Polymeric Surfactants Prepared from Water-Soluble
O-(2-Hydroxyethyl)cellulose

P. TALÁBA, I. SROKOVÁ, and P. HODUL

Department of Fibres and Textile, Faculty of Chemical Technology,
Slovak Technical University, SK-812 37 Bratislava

By partial hydrophobization of O-(2-hydroxyethyl)cellulose with chlorides of higher fatty acids (C_{12} and C_{18}) the new O-dodecanoyl-O-(2-hydroxyethyl)cellulose and O-octadecanoyl-O-(2-hydroxyethyl)cellulose have been synthesized and characterized by elemental and spectral analyses. The prepared derivatives reduce the surface tension of water and have a good emulsification efficiency.

Water-soluble derivatives of polysaccharides can exhibit properties of biodegradable polymeric surfactants after an appropriate chemical modification. The hydrophobization can be carried out by introducing alkyl or acyl groups with a higher number of carbon atoms (C_{10} up to C_{18}) to a low degree of substitution in such a way that the water solubility of the products is well-preserved. Both alkylation and acylation types of reaction have been realized under heterogeneous or homogeneous conditions using NaOH or pyridine as catalyst [1, 2]. Derivatives obtained by these partial hydrophobizations exhibit significant surface-active properties. In the previous paper [1] the preparation of O-(2-hydroxyethyl)cellulose containing O-dodecyl side chains which leads to products with excellent emulsification efficiency is described. Similar properties from the surface activity point of view have been reported for O-dodecyl-O-(2-sulfoethyl)cellulose [3].

The present work deals with the preparation of water-soluble O-(2-hydroxyethyl)cellulose containing O-dodecanoyl.or O-octadecanoyl side chains.

EXPERIMENTAL

Water-soluble hydroxyethylcellulose (HEC) used in this study had the following characteristics: polymerization degree $\overline{DP} = 600$, $\overline{M}_N = 123000$ g mol^{-1} (determined by viscometry), hydroxyethylation degree $DS_{HE} = 1.3$, and $w(ash) = 3.6$ %.

Dodecanoyl and octadecanoyl chlorides were commercial products (Merck). Distilled water was used for preparation of solution. The IR spectra were measured in KBr pellets using a PU 9800 FTIR device (Philips Analytical). The UV spectra were measured in the cadoxene—H_2O using a Specord UV VIS device (Zeiss, Jena).

Surface tension was determined at 25 °C according to Ref. [4] 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 of the numerical value of concentration. The ability of the prepared surfactants to form foams was determined at 25 °C by the Ross—Milles method [5] in the concentration range 1—2 g dm^{-3}. The foamability 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 oil-water (o/w) type were obtained using 10 cm^3 of paraffinic oil dyed with Sudan IV and 90 cm^3 of water containing 1.0 g of prepared derivatives, by means of a laboratory mixer. Emulsification was carried out according to Ref. [6]. 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.

O-Dodecanoyl-O-(2-hydroxyethyl)cellulose (DHEC) and O-Octadecanoyl-O-(2-hydroxyethyl)cellulose (OHEC)

5 g of HEC dried at 105 °C for 3 h was suspended in 50 cm^3 of anhydrous N,N-dimethylformamide (DMF) at constant stirring for 40—60 min at 90 °C. Then the reaction mixture was cooled at 50 °C and 1.4 cm^3 (0.018 mol) of anhydrous pyridine and 0.018 mol of dodecanoyl chloride (octadecanoyl chloride) were added into the solution. The reaction was allowed to proceed under stirring at 90 °C for 3 h. The polymer was pre-

Table 1. Modification of HEC with Dodecanoyl Chloride (LCH) and Octadecanoyl Chloride (SCH)

Compound	w(HEC) : w(LCH, resp. SCH)	Reaction time	Solubility in water	DS_R	w_i(calc.)/% w_i(found)/%	
		h			C	H
I	1 : 1	3.0	S	0.01*	47.28	7.10
					47.34	6.97
II	1 : 1	5.0	I	0.30	53.41	8.06
					53.34	7.96
III	1 : 1	10.0	I	0.30	53.41	8.06
					53.32	8.10
IV	1 : 1	20.0	I	0.30	53.41	8.06
					53.20	8.15
V	2 : 1	5.0	S	0.01*	47.28	7.10
					47.14	7.02
VI	3 : 1	5.0	S	0.01*	47.28	7.10
					47.20	7.12
VII	3 : 1	8.0	S	0.01*	47.28	7.10
					47.12	6.88
VIII	1 : 1	0.5	PS	0.25	54.96	8.39
					54.80	8.43
IX	1 : 1	3.0	PS	0.25	54.96	8.39
					54.62	8.14
X	1 : 1	5.0	I	0.30	56.13	8.59
					56.47	8.70
XI	1 : 1	10.0	I	0.30	56.13	8.59
					56.02	8.12
XII	1 : 1	20.0	I	0.30	56.13	8.59
					56.20	8.50
XIII	2 : 1	3.0	S	0.01*	47.43	7.13
					47.49	7.00
XIV	2 : 1	5.0	I	0.30	56.13	8.59
					55.96	8.25
XV	3 : 1	3.0	S	0.01*	47.43	7.13
					47.28	6.98
XVI	3 : 1	5.0	S	0.01*	47.43	7.13
					47.35	7.20

DS_R – degree of substitution by dodecanoyl or octadecanoyl groups; I, PS, S – compound insoluble, partially soluble, and soluble in water; *I—VII*: *O*-dodecanoyl-*O*-(2-hydroxyethyl)cellulose; *VIII—XVI*: *O*-octadecanoyl-*O*-(2-hydroxyethyl)cellulose; *DS_R determined from the UV spectra.

cipitated into 500 cm³ of acetone, filtered and washed with acetone. Then the final product (*I*) was dialyzed and evaporated under diminished pressure at 60 °C for 6 h to yield the DHEC (5.5 g) (degree of substitution (DS_R) ≈ 0.01).

The same procedure was used for preparation of the other DHEC (compounds *II—VII*) and OHEC (compounds *VIII—XVI*) derivatives, respectively, using different reaction conditions (Table 1). All prepared products were characterized by elemental analysis (Table 1) and water-soluble products (*I, V—VII, XIII, XV, XVI*) by the IR spectra (Table 2).

RESULTS AND DISCUSSION

For the preparation of acyl derivatives of hydroxyethylcellulose, the water-soluble HEC and chlorides of both dodecanic ($CH_3(CH_2)_{10}$—COCl, LCH) and octadecanic ($CH_3(CH_2)_{16}$—COCl, SCH) acids were used.

Partial hydrophobization of HEC was carried out,

similarly as the synthesis of cellulose stearate and oleate, respectively, or alkyl derivatives of HEC in anhydrous *N,N*-dimethylformamide (DMF) using pyridine as catalyst at ≈ 90 °C [1, 7, 8]. The mass ratios of HEC to chloride were from 1:1 to 3:1, and the reaction time 0.5—20 h. In order to prepare water-soluble derivatives, in this way we prepared the *O*-dodecanoyl-*O*-(2-hydroxyethyl)cellulose (DHEC) (*I—VII*) and the *O*-octadecanoyl-*O*-(2-hydroxyethyl)cellulose (OHEC) (*VIII—XVI*) varying in DS_R (Table 1). When modifying the HEC with dodecanoyl chloride at the mass ratio of 1:1, and at the reaction time longer than 5 h, derivatives with DS_R ≈ 0.3 (*II—IV*) partially soluble or insoluble in water were obtained. Modification of HEC with octadecanoyl chloride at the same mass ratio of reactants gave similar results in the whole range of reaction time of 0.5—20 h (*VIII—XII*). As can be seen from Table 1, the reaction time does not influence significantly the DS_R (degree of substitution with respect to the content of dodecanoyl and octadecanoyl groups, respectively) in the range of 5—

Table 2. IR Spectral Data of Water-Soluble Acyl Derivatives of HEC

Compound	$\tilde{\nu}/\mathrm{cm}^{-1}$				
	$\nu(\mathrm{OH})$	$\nu(\mathrm{CH3})$	$\nu(\mathrm{CH2})$	$\nu(\mathrm{C{=}O})$	$\gamma(\mathrm{C{-}H})$
I	3393	2926	2855	1753	847
V	3397	2926	2856	1747	845
VI	3392	2928	2855	1750	845
VII	3397	2926	2856	1755	843
XIII	3396	2924	2850	1747	842
XV	3397	2928	2854	1750	847
XVI	3393	2928	2855	1738	847

20 h. When the reaction time was lowered to 3 h, the mass ratio being unchanged (1:1), the significant decrease of DS_R (0.01) was achieved so that derivative *I* was already soluble in water. With the aim to prepare water-soluble derivatives, the mass ratio of reactants was changed to 2:1 and 3:1 under simultaneous change of the reaction time (Table 1). From the results achieved it is apparent that the mass ratio of HEC/acyl chloride considerably influences the DS_R. The water-soluble derivatives *I, V—VII, XIII,* and *XV, XVI* exhibit DS_R values ≈ 0.01 in comparison to derivatives *II—IV, VIII—XII,* and *XIV* which are insoluble ($DS_R \approx 0.3$).

The IR spectra of water-soluble derivatives are given in Table 2. In the spectra intense bands at $\tilde{\nu} \approx 1740 \mathrm{~cm}^{-1}$ corresponding to the ester C=O stretchings of the acyl groups were found. Intense absorption bands at $\tilde{\nu} = 2850$—$2928 \mathrm{~cm}^{-1}$ were assigned to stretching vibrations of the methylene and methyl groups, in accordance with data published in paper [9]. The UV spectra of prepared products show an absorption maximum at $\lambda = 258$ nm with the absorption edge at 300 nm. This was used to evaluate low DS_R values [10].

Surface-active properties of the water-soluble derivatives of HEC (*I, V—VII, XIII, XV, XVI*) were characterized by surface tension, critical micelle concentration (c.m.c.), foamability, and emulsifying power. From Figs. 1 and 2 it can be seen that the derivatives lower the surface tension of water and exhibit the typical dependence of surface tension on log of the concentration. In Table 3 the values of minimal surface tension (γ_{min}) and that of c.m.c. are summarized. The DHEC derivatives compared with the OHEC ones exhibit lower values of surface tension in the range of critical micelle concentration. The values γ_{min} for the DHEC derivatives (*I, V—VII*) ranged from 49.6 to 52.3 mN m^{-1} whereas those for the OHEC ones (*XIII, XV, XVI*) from 51.4 to 59.9 mN m^{-1}. Results achieved are higher when compared with values of γ_{min} for the *O*-dodecyl-*O*-(2-hydroxyethyl)cellulose [1] (31.5 mN m^{-1}) and the *O*-dodecyl-*O*-(2-sulfoethyl)cellulose [3] (37.8 mN m^{-1}). The determined surface tension val-
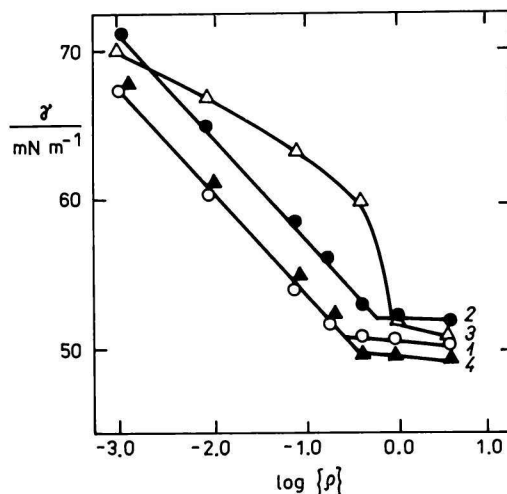

Fig. 1. Surface tension (γ) *vs.* log of the numerical value of concentration of the DHEC derivatives at 25 °C. *1.* Compound *I* (c.m.c. = 0.3 g dm^{-3}), *2.* compound *V* (c.m.c. = 0.6 g dm^{-3}), *3.* compound *VI* (c.m.c. = 1.0 g dm^{-3}), *4.* compound *VII* (c.m.c. = 0.4 g dm^{-3}).
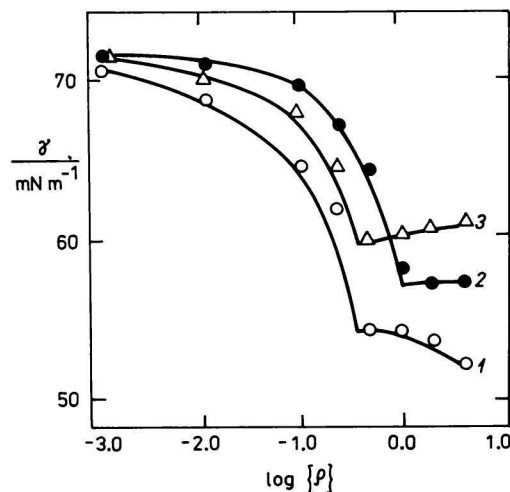

Fig. 2. Surface tension (γ) *vs.* log of the numerical value of concentration of the OHEC derivatives at 25 °C. *1.* Compound *XIII* (c.m.c. = 0.5 g dm^{-3}), *2.* compound *XV* (c.m.c. = 1.0 g dm^{-3}), *3.* compound *XVI* (c.m.c. = 0.5 g dm^{-3}).

ues can be accounted for in terms of low degree of substitution with respect to C_{12} and C_{18} acyl groups, respectively ($DS_R \approx 0.01$). The value γ_{min} for HEC is 61.6 mN m^{-1}, which agrees well with Ref. [1]. The HEC does not aggregate in bulk and does not form micelles [3].

Foamability of the water-soluble derivatives was estimated by the Ross—Milles method. In the studied range of concentration, the derivatives exhibit no significant foamability. The column heights after running out of the last drop (h_1) and that after 5 min (h_2) were 65 mm and 35 mm in the case of DHEC derivatives

Table 3. Values of γ_{min} and c.m.c. of Water-Soluble Acyl Derivatives of HEC with $DS_R \approx 0.01$ Compared to Those of Unmodified HEC

Compound	γ_{min} mN m^{-1}	c.m.c. g dm^{-3}
I	50.6	0.3
V	52.3	0.6
VI	51.1	1.0
VII	49.6	0.4
XIII	51.4	0.5
XV	56.1	1.0
XVI	59.9	0.5
HEC	61.6	–

Table 4. Emulsification Efficiency of Derivatives Expressed in Terms of the Height (mm) 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 to That of Tween 20

Compound	Oil layer (cream layer)			Type of emulsion
	h_1/mm	h_2/mm	h_3/mm	
V	0(0)	0(0)	1.5(2.0)	o/w
VI	0(0)	0(0)	4.0(2.5)	o/w
VII	0(0)	0(0)	11.0(5.0)	o/w
XIII	0(0)	0(0)	0(3.0)	o/w
XV	0(0)	0(0)	0(3.0)	o/w
XVI	0(0)	0(0)	0(3.0)	o/w
Tween 20	0(0)	0(0)	0(2.0)	o/w

and 35 mm and 20 mm for the OHEC ones, respectively.

The emulsification efficiency was characterized by the stability of the paraffinic oil-water emulsion (10 mass %). The results were compared with the commercially available emulsifier Tween 20. From Table 4 it can be seen that acyl derivatives of HEC have a pronounced emulsifying power which reaches the Tween 20 level. A discretely separated oil layer was observed after 24 h. The high emulsion efficiency can be explained by accepting a dual action of derivatives, *i.e.* the formation of interfacial films on the face boundaries with simultaneous affecting the continual phase viscosity in the role of molecular colloid.

Finally it can be concluded that acyl derivatives of higher fatty acids (C_{12}, C_{18}) of HEC with a low degree of substitution (≈ 0.01) represent new groups of polymeric surfactants with excellent emulsifying properties.

REFERENCES

1. Hodul, P., Antoš, K., Blažej, A., and Markušovská, E., *Tenside Detergents 22*, 114 (1985).
2. Talába, P., Sroková, I., and Hodul, P., *Vlákna a textil 2*, 155 (1995).
3. Talába, P., Sroková, I., Hodul, P., and Čík, G., *Chem. Papers 50*, 101 (1996).
4. Lunkenheimer, K. and Miller, R., *Tenside Detergents 16*, 312 (1979).
5. Lindner, K. (Editor), *Tenside – Textilhilfsmittel – Waschrohstoffe*. Wissenschaftlicher Verlag, Stuttgart, 1964.
6. Blažej, A., Hodul, P., Markušovská, E., Novák, L., Paulovič, M., and Vyskočil, I., *Tenzidy.* (Surfactants.) Alfa Publishers, Bratislava, 1977.
7. Itoh, I., Suzuki, H., Matsumoto, M., and Myiamoto, M., in *Cellulose, Structural and Functional Aspects.* (Kennedy, J. F., Phillips, G. O., and Williams, P., Editors.) P. 409. Ellis Horwood, Chichester, 1989.
8. Antoš, K., Hodul, P., Markušovská, E., Blažej, A., and Borovský, R., Czech. 214 392 (1984).
9. Samaranayake, G. and Glasser, W. G., *Carbohydr. Polym. 22*, 1 (1993).
10. Krkoška, P., Blažej, A., and Karas, K., *Chem. Zvesti 31*, 118 (1977).

Translated by J. Lokaj