J Surfact Deterg (2011) 14:179–184
DOI 10.1007/s11743-010-1225-4

ORIGINAL ARTICLE

Synthesis and Surface Active Properties of Novel Carbohydrate-based Cationic Surfactants

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Received: 23 December 2009 / Accepted: 20 July 2010 / Published online: 21 August 2010

Abstract The synthesis of new cationic carbohydrate surfactants is presented in this paper. The obtained surfactants have structures that are typical for saponins, which contain fatty amide hydrophobic chains and hydrophilic heads with cationic carbohydrate units. Their surface active properties and biodegradability have been studied. For two types, the biodegradability was above 85% and comparable to standard carbohydrate surfactants.

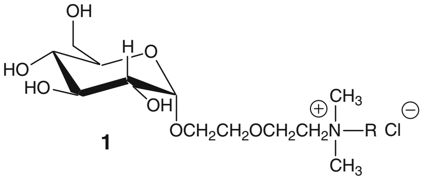
Keywords Cationic surfactants · Surface activity · Synthesis

Introduction

Carbohydrate surfactants make up a very important group of surface active compounds. Their principal advantage results from the fact that they are based on natural and renewable resources. Attention was paid fairly long ago to the possibility of using carbohydrate segments to substitute the hydrophilic section, which contained polyoxyethylene chains in traditional surface active compounds. Extensive research in that area was conducted as early as over 40 years ago [1]. Processes were then developed for the synthesis of basic groups of carbohydrate surfactants. Apart from alkylpolyglucosides, alkylglucamides may be classified as the most popular carbohydrate surfactants [2]. They are very similar to each other in regards to their properties.

Research on carbohydrate surfactants have been intensively promoted, and studies are oriented not only on nonionic surfactants but on ionic surfactants as well, because of their advantageous environmental performance. Many reports have been published in recent years on the synthesis of numerous interesting cationic surface active compounds which contained carbohydrate segments in their structures. Those compounds offer specific properties and fields of applications; their main outlets are: components of personal care products, flocculating and dispersing agents. Carbohydrate ethers with reactive alkylhalide groups make intermediates in the production of many of them.

A key stage in their synthesis is the etherification of glucose or other carbohydrates with aliphatic chlorohydroxyl compounds, such as: diethylene chlorohydrin, glycerol chlorohydrin, 2-chloroethanol or 3-chloro-1,2-propanediol [3–5]. The etherification of glucose with diethylene chlorohydrin gives a corresponding ether. This is then subjected to amination with dodecyl and to quaternisation with methyl chloride to yield the product **1**, which may be used in preparing hair and body care formulations.



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The same ether, in the reaction with 3-(N,N-dimethylamino)-propylamide of methacrylic acid, will yield a cationic monomer. Its polymerisation will produce a polymer with very good hair and body care properties [3].

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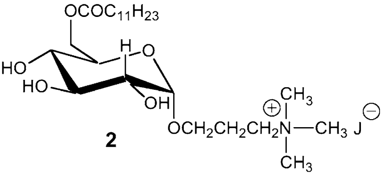
Analogical monomers were also obtained when ether was used which had been produced from carbohydrates and 3-chloro-1,2-propanediol [4].



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Another type of surface active compounds were derived from the etherification product of glucose with 3-chloro-1-propanol. That ether, when esterified with lauric acid and then quaternised with trimethylamine in the presence of NaJ, yields the product **2**, which additionally offers the softening properties [5].

The surface active compounds as described above comprise three specific structural fragments: carbohydrate segment, cationic centre and hydrophobic fatty chain.

This paper describes the synthesis of novel carbohydrate surfactants in which the etherification of a carbohydrate compound with aliphatic chloroalcohols is also a key step. The structures of novel surfactants are analogical to the surface active agents which have been discussed earlier. They were obtained according to the scheme shown in Fig. 1.

Experimental

Glucose was supplied by POCh. 3-(N,N-dimethylamino)-1-propylamine, 2-chloroethanol, 3-chloro-1,2-propanediol and palmitoyl chloride were supplied by Aldrich. All of these chemicals were of reagent grade. Stearoyl chloride (99.5%) was supplied by Chemical Factory "Zachem"–Bydgoszcz. Syntheses were conducted in thermostatted glass reactors delivered by Normschliff Gerätebau (Germany).

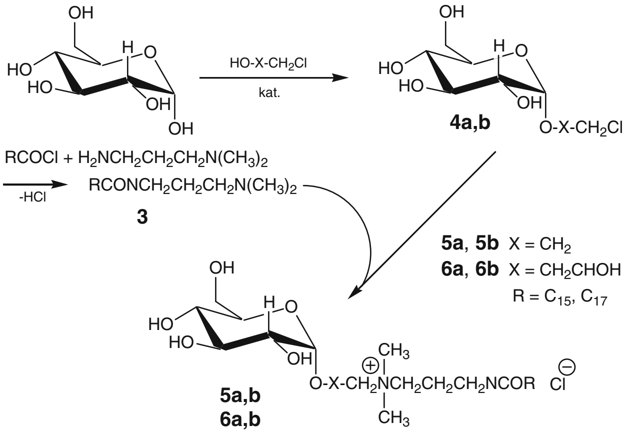


Fig. 1 Scheme for the synthesis of novel surfactants

The post-reaction mixture was analysed by the liquid chromatography method (HPLC), with the use of the GPC technique, for which the HP 1050 chromatograph with the RI4 detector (Varian) was employed. A chromatographic column Asahipak GF-310HQ 7.6 × 300 mm (Showa Denko, Japan) and DMF (with the admixture of 0.8% m/v of lithium chloride) as the eluent were used to separate the components. The eluent flow rate was adjusted to 0.5 ml/min and the column temperature was 40 °C. The samples of raw materials and products were dissolved in the eluent at the concentrations of 1% m/v (products) and 0.5% m/v (raw materials). The Cl^- content was determined by the potentiometric method, with the use of $AgNO_3$ solution.

Surface Tension Measurements

The surface tension of novel surfactants was measured by means of a Krüss K100 tensiometer using the dynamic Wilhelmy plate technique (DWPT), for various surfactant concentrations, at 20 °C. Demineralised water (conductivity < 0.055 μS; surface tension $= 72.8$ mN/m) was used to prepare the solutions; the water was purified in a deionisation kit.

Biodegradability

The biodegradability of aqueous solutions of new surfactants was verified according to the procedure ISO 9888: 1991 (static test, Zahn–Wallens method) and according to the method which was provided in OECD Guidelines for the Testing of Chemicals—OECD 302 B.

The biodegradability of new surfactants was studied for 1 wt % aqueous solutions, with the use of activated sludge from a sewage treatment plant as the inoculum. Solutions of compounds **5a** and **5b** were investigated. Their biodegradability was evaluated by measuring the changes in COD over 28 days.

Synthesis of Quaternary Surface Active Compounds

*Synthesis of 3-(N,N-Dimethylamino)-1-Propylamides (**3**)*

25.5 g of dimethylpropylamine were dissolved in toluene (450 ml) and that solution was charged to the reactor. The nitrogen blow-in was then activated and acid chloride was added dropwise. The temperature was maintained at 30 °C. When the addition of acid chloride had completed (after about 1.5 h), the mixture was agitated for another 30 min and it was left to stand until the next day. The obtained suspension was transferred to the solution of 20 g NaOH in 500 ml of water. After a short agitation, the precipitate which separated from the solution was filtered and dried. The final product had the form of a white powder.

*Synthesis of Chloroalkyl Ethers of Glucose (**4a, b**)*

0.36 mol of glucose (65 g), 1.8 mol of chloroalcohol and a catalyst (Amberlyst 15, 9.3 g) were placed in the reactor. The temperature was adjusted to 70 °C (thermostat) and agitation was started. After the glucose was dissolved completely, the agitation action was continued for 1 h. Complete conversion was also confirmed by no glucose being present in the TLC chromatogram. The catalyst was separated and the solution was concentrated at a temperature <90 °C (2 mmHg) to obtain thick syrup. After cooling the syrup down, it was washed with acetone (3 × 30 mL) and the product was held at elevated temperature, under nitrogen atmosphere, to remove the remaining solvent. The obtained ether **4a, b** had the form of a syrup which was nearly colourless to yellow–brown, and which solidified at room temperature.

*Synthesis of Cationic Surfactants (**5a, b** and **6a, b**)*

The following components were placed in the reactor: 0.06 mol of ether **4** and 15 mL of water. These were agitated at about 40 °C until a homogeneous solution was formed. Then, amide **3** was added (0.06 mol) with continuous mixing. The reactor content quickly became a very thick paste, hence, the temperature was increased to 50 °C. After 6 h, complete conversion of ether was confirmed (by the TLC method). The crude product was washed twice with acetone to eliminate residual 2-chloroethanol or 3-chloro-1,2-propanediol and it was dried. The product had the form of a white–grey paste.

Results and Discussion

3-(N,N-dimethylamino)-1-propylamides were initially synthesised with the use of triethylamine to absorb hydrogen chloride which was evolved in the process. The syntheses were conducted at 20–25 °C and at the diamine:acid chloride molar ratio of 1:0.9/1:1.1, and excess triethylamine in relation to diamine amounted for 20% m/m. The yield of amides was 93.5–94.5%, but the product purity (GC) was never better than 90%. Those amides may also be produced in the classical Schotten–Baumann reaction, in the aqueous-alkaline medium. However, that method presented some difficulties at the stage of produce recovery. The amide suspension was a fine-grained structure and its filtration was an onerous task. Another method for the production of fatty amides is based on the synthesis with the use of a solvent [6]. That method turned out to be more efficient. Instead of harmful benzene, safer toluene was used. The yield of amides was 93.4–94.6%, while the product purity was over 99%.

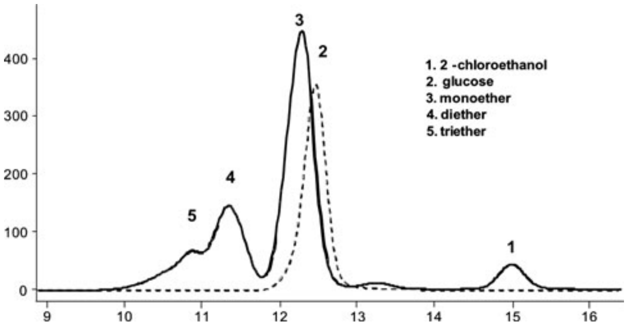
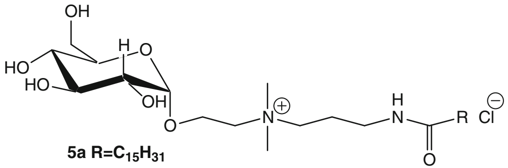


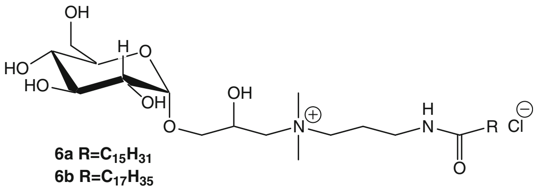
Fig. 2 GPC chromatogram of 1-O-(2-chloroethyl)glucose **5a**

The synthesis of chloroalkyl ethers of glucose has been described previously [7]. Figure 2 presents the GPC chromatogram for ether **4a**. The product, apart from glucose and 2-chloroethanol (about 7% m/m), also contains 1-O-(2-chloroethyl)glucose oligomers which were formed under synthesis conditions. The composition of ether **4b** was similar.

These ethers were then subjected to quaternisation with the use of amides **3**, and cationic surfactants **5** and **6** were obtained in that way.



5a R=$C_{15}H_{31}$
5b R=$C_{17}H_{35}$



6a R=$C_{15}H_{31}$
6b R=$C_{17}H_{35}$

The results of the synthesis of new surfactants are shown in Table 1.

Table 1 Results of the synthesis of novel cationic surfactants

Product	Dry matter (%)	Content of [Cl$^-$] (%)	Content of cationic compounds[a] (%)
5a	82.1	4.31	96.0
5a	84.1	5.21	96.5
6b	82.6	3.24	97.9
6b	83.8	4.22	98.1

[a] Calculated on a dry weight basis

Surface Active Properties

Determination of Surface Tension Isotherms

Figures 3 and 4 show surface tension isotherms for the novel surfactants. These isotherms were analysed to establish the *cmc* values for all compounds. The results are presented in Table 2.

Once established, those values made it possible to calculate the following physical–chemical parameters which describe individual surface active compounds:

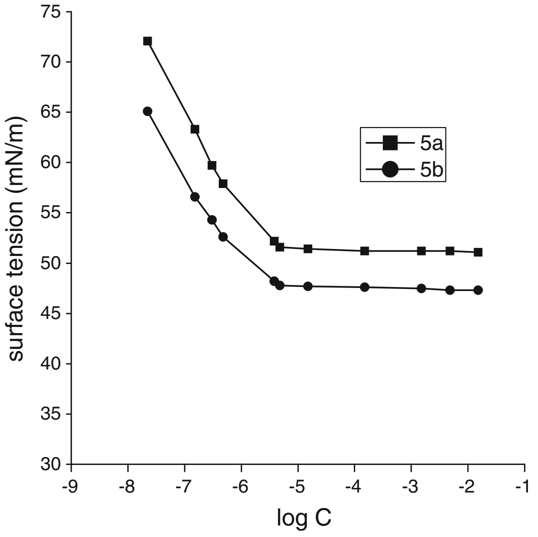


Fig. 3 Surface tension vs. –log *c* (concentration) of compounds **5a** and **5b**

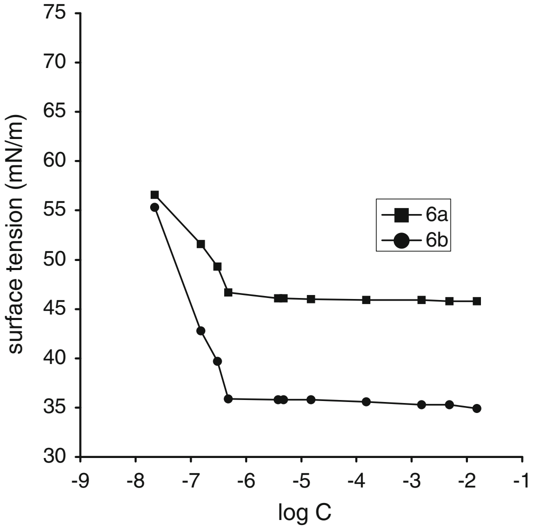


Fig. 4 Surface tension vs. –log *c* (concentration) of compounds **6a** and **6b**

1. Surface excess:

$$\Gamma_{cmc} = -\frac{1}{2.303RT} \cdot \frac{\partial \gamma_{cmc}}{\partial \log C_{cmc}}$$

2. Specific surface area:

$$A_{cmc} = \frac{10^{20}}{N \cdot \, \Gamma_{cmc}} (\text{Å}^2),$$
$$N\text{:Avogadro's number } (6.022 \times 10^{23})$$

3. Free energy of micellisation:

$$\Delta G_{cmc} = 2.303RT \, \log C_{cmc} \, (\text{kJ/mol})$$

The calculation results are shown in Table 3.

Determination of the Krafft Point

The Krafft point values for novel surfactants were measured for $C = 0.2\%$ m/m, which corresponds to about 7×10^{-6} mol/L, so it is close to *cmc*. The weighed amount of sample (content of active component 95–97% m/m) was placed in 100 ml of distilled water and left to stand overnight. The obtained suspension was heated up to complete dissolution and then cooled down to 5 °C. The Krafft point was found when the sample was heated up at the rate of 4 °C/min. The results are presented in Table 4.

Table 2 Results for *cmc* values

Compound	C (mol/L)	γ_{cmc} (mN/m)
5a	5.01×10^{-6}	51.5
5b	5.25×10^{-6}	47.8
6a	4.78×10^{-7}	46.1
6b	5.01×10^{-7}	35.9

Table 3 Surface properties of novel surfactants

Compound	$10^6\ \Gamma_{cmc}$ (mol/m^2)	A_{cmc} (Å^2)	ΔG_{cmc} (kJ/mol)
5a	1.17	141	29.93
5b	1.05	157	29.82
6a	4.25	39	35.70
6b	2.15	76	35.58

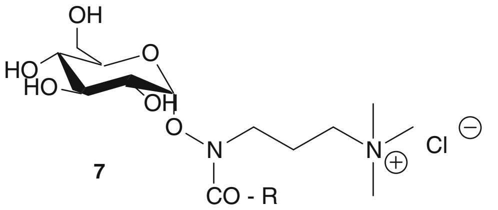
Table 4 Krafft point values

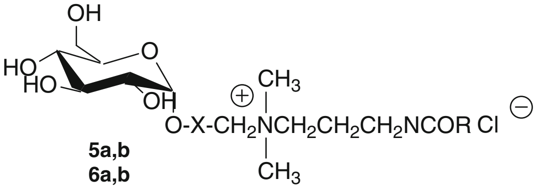
Compound	C (mol/L)	Krafft point (°C)
5a	7.1×10^{-6}	30–32
5b	6.9×10^{-6}	>65
6a	7.0×10^{-6}	50–52
6b	7.4×10^{-6}	>65

The following structural elements may be distinguished in the novel surfactants:

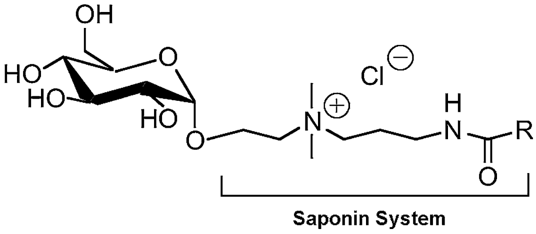
- Respectively big fragment with hydrophilic performance which comes from glucose
- Quaternary ammonium group
- Hydrophobic fatty segment

Those compounds may be classified as cationic surfactants with the extended hydrophilic constituent. The study of the literature sources indicates that few compounds of that type have been described. Based on the available source reports, one may only draw some general conclusions on the properties and potential applicability of such compounds. Compounds with similar structures were described in the patent [8] **7** and in the review [9].





The patent, however, does not comment on the surface active properties, but it only states that those compounds offer some specific properties which make them recommended for the hair conditioning formulations as well as flocculants and pigment dispersants. The obtained new compounds may also be taken as the saponin-type surfactants [9].



The saponin surfactants are used as components in hair care products and as emulsifiers. The addition of a carbohydrate radical may bring a number of advantageous properties to such products, such as:

- Better skin tolerance
- Superior emulsifying performance etc.

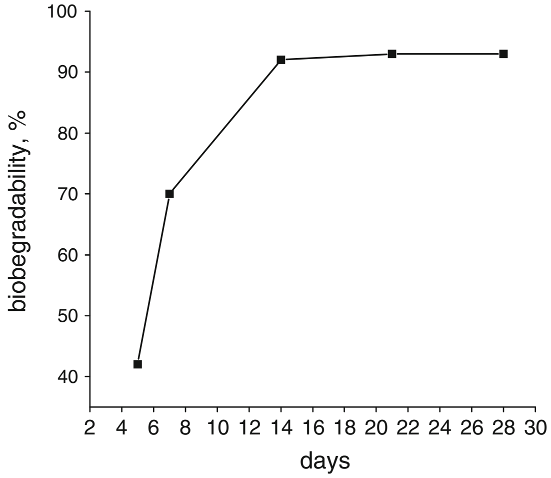


Fig. 5 Biodegradability of surfactant **6a**

Moreover, the presence of a quaternary ammonium group adds good germicidal and preservative properties to such compounds [9]. Those features are essential in the case of carbohydrate surface active compounds, for which the addition of a preservative is required in many instances.

The obtained new surface active compounds also appear to be favourable from the viewpoint of biodegradability. Their biodegradability is compared with that of selected carbohydrate surfactants below:

	Biodegradability (%)
Esters of saccharose	99–100
Aldonamide C_{18}	83 [9]
Aldonamide C_{12}	90 [9]
Compound **5a**	89
Compound **6a**	93

Figure 5 provides the biodegradation profile for the surfactant **6a** (aqueous solution with the concentration of 1% m/m) versus time. As can be seen, its maximum biodegradability can be achieved as soon as after only 14 days.

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Author Biographies

Janusz Nowicki (born 1954) graduated in 1978 from the Faculty of Chemistry, Wrocław University of Technology, Poland. Since 1980, he has worked at the Institute of Heavy Organic Synthesis “Blachownia” as a specialist in organic synthesis. In 1992, he obtained a Ph.D. at the Technical University of Łódź. His field of research covers the organic synthesis of specialty organic chemicals and heterogenous catalysis.

Adam Sokołowski (born 1941) studied chemistry from 1966 to 1971 at Wrocław University of Technology and received his Ph.D. at the same university in 1977. He is presently a professor of chemistry in the Department of Chemical Engineering. His work focuses on the surface properties of binary phases, microemulsions and the engineering of dispersed phases.

Dagmara Reksa (born 1983) graduated in 2008 from Wrocław University of Technology, Faculty of Chemistry, where she is now a Ph.D. student in the Department of Chemical Engineering. Her research interests include the surface properties of binary phases, microemulsions and ionic liquids as solvents.