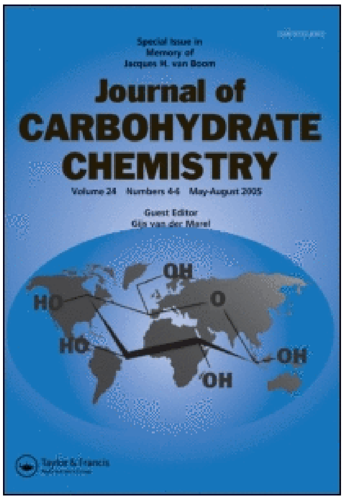

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CELLULOSE-BASED BIODEGRADABLE POLYMERIC SURFACTANTS

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ABSTRACT

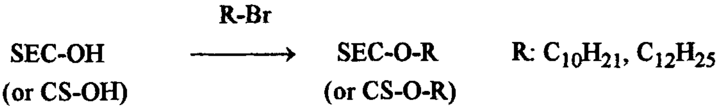
In this paper is reported the partial hydrophobization of *O*-(2-sulfoethyl)cellulose (SEC) using 1-bromododecane, 1-bromodecane, and 1-bromododecane with cellulose sulfate (CS), respectively, and characterization of the reaction products by both elemental and spectral analyses. The surface tension, critical micelle concentration (c.m.c.), foaming, emulsifying, detergency and antiredeposition power of the products were also studied. All prepared derivatives reduce the surface tension and exhibit remarkable emulsifying properties. Alkylated SECs were observed to have improved foaming, emulsifying and antiredeposition characteristics compared to the SECs.

INTRODUCTION

Water-soluble derivatives of polysaccharides can exhibit properties of biodegradable polymeric surfactants after an appropriate chemical modification. The hydrophobization of certain hydrophilic polysaccharides can be carried out by conversion to ethers or esters containing long alkyl or acyl groups (C_{10} - C_{18}). In previous papers[2,3] the partial hydrophobization of a water soluble *O*-(2-hydroxyethyl)cellulose (HEC) using alkyl or acyl halogenides was reported. The reaction conditions are governed to obtain products with a low DS and preserved water solubility. Prepared derivatives reduce the surface tension and have excellent emulsification efficiency. The present work deals with preparation of partially hydrophobized *O*-(2-sulfoethyl)cellulose (SEC) with a C_{12}- alkyl side chain, and cellulose sulfate (CS) with C_{10}-C_{12}-, respectively.

RESULTS AND DISCUSSION

New cellulose *O*-alkyl ethers *O*-dodecyl-(2-sulfoethyl)cellulose (SECL), *O*-decyl- and *O*-dodecyl-*O*-cellulose sulfate, respectively, were prepared according to the reaction scheme:



$$\begin{array}{ccc} \text{SEC-OH} & \xrightarrow{\text{R-Br}} & \text{SEC-O-R} \qquad \text{R: } C_{10}H_{21}, C_{12}H_{25} \\ \text{(or CS-OH)} & & \text{(or CS-O-R)} \end{array}$$

The water-soluble sodium salt of *O*-(2-sulfoethyl)cellulose (SEC) with DS_S=0.5 (degree of substitution by sulfoethyl groups) was obtained by reaction of cellulose with the sodium salt of 2-bromoethanesulfonic acid in the DMSO-SO_2-DEA system under homogeneous conditions, catalyzed by pyridine. The substitution of the hydroxyl groups of cellulose was confirmed by the IR spectra which agreed well with the data published.[4] The sodium salt of SEC was subsequently modified with 1-bromododecane (BDD) in dry DMF (dimethylformamide) using pyridine as a catalyst. Mass ratios of reactants, reaction temperature and the results from elementary analysis are given in Table 1. From the four derivatives SECL synthesized the one with DS_A=0.8 (degree of substitution by alkyl groups) was insoluble in water (SECL-4). It is evident, that the higher the mass ratio of the reactants w(SEC):w(BDD) at constant reaction time (3.5 h), the higher the DS_A (SECL-2 and 3). At constant mass ratio (1:5), DS_A increased with increasing reaction time. Optimum conditions for obtaining water-soluble derivatives are at mass reactant ratios of 1:3 - 1:5 and reaction time between 3.5 - 5.0 h.

The cellulose sulfate of lower molecular mass ($\overline{M}_w$=27,800) (CS-A) with DS_S=1.1 (calculated from the sulfur content and elementary analysis as well) was obtained by esterification of cellulose with chlorosulfonic acid in pyridine.[5] Modification of CS-A with BDD in the DMF/H_2O (1:1) system[2] homogeneously as well as heterogeneously in non-aqueous DMF,[2,3] using NaOH as catalyst in both media. By varying the reaction conditions (Table 1), LCS-A derivatives with low DS_A (0.01-0.1) were prepared. The cellulose sulfate (CS-B) of higher molecular mass was modified in the DMF/H_2O (1:1) system with BD and BDD, respectively. At the moderate reaction conditions used, the DS_A achieved was very low (~0.01) in both cases (Table 1).

Table 1. Synthesis and Elemental Analyses of Cellulose Derivatives

Compound	CD/ BDD (g/g)	Reaction time (h)	Reaction temperature (^oC)	DS_A	Elemental analyses Calcd/Found C (%)	H (%)	S (%)
SECL-1	1:3	3.5	90-100	0.30	47.75	7.21	6.00
					47.25	7.10	6.13
SECL-2	1:5	3.5	90-100	0.50	52.00	8.00	5.33
					52.18	7.06	5.47
SECL-3	1:5	5.0	90-100	0.70	55.39	8.63	4.79
					54.96	8.42	4.85
SECL-4[a]	1:5	7.0	90-100	0.80	56.85	8.90	4.56
					56.79	8.95	4.60
LCS-A-1	1:5	1.5	50	0.06	32.38	4.65	13.19
					32.18	4.50	13.25
LCS-A-2	1:5	3.0	50	0.01	32.25	4.49	11.24
					32.10	4.58	11.05
LCS-A-3	1:3	5.0	90-100	0.10	32.38	4.65	13.19
					32.45	4.70	13.10
DCS-B	1:5[b]	2.0	50	0.01	36.05	5.02	7.86
					35.90	5.22	7.15
LCS-B	1:5	2.0	50	0.01	35.99	5.01	7.86
					35.60	5.24	7.58

a. Insoluble in water. b. CD/BD. DS_A - Degree of substitution by alkyl groups. CD - Cellulose derivative.

The IR spectral data of all water-soluble alkylated derivatives are summarized in Table 2. They correspond well with the data published in paper[4] and support the alkylation of the derivatives.

Surface active properties of the water-soluble derivatives were characterized as to their surface tension, critical micelle concentration (c.m.c.), foaming, emulsifying, antiredeposition and detergency properties. SECL derivatives show a pronounced surface activity (Figure 1). The curves of the surface tension *vs.* log concentration resemble those of classic surfactants. SECL-3 with the highest DS_A was the most effective in reducing the surface tension (γ_{min}=37.8 mN.m^{-1} at c=2.5 kg.m^{-3}). Values of c.m.c. ranged in 0.75 - 0.90 kg.m^{-3}. Similar results have been reported for *O*-dodecyl- derivatives of HEC.[2] In contrast to LCS-A-1 and LCS-A-3, the LCS-A-2, DCS-B and LCS-B derivatives did not exhibit

Table 2. IR Spectral Data of the Synthesized Compounds

	υ / cm^{-1}					
Compound	$\upsilon(CH_3)$	$\upsilon(CH_2)$	$\upsilon(OH)$	$\upsilon_s(SO_2)$	$\upsilon_{as}(SO_2)$	$\gamma(C\text{-}H)$
SECL-1	2922	2851	3391	1166	1377	843
SECL-2	2921	2851	3397	1170	1381	847
SECL-3	2921	2851	3393	1169	1381	845
LCS-A-1	2926	2855	3484	1162	1375	---
LCS-A-2	2928	2856	3453	1174	1419	---
LCS-A-3	2926	2855	3454	1168	1380	---
DCS-B	2905	----	3458	1156	1375	808
LCS-B	2905	----	3453	1159	1377	808

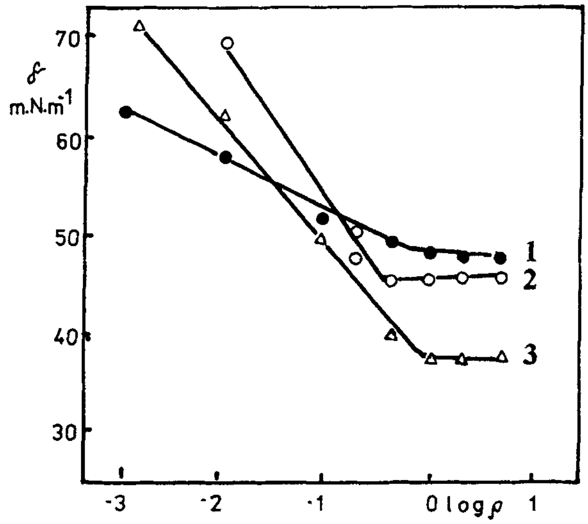


FIG. 1. Surface tension (γ) *vs.* log concentration of the SECL derivatives at 25 °C. 1. Compound SECL-1 (c.m.c. = 0.7 kg.m^{-3})., 2. compound SECL-2 (c.m.c. = 0.7 kg.m^{-3})., 3. compound SECL-3 (c.m.c. = 0.9 kg.m^{-3}).

a significant drop of surface tension what can be related to the small DS_A (~0.01) of these samples. The respective values of minimal surface tension for LCS-A-1 and LCS-A-3 were γ_{min}=57.6 mN.m^{-1} and γ_{min}=39.8 mN.m^{-1}, respectively. Values of c.m.c. ranged in 0.74 - 1.17 kg.m^{-3}.

SECL exhibits a high foaming power comparable with that of Tween 20 (oxyethylated monolauransorbitol).[6] The best results from the point of the complex of properties studied were achieved with the derivative SECL-3 (DS_A=0.7). At concentration below 1 kg.m^{-3}, no foaming was observed (Figure 2). The foaming properties of alkylated cellulose sulfate derivatives are not significant.

The emulsification efficiency was determined by evaluation of the stability of 10% o/w emulsions using paraffinic oil. In the procedure 10% wt. of surfactants on the oil base were used.

The results were compared with the commercial emulsifier Tween 20.[6] As can be seen from Table 3 all cellulose derivatives have pronounced emulsifying power which reaches the Tween 20 level. Except for LCS-B, a discrete separated oil layer was observed in all cases after 24 h. The high emulsion efficiency can be elucidated by considering a dual action of derivatives, *i.e.* the formation of interfacial films on the face boundaries while simultaneously affecting the continual phase viscosity in the role of a molecular colloid.

Evaluation of the washing power (WP) of the alkylated cellulose derivatives in both neutral and alkaline medium (containing Na_2CO_3) using oily-soil with particles of soot is given in Table 4. All derivatives show rather low WP values in neutral medium compared to that of the standard LAS. Higher values were established in alkaline medium due to increase of the dispersing effect. Best results were obtained in the case of the LCS-A-3 surfactant with the highest DS_A (~0.1). The low-substituted derivatives do not create micelles in bulk phase and thus they do not show a solubilizing effect on the oily soil components. Both surfactants LCS-A-1 and LCS-A-3 form micelles. Derivative LCS-A-3 can better stabilise the soil in the washing bath, the result of which is the higher final WP value.

The results from antiredeposition efficiency of alkylated cellulose sulfates are given in Table 5. The derivatives LCS-A-1, LCS-A-3, LCS-B and original cellulose sulfate (CS-B) exhibit lower values of antiredeposition efficiency in comparison to carboxymethylcellulose (CMC). The synergistic effect of derivatives with CMC was also examined. The results indicate a strong synergistic effect for LCS-A-3 derivative with DS_A~0.1 up to the value of 41.9%. A weaker synergistic effect was observed in the case of the LCS-B derivative which has the lowest DS_A.

In conclusion, it was confirmed that the partial hydrophobization by long alkyl chains of water-soluble cellulose derivatives yields products with significant surface-active properties. These polymeric surfactants represent a special group of surface-active substances which can be interposed between fully synthetic surfactants and biosurfactants. Similar as other low substituted cellulose surfactants[2] they are biodegradable.

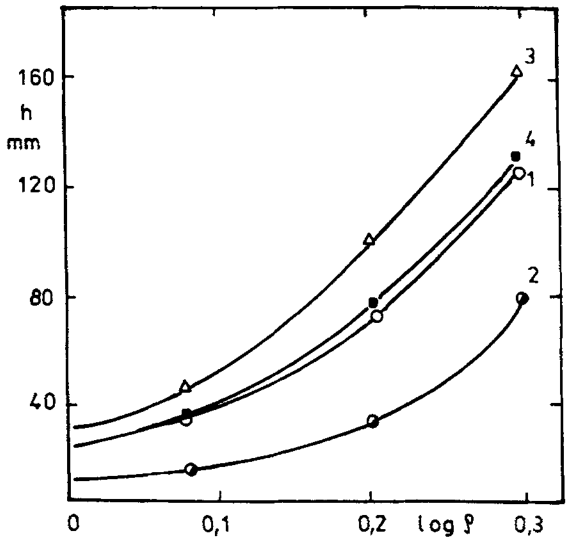


FIG. 2. Foamibility of the SECL derivatives expressed in terms of the height of the foam column after outflow of the last drop of solution (h_1) and after 5 min (h_2) at different log concentrations. 1. h_1 (compounds SECL-1, 2)., 2. h_2 (compounds SECL-1, 2)., 3. h_1 (compound SECL-3)., 4. h_2 (compound SECL-3).

Table 3. Emulsification Efficiency of Derivatives Expressed in Terms of the Height of Cream Column Formed as a Function of Storage Time after 5 min (h_1), 1 h (h_2), and 24 h (h_3) Compared with Tween 20

	Oil layer (cream layer)/mm			Type of
Compound	h_1	h_2	h_3	emulsion
SECL-1	0(10)	0(10)	4(10)	o/w
SECL-2	0(10)	0(10)	3(10)	o/w
SECL-3	0(10)	0(10)	1(10)	o/w
LCS-A-1	0(2)	0(3)	2(6)	o/w
LCS-A-2	0(4)	0(5)	0(7)	o/w
LCS-A-3	0(1)	0(2)	3(6)	o/w
DCS-B	0(0)	0(3)	1(4)	o/w
LCS-B	0(0)	1(6)	2(7)	o/w
Tween 20	0(0)	0(0)	0(2)	o/w

Table 4. Washing Power of Synthesized Derivatives

Compound	Washing power / %	
	Neutral detergency	Alkaline detergency
LCS-A-1	11.3	20.0
LCS-A-3	16.9	28.4
CS-A	5.4	18.9
DCS-B	2.7	11.1
LCS-B	2.8	6.1
CS-B	2.2	—
LAS	29.0	35.0

LAS - sodium dodecylbenzene sulfonate

Table 5. Antiredeposition Efficiency of Synthesized Derivatives

Compound	Degree of whiteness		Antiredeposition efficiency U / %
	Before washing	After washing	
CMC	0.85	0.55	30.9
LCS-A-1	0.85	0.49	16.2
LCS-A-3	0.85	0.52	24.1
LCS-A-1+CMC	0.85	0.57	34.1
LCS-A-3+CMC	0.85	0.60	41.9
CS-B	0.85	0.43	1.5
LCS-B	0.85	0.47	12.5
LCS-B+CMC	0.85	0.51	19.7
A	0.85	0.42	—

LCS-A-1+CMC - cotton fabric scoured in a bath containing 1.0 mL of CMC (c=5 kg.m^{-3}) and 1.0 mL of LCS-A-1 (c=5 kg.m^{-3}), *etc.*

A - cotton fabric scoured in a bath of soil without the addition of an antiredeposition agent

EXPERIMENTAL

Materials and general procedures. Microcrystalline cellulose powder with $\overline{M}_w$=26,000 and cellulose with $\overline{M}_w$=80,000 (determined by viscosimetry) were used as cellulose samples. The sodium salt of 2-bromoethanesulfonic acid, 1-bromodecane (BD), 1-bromododecane (BDD) were from Merck. CMC with $\overline{M}_w$=570,650 and DS=1 was of commercial product (Hercules).

IR spectra were measured on KBr pellets using a PU 9 800 FTIR device (Philips Analytical). Surface tension was determined at 25 °C according to reference 7 using the Lecompte du Nouy device in the concentration range 0.001-5 kg.m^{-3}. The critical micelle concentration was estimated from the plot of the surface tension *vs.* log concentration. The foaming ability of the surfactants was determined at 25 °C by the Ross-Milles method[8] in the concentration range 1-2 kg.m^{-3} and expressed as the height of the foam column formed after the outflow of the last drop of solution (h_1) and that after 5 min (h_2). Emulsification was carried out according to reference 6. Emulsions of the o/w type were obtained using 10 mL of paraffin oil dyed with SUDAN IV and 90 mL of water containing 1.0 g of prepared cellulose derivative by means of a laboratory mixer. The stability of emulsions was estimated in three different time intervals after the emulsions were prepared, *i.e.* 5 min (h_1), 1 h (h_2), and 24 h (h_3) and is expressed in terms of cream layer formed onto surface. The antiredeposition efficiency was determined by the method of Stupel[9] measuring the degree of whiteness of a cotton fabric prior to and after laundering in a bath of soil. The whiteness of cotton fabrics was measured using a Leukometer apparatus (by Carl Zeiss Jena) equipped with a white filter. Detergency power was assessed by measuring the reflectance of artificially soiled cotton fabrics after washing in aqueous derivatives solutions, using standard cotton fabrics[6]. The bath volume was 100 mL (concentration of derivatives c=3 kg.m^{-3}), 0.2 g of Na_2CO_3 (alkaline detergency) at 80 °C. Fabrics samples were then washed and finally dried at 60 °C for 1 h.

Sodium salt of *O*-(2-sulfoethyl)cellulose. Cellulose (1 g) dried at 105 °C for 3 h was suspended in anhydrous DMSO (20 mL) at constant stirring and DMSO-SO_2-DEA (12 mL) prepared according to reference 10 were added to the suspension. Then, anhydrous pyridine (1 mL) and the sodium salt of 2-bromoethanesulfonic acid (1.5 g) dissolved in DMSO (10 mL) were added. The reaction mixture was stirred at 50-60 °C for 15 h. The polymer was precipitated into 500 mL of acetone, filtered and washed with acetone. The product was dialyzed, concentrated under diminished pressure at 60 °C to yield the sodium salt of SEC (1.2 g) (DS_S=0.5). IR (KBr) 3410 (OH), 2903 (CH_2), 1373 $(SO_2)_{as}$, 1163 $(SO_2)_S$.

Anal. Calcd: C, 37.00., H, 5.10., S, 7.10. Found: C, 36.78., H, 4.09., S, 7.17.

***O*-Dodecyl ether of *O*-(2-sulfoethyl)cellulose.** To a stirred mixture of the SEC (1.1 g) and anhydrous DMF (50 mL), pyridine (2 mL) and, after 1 h BDD (5.5 g) in DMF (5 mL) was added. The reaction was stirred at 90-100 °C for 3.5 h. The mixture was then poured into 50 mL of distilled water. The precipitate was filtered off and the filtrate extracted twice with 50 mL of benzene in order to remove the unreacted 1-bromododecane. The water layer was concentrated at 60 °C under vacuum. The product was filtered off and extracted with diethyl ether in a Soxhlet apparatus for 10 h. The yield of the alkylated derivative SECL-2 was 1 g (DS_A=0.5). The same procedure was used for SECL-1, 3 and 4 by varying reaction conditions. The final products were dried at 60 °C for 3 h and characterized by elemental analysis and infrared spectra.

Cellulose sulfate. The sulfation of both cellulose samples was carried out according to the procedure described in reference 5. The obtained products CS-A and CS-B have DS_S ~1.1 and $\overline{M}_n$=27,800 and 80,800, respectively (determined by osmometry). IR (KBr) 3429 (OH), 1385 $(SO_2)_{as}$, 1170 $(SO_2)_s$. The content of S was 13.7 (CS-A) and 13.5% (CS-B).

***O*-Dodecyl ether of *O*-cellulose sulfate.** Under homogeneous conditions, CS-A (4.7 g) was dissolved in distilled water (45 mL). A solution of NaOH (0.9 g) in water (3 mL) was then added. The mixture was stirred at room temperature for 1.5 h. Then BDD (23.5 g) in DMF (48 mL) was added dropwise under stirring and reaction proceeded at 50 °C for 1.5 h. After cooling the reaction mixture to room temperature, it was poured into 800 mL of ethanol. The product was filtered, washed with 200 mL of ethanol and finally dried over P_2O_5 for 5-6 h in vacuum to yield LCS-A-1. LCS-A-2 was prepared by the same procedure as under reaction conditions given in Table 1. Under heterogeneous conditions, CS-A (3 g) was dispersed in DMF (90 mL), then powdered NaOH (0.75 g) was added to the reaction mixture. After stirring at 80 °C for 20 min, and subsequent cooling to 30 °C, BDD (9 g) (wt. ratio CS-A:BDD=1:3) was added and the reaction allowed to proceed at 90-100 °C for 5 h. After cooling to room temperature the mixture was poured into 650 mL of ethanol. The product was filtered, washed with 200 mL of ethanol and finally dried over P_2O_5 for 24 h, yielding LCS-A-3 (1.9 g).

***O*-Decyl ether of *O*-cellulose sulfate (DCS-B) and *O*-dodecyl-*O*-cellulose sulfate (LCS-B).** The procedure is similar as is described for preparation of LCS-A-1 and LCS-A-2.

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