New Alkylated *O*-(2-Sulfoethyl)cellulose and Its Properties

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Dedicated to Professor Ing. K. Antoš, CSc., in honour of his 70th birthday

New *O*-(2-sulfoethyl) derivatives of cellulose substituted with *O*-dodecyl chains have been synthesized and characterized by elemental and spectral analyses. The prepared derivatives exhibit significant surface-active properties, the emulsification efficiency, and foamability.

Introduction of suitable substituents into the macromolecule of cellulose enables to prepare derivatives with various new properties (polymer with a liquid-crystalline structure, Langmuir—Blodgett films, tensides, and carriers for immobilization of enzymes) [1, 2].

By chemical modification of cellulose with 2-haloalkylsulfonates, the water-soluble *O*-sulfoalkyl-celluloses can be obtained which have utilization in technological applications and also as an intermediate for other modifications of cellulose [3]. *O*-Sulfoethylcellulose and its derivatives may serve as wetting agents and show antiredepositive effects [3].

This type of modification is usually carried out in aqueous alkaline medium which promotes the destruction of cellulose. A lower degradation is observed in the presence of an immiscible solvent like chloroform, higher alcohols, *etc.*, in the reaction medium. However, the alkylation reaction proceeds under more heterogeneous conditions which limits the degree of substitution [3].

Water-soluble derivatives of polysaccharides (*O*-(2-hydroxyethyl)cellulose, *O*-carboxymethylcellulose) can exhibit properties of biodegradable polymeric surfactants [4, 10] after an appropriate chemical modification, *e.g.* by introducing alkyl or acyl groups with number of carbon atoms C_{10} up to C_{18} into an appropriate low degree of substitution.

The present work deals with preparation of the sodium salt of *O*-sulfoethylcellulose in a homogeneous medium using dimethyl sulfoxide (DMSO)—SO_2—diethylamine (DEA) as cellulose solvent as well as a derivative containing *O*-dodecyl side chains.

EXPERIMENTAL

Microcrystalline cellulose powder was used as a cellulose sample with the polymerization degree $\overline{DP} = 160$ and $\overline{M}_m = 26000$ g mol⁻¹ (determined by viscosimetric measurements).

The sodium salt of 2-bromoethanesulfonic acid (Merck), 1-bromododecane (laurylbromide, LB) and other used chemicals were of anal. grade purity. Distilled water was used for preparation of solutions. The IR spectra were measured in KBr pellets using a PU 9800 FTIR device (Philips Analytical).

Surface tension was determined at 25 °C according to Ref. [5] using the Lecompte du Nouy device in the concentration range 0.001—5 g dm⁻³. The critical micelle concentration was estimated from the plot of the surface tension *vs.* log concentration. The ability of the prepared surfactants to form foams was determined at 25 °C by the Ross—Milles method [6] in the concentration range 1—2 g dm⁻³. The foaming power is 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). Emulsions of the o/w type were obtained using 10 cm³ of paraffinic oil dyed with SUDAN IV and 90 cm³ of water containing 1.0 g of *O*-dodecyl-*O*-(2-sulfoethyl)cellulose by means of a laboratory mixer. Emulsification was carried out according to Ref. [7]. 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 on the surface (Table 3).

Table 1. Alkylation Conditions of the Sodium Salt of O-(2-Sulfoethyl)cellulose (SEC) ($DS_S = 0.5$) with 1-Bromododecane (LB)

Compound	$w(SEC):w(LB)$	Reaction time h	DS_L	$w_i(calc.)/\%$ $w_i(found)/\%$		
				C	H	S
I	1:5	5.0	0.7	55.39	8.63	4.79
				54.96	8.42	4.85
II	1:5	3.5	0.5	52.00	8.00	5.33
				52.18	7.06	5.47
III	1:3	3.5	0.3	47.75	7.21	6.00
				47.25	7.10	6.13
$IV*$	1:5	7.0	0.8	56.85	8.90	4.56
				56.79	8.95	4.60

*Compound insoluble in water; DS_S – degree of substitution by 2-sulfoethyl groups; DS_L – degree of substitution by dodecyl (lauryl) groups.

Table 2. IR Spectral Data of the Synthesized Compounds

Compound	$\tilde{\nu}/cm^{-1}$					
	$\nu(CH_3)$	$\nu(CH_2)$	$\nu(OH)$	$\nu_s(SO_2)$	$\nu_{as}(SO_2)$	$\nu(C—H)$
I	2922	2851	3391	1166	1377	843
II	2921	2851	3397	1170	1381	847
III	2921	2851	3393	1169	1381	845

Sodium Salt of O-(2-Sulfoethyl)cellulose (SEC)

1 g of cellulose dried at 105 °C for 3 h was suspended in 20 cm³ of anhydrous DMSO at constant stirring and 12 cm³ of DMSO—SO₂—DEA prepared according to Ref. [8] were added to the suspension. Then, 1 cm³ of anhydrous pyridine and 1.5 g of sodium salt of 2-bromoethanesulfonic acid dissolved in 10 cm³ of DMSO were added. The reaction mixture was stirred for 15 h at 50—60 °C. The polymer was precipitated into 500 cm³ of acetone, filtered and washed with acetone. The product was dialyzed, evaporated under diminished pressure at 60 °C for 8 h to yield the sodium salt of SEC (1.2 g) (degree of substitution (DS) = 0.5).

Elemental analysis: w_i(calc.): 37.00 % C, 5.10 % H, 7.10 % S; w_i(found): 36.78 % C, 4.09 % H, 7.17 % S. IR spectrum (KBr pellet), $\tilde{\nu}/cm^{-1}$: 3410 ν(OH), 2903 ν(CH₂), 1373 ν_{as}(SO₂), 1163 ν_s(SO₂).

O-Dodecyl-O-(2-sulfoethyl)cellulose (O-Lauryl-O-(2-sulfoethyl)cellulose (LSEC))

To a stirred mixture of 1.1 g of the sodium salt of SEC (DS = 0.5) and 50 cm³ of anhydrous N,N-dimethylformamide (DMF), 2 cm³ of pyridine and, after 1 h, 5.5 g of 1-bromododecane in 5 cm³ of DMF were added. The reaction was allowed to proceed under stirring at 90—100 °C for 3.5 h. The mixture was then poured into 50 cm³ of distilled water. The precipitate was filtered off and the filtrate extracted twice with 50 cm³ of benzene in order to remove the unreacted 1-bromododecane. The water layer was concen-

trated 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 (LSEC) was 1 g ($DS_L = 0.5$). The same procedure was used for preparation of the LSEC derivatives having $DS_L = 0.3$ and 0.7, respectively, using different reaction conditions (Table 1). The final products were dried at 60 °C for 3 h and characterized by elemental analysis (Table 1) and infrared spectra (Table 2).

RESULTS AND DISCUSSION

A new cellulose derivative, O-dodecyl-O-(2-sulfoethyl)cellulose (LSEC) was prepared by two successive alkylations. In the first step, the water-soluble sodium salt of O-(2-sulfoethyl)cellulose (SEC) with $DS_S = 0.5$ was prepared by reaction of cellulose with the sodium salt of 2-bromoethanesulfonic acid. The reaction was carried out in the homogeneous medium of DMSO—SO₂—DEA, the mass ratio being 1:1.5, with the catalytic amount of pyridine. Evidence of substitution of the hydroxyl groups of cellulose anhydroglucose units was obtained from the IR spectra, which agreed well with the data published [9].

The prepared sodium salt SEC was subsequently modified with 1-bromododecane (LB) in such a way that the water solubility of the product was preserved. The reaction was performed in DMF using pyridine as a catalyst. Mass ratios of reactants and temperature are given in Table 1.

From among four alkylated derivatives LSEC synthesized one with $DS_L = 0.8$ was insoluble in water. The higher mass ratio $w(SEC):w(LB)$ at the same

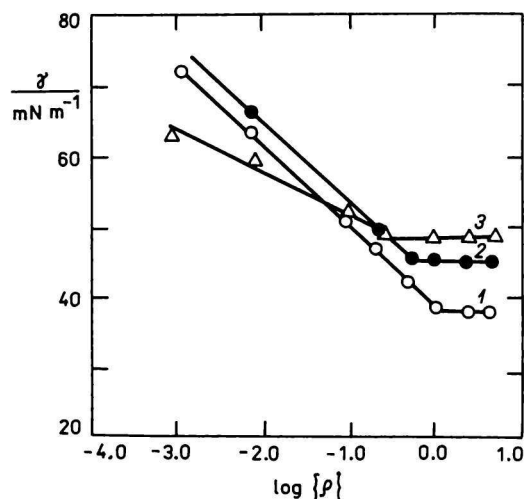**Fig. 1.** Surface tension (γ) *vs.* log concentration of the LSEC derivatives at 25 °C. *1.* Compound *I* (c.m.c. = 0.90 g dm^{-3}); *2.* compound *II* (c.m.c. = 0.77 g dm^{-3}); *3.* compound *III* (c.m.c. = 0.75 g dm^{-3}).

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)

Compound	Oil layer (cream layer)			Type of emulsion
	h_1/mm	h_2/mm	h_3/mm	
I	0(10)	0(10)	1(10)	o/w
II	0(10)	0(10)	3(10)	o/w
III	0(10)	1(10)	4(10)	o/w

reaction time (3.5 h), the higher DS$_L$ (LSEC *II* and *III*). When the mass ratio was constant (1:5), with longer reaction time DS$_L$ increased (LSEC *II* and *IV*). The best results were obtained with the mass ratio in the range of 1:3 to 1:5 and the reaction time of 3.5 to 5 h.

The IR spectra of these products are given in Table 2. The data obtained correspond well with the data published in paper [9] and support the structure of prepared LSEC derivatives.

The surface tension, critical micelle concentration (c.m.c.), both foaming and emulsifying power of the prepared products were also studied.

The LSEC derivatives *I—III* have a pronounced surface activity. The curves of the surface tension *vs.* log concentration have typical shape of classic surfactants (Fig. 1). The LSEC *I* product was the most effective in reducing the surface tension (γ_{min} = 37.8 mN m^{-1} at c = 2.5 g dm^{-3}). Values of c.m.c. ranged in 0.75—0.90 g dm^{-3}. Similar results were obtained with *O*-dodecyl derivatives of *O*-(2-hydroxyethyl)cellulose [4].
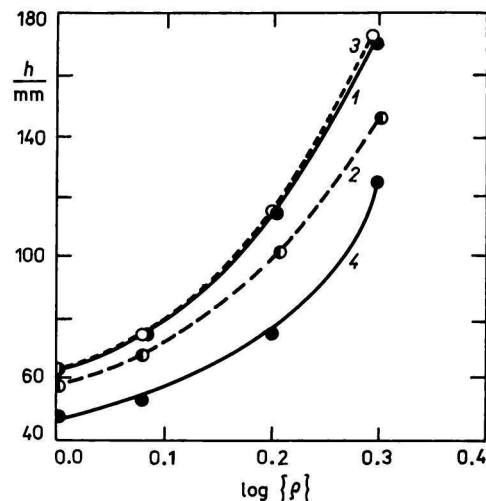
Fig. 2. Foamability of the LSEC derivatives expressed in terms of the height of the foam column after outflow of the last drop of solution (h_1) and after 5 min (h_2) at different log concentrations. *1.* h_1 (compound *I*); *2.* h_2 (compound *I*); *3.* h_1 (compounds *II, III*); *4.* h_2 (compounds *II, III*).

The LSEC derivatives exhibit excellent emulsifying properties (Table 3) comparable with those of the commercial product Tween 20 [7].

LSEC exhibits also a higher foaming power compared with Tween 20 [7]. The best results from the point of the complex properties studied were achieved with the derivative LSEC *I* (DS$_L$ = 0.7). When the concentration was below 1 g dm^{-3} no foaming was observed (Fig. 2).

In conclusion, it was confirmed that the partial hydrophobization of water-soluble SEC derivatives with dodecyl group leads to products with good surfactant properties.

These polymeric surfactants based on water-soluble cellulose derivatives represent a special group of surface-active substances which can be interposed between fully synthetic surfactants and biosurfactants.

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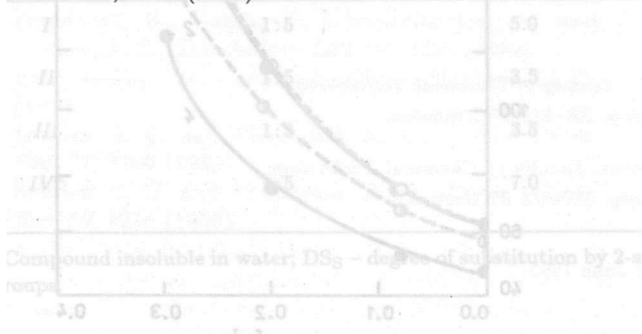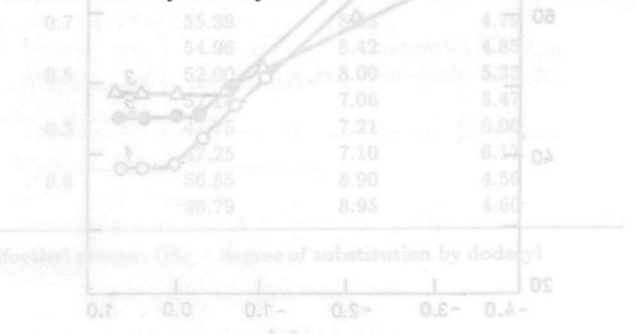
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