–230°C but this is where decomposition occurs and so positive identification and measurement is difficult. From optical microscopy, the crystals transformed between 122°C and 152°C to give a liquid crystalline phase which melted at 240–241°C.

C16-lactitol exhibited two endotherms at 43–58°C (maximum at 53°C; enthalpy approximately 21.7 kJ mol⁻¹) and 205–221°C (maximum at 216°C; enthalpy approximately 4.3 kJ mol⁻¹). From optical microscopy, the crystals transformed at 82–103°C to an anisotropic liquid crystalline

phase which melted at 229–231°C to an isotropic liquid.

3.2. Lyotropic phase transitions

All six surfactants have a region in their surfactant/water phase diagram that is isotropic micellar (L₁). In increasing surfactant concentration gradient experiments, the C8 and C12 lactose and lactitol mono-esters had optical textures consistent with the sequential formation of hexagonal (H₁) and lamellar (L_α) phases. For the C16 lactose and lactitol mono-esters only textures characteristic of lamellar (L_α) phases were seen. The lyotropic behaviour of the six mono-esters is consistent with what would be expected from geometric packing constraints [30] and the behaviour pattern ascertained from the analysis of a large number of other carbohydrate-based surfactants [29].

3.3. Air–water surface tensions

The surface tension curves for the six surfactants are shown in Fig. 2. Table 1 lists the critical micelle concentrations (cmc), surface tensions at the cmc (γ_{cmc}) and minimum surface tensions (γ_{min}) that were obtained from the surface tension curves. For each surfactant, the cmc was identified as the surfactant concentration (c) where the gradient, $d\gamma/d \log c$, abruptly changed from the maximum value to a smaller value [31]. There is little to be gained from comparing the surface tension data for commercial preparations of sucrose ester surfactants, which contain mono-, di- and tri-esters, with the

Table 1
Air–water surface tension data

Surfactant	cmc (mM; wt%)	A_o (Å ²) ± 5	γ_{CMC} (mN m ⁻¹)	γ_{Min} (mN m ⁻¹)	$\Delta G_{\text{mic}}^{\circ}$ (kJ mol ⁻¹)
Lactose mono-octanoate	2.63; 0.12	32	33.7	30.6	–24.7
Lactitol mono-octanoate	2.75; 0.13	36	33.1	25.7	–24.6
Lactose mono-dodecanoate	0.427; 0.022	41	35.0	34.4	–29.2
Lactitol mono-dodecanoate	0.427; 0.022	43	34.0	33.8	–29.2
Lactose mono-hexadecanoate	9.55×10^{-3} ; 0.00056	36 ^a	38.4	36.9	–38.6
Lactitol mono-hexadecanoate	7.59×10^{-3} ; 0.00044	22 ^a	39.3	35.9	–39.2

^aGreater uncertainty than other A_o values because of low [Surfactant].

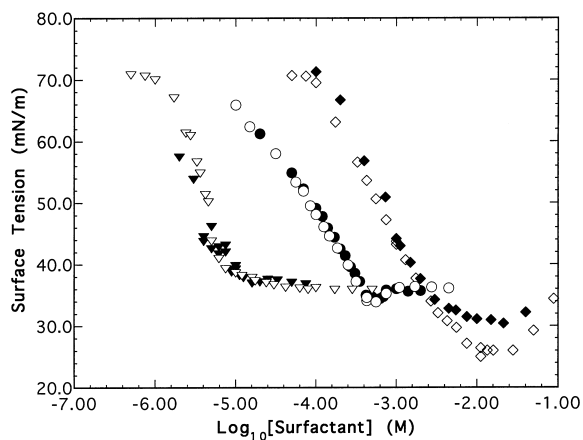


Fig. 2. Air–water surface tension as a function of the logarithm of the surfactant concentration for lactose mono-octanoate (◆), lactitol mono-octanoate (◇), lactose mono-dodecanoate (●), lactitol mono-dodecanoate (○), lactose mono-hexadecanoate (▼), and lactitol mono-hexadecanoate (▽).

lactose and lactitol mono-esters. There is surface tension data for the pure sucrose 6-dodecanoate isomer [32] that can be compared to the results in Table 1. The C12-lactose and C12-lactitol surfactants have cmc values that are similar to that of sucrose 6-dodecanoate (cmc=0.455 mM) [32]. The γ_{cmc} values for the C12-lactose and C12-lactitol surfactants are slightly lower than the value for sucrose 6-dodecanoate ($\gamma_{\text{cmc}} = \gamma_{\text{min}} = 37.4 \text{ mNm}^{-1}$) [32]. This difference in the γ_{cmc} values corresponds to the fact that, for concentrations in the vicinity of the cmc, the number of surfactant molecules per unit area at the air–water interface is greater for the lactose and lactitol mono-esters than it is for the sucrose mono-ester (see below).

The surface tension data for each surfactant were treated in terms of the Gibbs adsorption equation to calculate the amount of surfactant adsorbed per unit area of air–water interface. The maximum adsorption density (Γ_{max}), in mol m^{-2} , and the minimum area per surfactant molecule at the air–water interface (A_0), in \AA^2 , were determined from the relationships [33]

$$\Gamma_{\text{max}} = - \frac{1}{2.303RT} \lim_{c \rightarrow \text{cmc}} \left| \frac{d\gamma}{d \log c} \right| \quad (1)$$

$$A_0 = \frac{10^{20}}{N\Gamma_{\text{max}}} \quad (2)$$

where R is the gas constant, T is the absolute temperature, and N is Avogadro's number. The A_0 values are provided in Table 1. The A_0 value for the C12-lactose and C12-lactitol surfactants are significantly lower than the A_0 value of 56 \AA^2 for sucrose 6-dodecanoate [32]. It is difficult to know whether this is due to (i) an inherent differ-

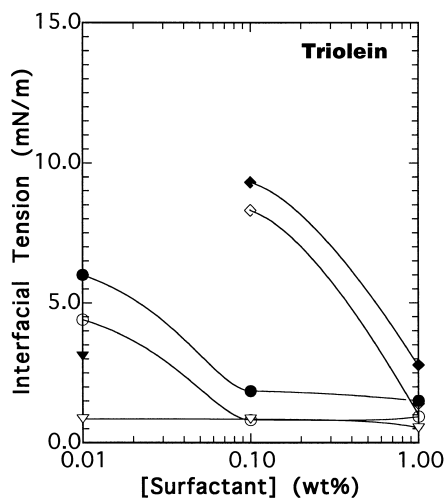
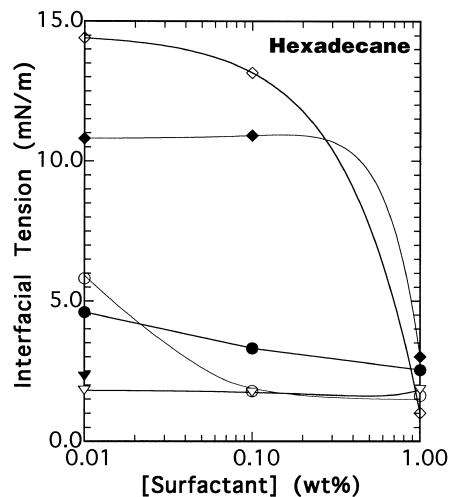


Fig. 3. Oil (hexadecane or triolein)–water interfacial tension as a function of the initial concentration of the surfactant in the aqueous solution: lactose mono-octanoate (◆), lactitol mono-octanoate (◇), lactose mono-dodecanoate (●), lactitol mono-dodecanoate (○), lactose mono-hexadecanoate (▼), and lactitol mono-hexadecanoate (▽). The lines are drawn solely to aid the eye in connecting data.

ence in the way sucrose headgroups pack at the air–water interface compared to lactose and lactitol headgroups, or (ii) synergistic effects that allow a population of mixed mono-ester isomers to pack to a smaller average area per molecule than a pure mono-ester isomer.

The standard free energy of micellization ($\Delta G_{\text{mic}}^{\circ}$) for each surfactant was calculated by

using the expression [33]

$$\Delta G_{\text{mic}}^{\circ} = RT \ln(\text{cmc}/55.5) \quad (3)$$

Table 1 contains the $\Delta G_{\text{mic}}^{\circ}$ values. Because the cmc values are similar, the calculated $\Delta G_{\text{mic}}^{\circ}$ values for the C12-lactose and C12-lactitol surfactants are similar to that for sucrose 6-dodecanoate [32].

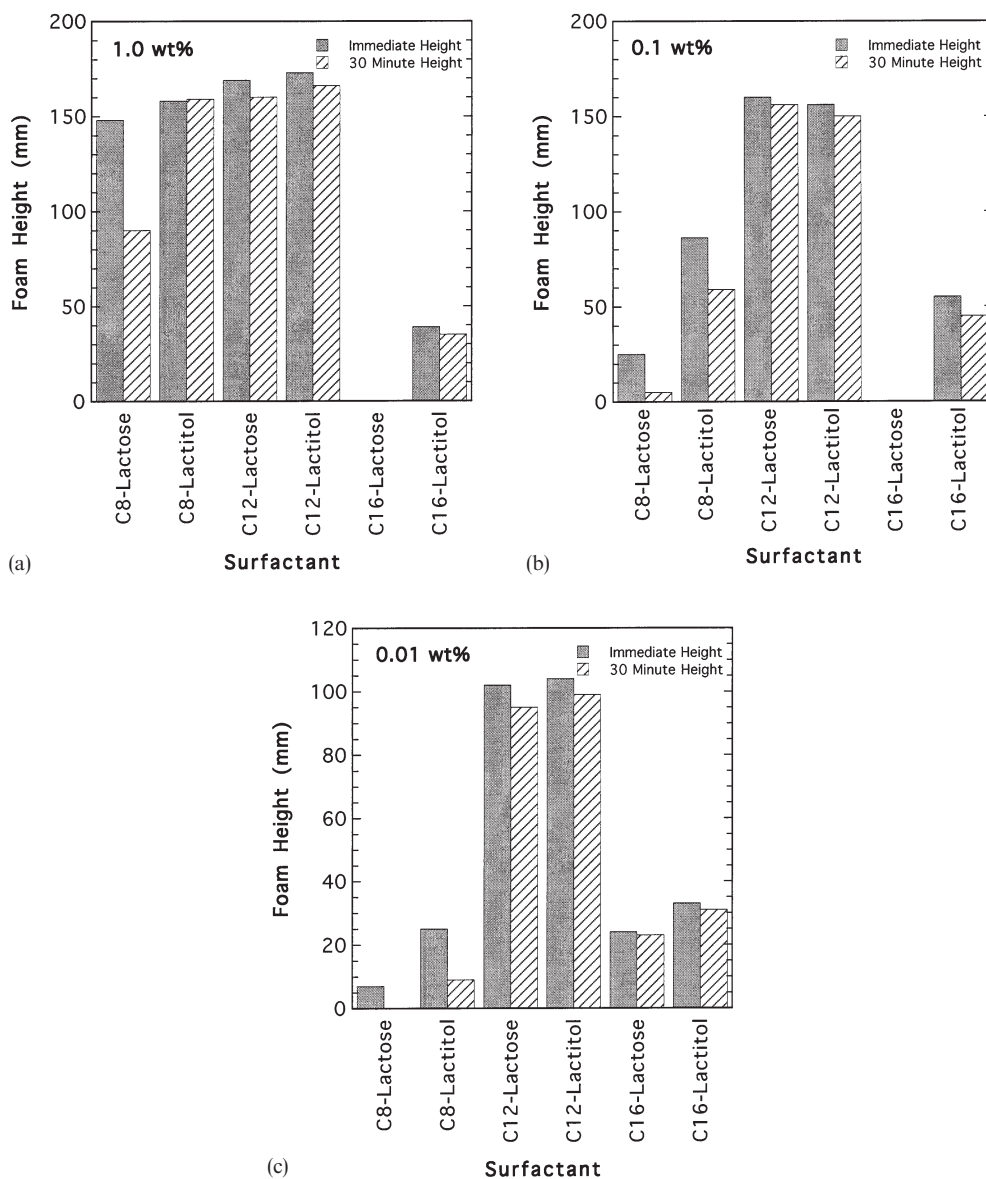


Fig. 4. Ross–Miles foam heights at time zero and after 30 min. Three surfactant concentration were studied; 0.01, 0.1 and 1.0 w/w%.

3.4. Oil–water interfacial tensions

The interfacial tensions for aqueous surfactant solutions in contact with hexadecane and triolein are shown in Fig. 3. There are no data reported for 0.01 wt.% C8-lactose and C8-lactitol in the triolein system because it was not possible to generate stable spinning drops at this concentration. Once the concentration is above the cmc, see Table 1, the interfacial tensions plateau at 3.5–0.5 mN m⁻¹. There is a trend that the longer chain surfactants have slightly lower interfacial tensions than their shorter chain homologues. Above, the cmc, there is no difference, within experimental error, between a lactose and lactitol surfactant of equivalent chain length. The interfacial tensions suggest that the lactose and lactitol mono-esters would be good emulsifiers [34].

3.5. Ross–Miles foam heights

The foam height results are displayed in Fig. 4. Above the cmc, with the exception of C8-lactose, the foams are very stable, as there is only a slight decrease in height over 30 min of standing. The mono-dodecanoates are clearly the best foam forming surfactants. Above the cmc, there is no significant difference between the initial foam height for a lactose and lactitol surfactant of equivalent hydrophobe. The foam height behaviour of the C12 mono-esters is similar to that of Teric LA8 and Teric 12A9, which are polydisperse C12 ethoxylates with respective averages of 8.0 and 9.0 mol of ethylene oxide. For Teric LA8 the initial (and 30 min) foam heights in mm are 178 (167), 131 (119) and 57 (49) for 1.0, 0.1 and 0.01 wt% solutions, respectively [35]. For Teric 12A9 the initial (and 30 min) foam heights in mm are 166 (163), 117 (112) and 45 (44) for 1.0, 0.1 and 0.01 wt% solutions, respectively [35].

3.6. Modified Shapiro tape wetting

The cotton tape wetting results for the six surfactants are shown in Fig. 5. The lactitol surfactants may be marginally better cotton tape wetting agents than the equivalent chain length lactose surfactants. Compared with some nonionic poly

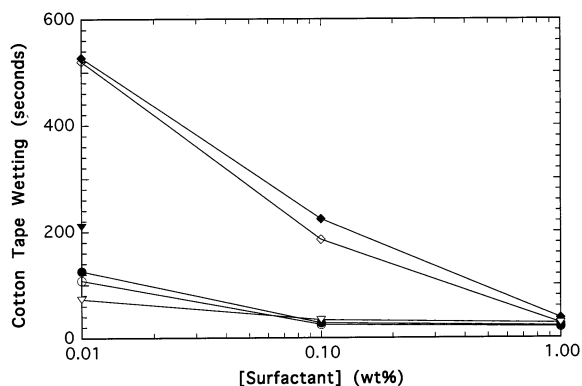


Fig. 5. Rate of tape wetting as a function of the initial concentration of the surfactant in the aqueous solution: lactose mono-octanoate (◆), lactitol mono-octanoate (◇), lactose mono-dodecanoate (●), lactitol mono-dodecanoate (○), lactose mono-hexadecanoate (▼), and lactitol mono-hexadecanoate (▽).

ethoxylate surfactants, lactose and lactitol surfactants are relatively poor cotton wetting agents. For example, Teric 12A9 in an identical modified Shapiro test wets cotton in 2, 10 and 61 s for 1.0, 0.1 and 0.01 wt% solutions, respectively [35].

4. Conclusion

There is little difference between the physicochemical properties of lactose and lactitol mono-esters of equivalent chain length in the C8, C12 and C16 study group. These carbohydrate-based surfactants display thermotropic and lyotropic phase transitions, exhibit good surface and interfacial activity, and some are good foamers.

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