ECO-TECHNOLOGIES FOR OBTAINING CARBOHYDRATES BASED SURFACTANTS

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Abstract

Carbohydrate based surfactants represent an alternative to surfactants produced from petrochemical raw materials. They can be prepared from various renewable vegetable raw materials in a large structural diversity. This class of surfactants presents high surface active properties and functionalities, being use in different industrial areas. The development of carbohydrate based surfactants is possible due to their higher biodegradability and lower toxicity. Two carbohydrate based surfactants, galactose palmitate and bolaamphiphilic surfactant 1,12-dodecanedioyl digalactose, were synthesized by reacting the galactose with fatty acid chlorides, in aqueous medium, alkaline catalysis, at room temperature, following the principles of green chemistry. The structures of synthesized surfactants were proved by FT-IR analysis. The surface activity of galactose palmitate was demonstrated by a low surface tension at the interface water/oil.

Keywords*: Bio-based surfactants, Carbohydrates, Eco-technologies*

1. Introduction

Carbohydrates based surfactants constitute a class of surfactants with special characteristics, whose industrial development took place only after the legislative restrictions on environmental protection were increased, in conjunction with the natural decline of traditional petrochemicals sources. The increasing use of carbohydrates is given by the intrinsic qualities of carbohydrates: polyhydroxy combinations of vegetable origin, high purity, minimum ecological impact, lack of toxicity. Occurrence of appropriate technologies and the evolution of specific engineering processes for obtaining derivatives of carbohydrates, inclusive of the surfactants also allowed the development of this class. Carbohydrates based surfactants are constituted by a carbohydrate moiety derived from renewable plant resources linked to one or more natural triglycerides or derivatives through ester, thioester, ether, amine, or/and amide group [1-5]. Alkylpolyglucosides is the most important representatives of carbohydrates based surfactants, characterized by hydrophilic behavior similar to a classic polyethoxylated nonionic surfactant (C_{12} -C_{14} fatty alcohol ethoxylate with 6-8 mol EO), superior biodegradability, stability to electrolytes and to the alkali, high foaming power and low toxicity. Ester derivatives are represented especially by sorbitan and esters of sucrose. Sorbitan esters have specific uses in the food industry, cosmetics and pharmaceuticals. There are several routes to synthesized ester derivatives of carbohydrates.

A method to synthesize ester derivatives of carbohydrates involves transesterification of a triglyceride or fatty acid methyl ester with carbohydrate, using dimethylformamide or dimethylsulfoxide as solvent, in alkaline catalysis, at 90°C [6]. The synthesis of ester derivatives of carbohydrates can be performed in anhydrous liquid system (acetic acid) in the presence of organic acid chloride and a catalyst (potassium carbonate), at 90°C [7].
In the present study two carbohydrate based surfactants, galactose palmitate and bolaamphiphilic surfactant 1,12-dodecanedioyl digalactose, were synthesized through processes with reduced environmental impact achieved by using renewable raw materials (carbohydrates), aqueous reaction medium and low reaction temperature. Esters of galactose were synthesized by reacting the galactose with fatty acid chlorides, in aqueous medium, alkaline catalysis, at room temperature. The structures of synthesized surfactants were verified by FT-IR. Interfacial tension between water and a solution of galactose palmitate solubilised in paraffin oil was determined by Du Nouy ring method.

2. Experimental

2.1 Synthesis of galactose palmitate

The surfactant galactose palmitate was synthesized following the procedure presented in figure 1.

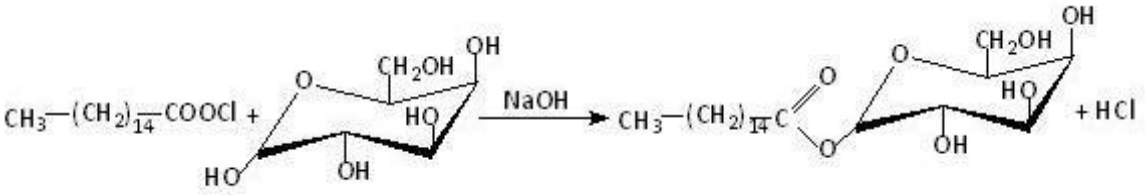

Figure 1 The synthesis reaction of galactose palmitate

In a reaction vessel of 250 mL capacity, equipped with dropping funnel, thermometer and electric stirrer 18 g (0,1 mol) D(+) galactose was introduced and allowed to disolve in 75 mL distilled water. The pH was adjusted to 8 using 25% NaOH solution.
To this solution was added dropwise 8,24 g (0,1 mol) palmitoyl chloride. During palmitoyl chloride addition the temperature was kept constant at 25°C, and if necessary a solution of NaOH was added to maintain a constant pH of 9-10. After the entire amount of palmitoyl chloride was added the reaction was allowed to complete for 1 hour . The product was filtered under vacuum and washed on the filter with distilled water to remove traces of unreacted carbohydrate. The filtrate is then oven dried at a temperature less than 50°C, in order to avoid the product degradation.

2.2 Synthesis of 1,12-dodecanedioyl digalactose

The surfactant 1,12-dodecanedioyl digalactose was synthesized following the procedure presented in figure 2.

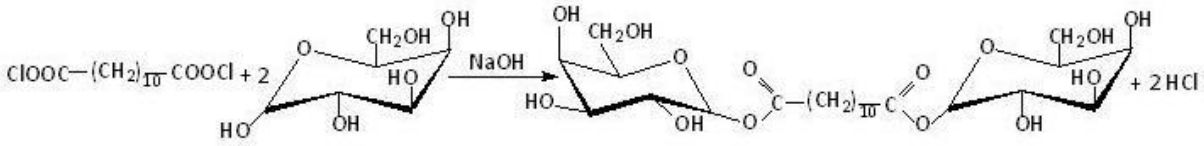

Figure 2 The synthesis reaction of 1,12-dodecanedioyl digalactose

In a reaction vessel of 250 mL capacity, equipped with dropping funnel, thermometer and electric stirrer 13 g (0,07 mol) D(+) galactose was introduced and allowed to dissolve in 75 mL distilled water. The pH was adjusted to 8 using 25% NaOH solution. To this solution was added dropwise 9,35 g (0,035 mol) dodecanedioyl dichloride. During dodecanedioyl dichloride addition the temperature was kept constant at 25°C, and if necessary a solution of NaOH was added to maintain a constant pH of 9-10. After the entire amount of dodecanedioyl dichloride was added the reaction was allowed to complete for 1 hour. The product was processed according to pct. 2.1.

2.3 FTIR spectroscopy

The raw materials (D(+) galactose, palmitoyl chloride, dedecanedioyl dichloride) and surfactants (galactose palmitate and 1,12-dodecanedioyl digalactose) were analysed by Fourier transform infrared spectroscopy (FTIR), KBr pellet procedure, with a Spectrum GX, Perkin Elmer instrument.

2.4 Interfacial tension

The interfacial tension was measured with a KSV Sigma 700 automated tensiometer. The measurements for interfacial tension were performed using the Du Nouy ring technique. The fluid with greater density was poured in the vessel, followed by lower density fluid. The vessel was placed on the platform and the Du Nouy ring was completely immersed in lighter fluid until the ring is a few mm above the interface between two immiscible liquids. The software will measure the interfacial tension when moving the ring from one phase to another.

3. Results and Discussion

The synthesis performed in order to obtain carbohydrates based surfactants took into account the principles of green chemistry: use of renewable raw materials (D(+) galactose), the use of safe solvents and mild reaction conditions (aqueous reaction medium), increased efficiency energy (low reaction temperature). The synthesis reaction selected for this type of surfactants is the esterification of D(+) galactose in an aqueous medium, in alkaline catalysis, using an acid chloride, known to have a high reactivity. In order to prevent as far as possible side reactions, the temperature should be kept low, and the acid chloride is added slowly, in small quantities.
The structures of galactose palmitate and 1,12-dodecanedioyl digalactose were characterized by FTIR spectroscopy, as presented in figures 3 and 4.

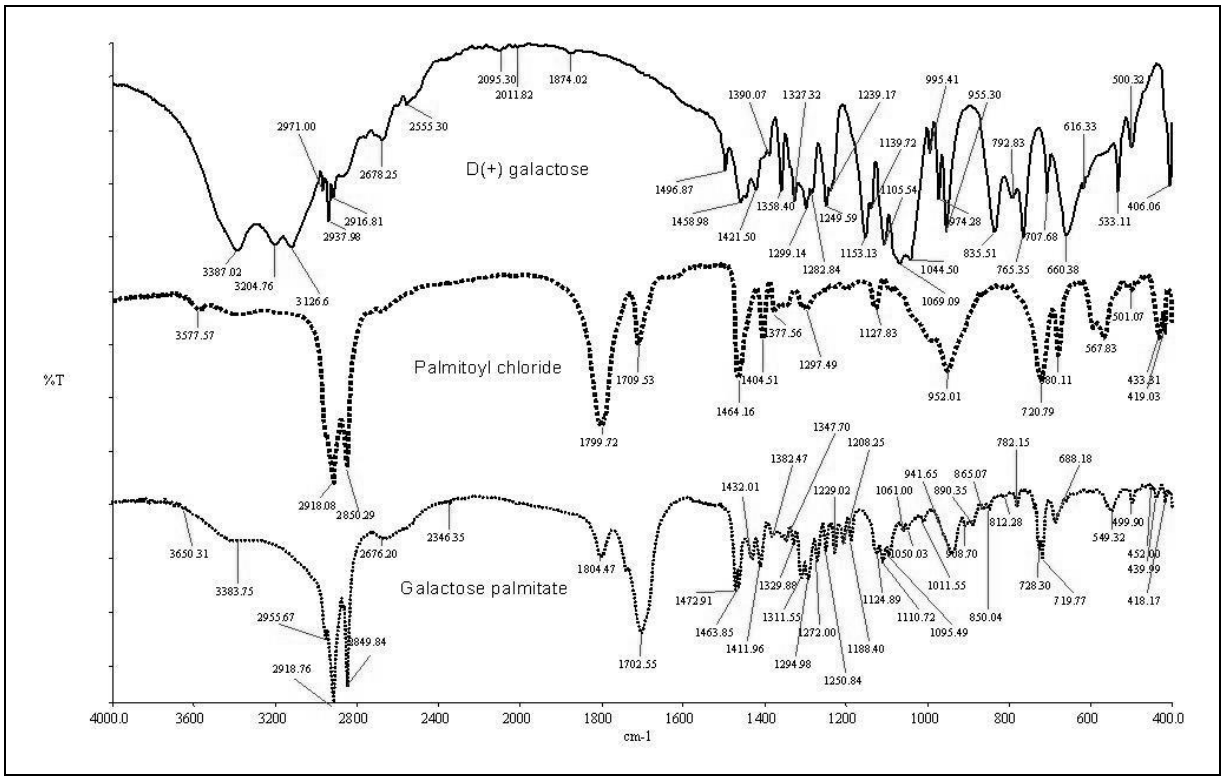

Figure 3 FTIR spectra of galactose palmitate and raw materials

For D (+) - galactose the hydroxyl groups give absorption bands at 3387 cm^{-1}, 3205 cm^{-1}, 3127 cm^{-1}. Two absorption bands assigned to O-CH bond appear at 1422 cm^{-1} and 1390 cm^{-1}. The spectral region between 1153 and 765 cm^{-1} is a complex sequence of peaks due mainly to C–O bond. In the 3000–2700 cm−1 region D(+) galactose shows few absorption bands: 2938 cm^{-1}, 2917 cm^{-1}, 2678 cm^{-1} assigned to CH_2 and 2971 cm^{-1} assigned to CH_3.

Palmitoyl chloride presents the characteristic absorption bands: CH_2 group stretching vibration appears at 2918 cm^{-1} and 2850 cm^{-1}. CH_2 vibration deformation appears as a double band at 1464 cm^{-1} and 1405 cm^{-1}. $(-(CH2)_n-,n>3)$ appears at 722 cm^{-1}, corresponding to long chain hydrocarbon. C=O bond characteristic band appears at much higher frequency than in the case of anhydrides, esters or amides of carboxylic acids: 1800 cm^{-1}.

The presence of absorption bands at 1703 cm^{-1} specific to the group C = O and at 1188 cm^{-1} specific to the group C-O-C in the spectrum of galactose palmitate, along with the characteristic absorption bands from reactants, with small shifts, indicate the esterification of palmitoyl chloride with D(+) galactose. The product contain traces of palmitoyl chloride due to the presence of C = O band at 1805 cm^{-1} and C-Cl band at 688 cm^{-1}.

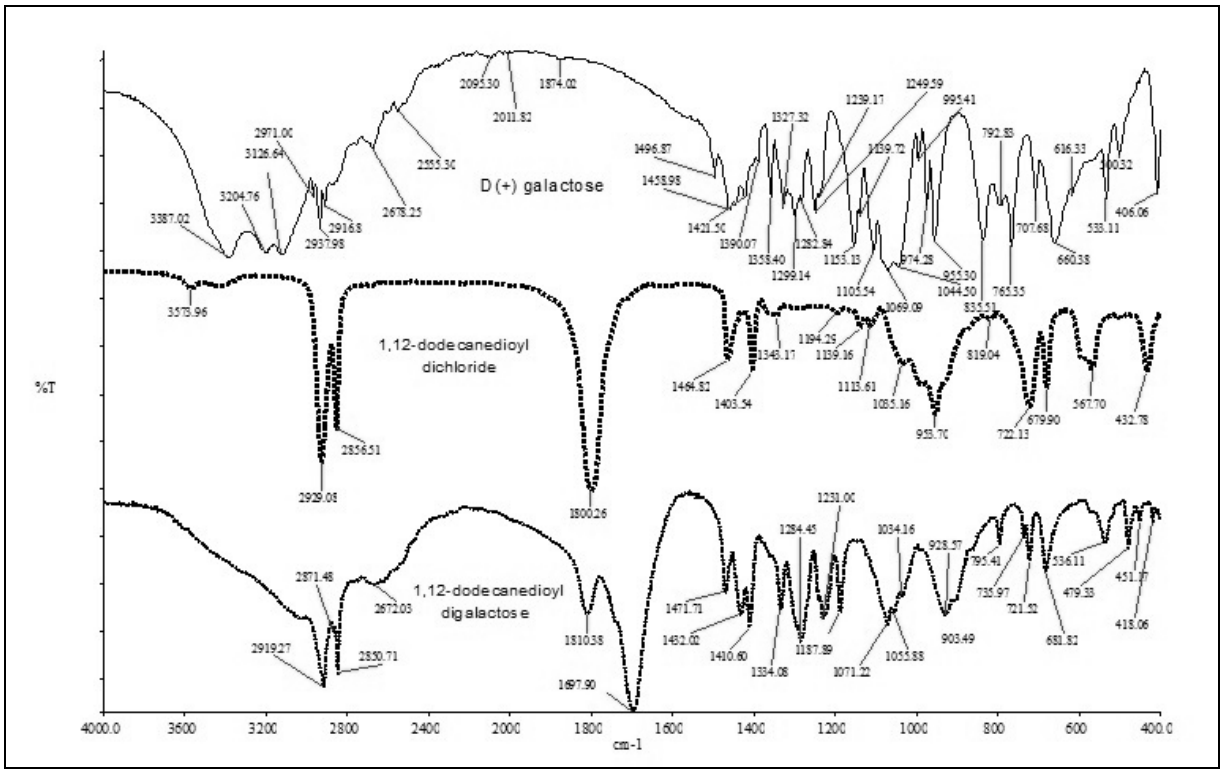

Figure 4 FTIR spectra of 1,12-dodecanedioyl digalactose and raw materials

Dodecandioyl dichloride presents characteristic absorption bands in FTIR spectrum: CH_2 group stretching vibration at 2929 cm^{-1} and 2857 cm^{-1}, CH_2 vibration deformation at 1465 cm^{-1} and 1404 cm^{-1}, $(-(CH2)_n-, n>3)$ at 722 cm^{-1}, corresponding to long chain hydrocarbon. Dodecanedioyl dichloride shows a strong C=O band at 1800 cm^{-1}, also a C-Cl stretch at 680 cm^{-1}.

The esterification reaction is proved by the absorption bands found also in reactants spectra, with small shifts, but especially by the absorption bands at 1698 cm^{-1} specific for the group C=O and at 1188 cm^{-1} specific for the group C-O-C. At the same time it should be noted that the product contains traces of dodecanedioyl dichloride due to the presence of C = O band at 1810 cm^{-1} and C-Cl band at 682 cm^{-1}.

In order to test the surface activity of surfactants based on carbohydrates, tests of solubility have performed thereof in various solvents, both products being insoluble in water. Tests have shown that galactose palmitate was soluble in paraffin oil and 1,12-dodecanedioyl digalactose was soluble in hot ethyl alcohol.

Evaluation of the surface activity of galactose palmitate (PGal) was performed by determining interfacial tension of water / surfactant solution using automated tensiometer KSV, Sigma 700. The table below shows the values of interfacial tension at 0.5% surfactant solution in paraffin oil (PO) / distilled water interface compared to the interfacial tension at paraffin oil / distilled water interface.

Table 1 Surface activity of galactose palmitate

System	**Interfacial tension (mN/m)**
PO/water	28.13
0.5% PGal in PO/ water	13.26

The analysis of experimental data showed that the system galactose palmitate/paraffin oil significantly reduces the interfacial tension compared with the system paraffin oil / water.

4. Conclusions

Ester derivatives of galactose were synthesized through a process with reduced environmental impact. Esterification reaction was performed in in accordance with the principles of green chemistry: use of renewable raw materials (galactose), use of safe solvents and reaction conditions (aqueous medium), increased energy efficiency (reaction temperatures up to 25°C). The structures of synthesized surfactants galactose palmitate and 1,12-dodecanedioyl digalactose were verified by FT-IR. The system galactose palmitate/paraffin oil significantly reduces the interfacial tension compared with the system paraffin oil / water.

Acknowledgements

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References

1. Gatard S., Nasir M. N., Deleu M., Klai N., Legrand V., Bouquillon S. *(*2013) Bolaamphiphiles Derived from Alkenyl L-Rhamnosides and Alkenyl D-Xylosides: Importance of the Hydrophilic Head, *Molecules*, **18**, 6101-6112

2. Habulin, M., Šabeder, S. and Knez, Ž. (2008) Enzymatic synthesis of sugar fatty acid esters in organic solvent and in supercritical carbon dioxide and their antimicrobial activity, *The Journal of Supercritical Fluids*, **45**(3), 338-345

3. Pestman, J. M., Terpstra, K. R., Stuart, M. C., van Doren, H. A., Brisson, A., Kellogg, R. M., & Engberts, J. B. (1997) Nonionic bolaamphiphiles and gemini surfactants based on carbohydrates. *Langmuir*, ***13***(25), 6857-6860

4. Eastoe, J., Rogueda, P., Howe, A. M., Pitt, A. R., & Heenan, R. K. (1996). Properties of new glucamide surfactants. *Langmuir*, *12*(11), 2701-2705.

5. Schuur, B., Wagenaar, A., Heeres, A., & Heeres, E. H. (2004). A synthetic strategy for novel nonsymmetrical bola amphiphiles based on carbohydrates, *Carbohydrate research*, ***339***(6), 1147-1153.

6. Plat T., Linhardt R.J. (2001) Syntheses and applications of sucrose-based esters, *Journal of Surfactants and Detergents*, **4**(4), 415-421

7. Sandra Kea, Charles E. Walker, Eric Kline, 1987, Sugar esters and an improved anhydrous method of manufacture, *US Patent 4683299*