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# Biodegradable Polymeric Surfactants from O-(Carboxymethyl)starch

## Abstract

This contribution/study deals with partial hydrophobisation of O-(carboxymethyl)starches (CMS, DS = 0.1 and 0.3) with alkylamine (C<sub>6</sub>, C<sub>10</sub>, and C<sub>12</sub>). The reaction was performed in methanol and dimethylsulfoxide with Dimethylaminopyridine (DMAP) as catalyst under classical heating and compared to the reaction performed with the assistance of microwave energy. The derivatives obtained were characterised by FT-IR spectroscopy and elemental analysis. Surface-activity and functional properties related to their application in textile finishing and the laundry process - washing power and antiredepositional efficiency were studied. Some of the tested derivatives exhibited excellent emulsifying efficiency and detergent performance properties.

**Key words:** carboxymethylstarch, polymeric surfactants, amidation, microwave heating, emulsifying efficiency, washing power.

cellulose (CMC) [5, 6], and pullulan [7]. Increasing interest has been focused on the structure-solution property relationship of amphiphilic polysaccharides [8 - 10]. The associative behaviour of hydrophobically modified CMC and Carboxymethyl pullulan (CM-pullulan) were studied after the amidation of these polysaccharides. Hexadecylamine derivatives of CMC or CM-pullulan were prepared by activation of their acid form using N,N-dicyclohexylcarbodiimide (DCCI) in DMSO [6, 7].

In our laboratory the hydrophobization of various polysaccharides was investigated, such as HEC [11], CMC [12], xylan [13], and carboxymethylstarch (CMS) [14, 15] by the esterification of hydroxyl groups using classical (with acylchloride and mixed anhydride) and unconventional methods (transesterification of methylesters of fatty acids or rape seed oil).

The aim of this research work was the amidation of carboxymethylstarch with various DS of carboxymethyl groups (0.3 and 0.1) under classical and microwave heating, which led to the preparation of new biopolymers with interesting properties.

In this article we report on the hydrophobisation of CMS with partial substitution of the carboxyl groups with hexyl-, decyl- and dodecylamine, the characterisation of the obtained derivatives, determination of their surface activity and detergent performance properties.

## Experimental

### Materials and methods

O-(Carboxymethyl)starch samples with DS<sub>CM</sub> = 0.1 and 0.3 were gifts from Prof.

T. Heinze (Friedrich-Schiller University of Jena), dodecyl-, decyl- and hexylamine were purchased from Fluka AG, RUCHS SG, (Switzerland), 4-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCCI) were from SIGMA-Aldrich Chemie, Steinheim (Germany).

The derivatives were characterised by FT-IR spectra (in KBr pellets, 2 mg/200 mg) obtained on a NICOLET Magna 750 spectrophotometer with a DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of 4 cm<sup>-1</sup>.

### Alkylamidation of carboxymethyl starch (CMS)

**Reaction in MeOH.** 1 g of CMS (DS = 0.1 and 0.3, in H<sup>+</sup> form) was dispersed into 15 ml MeOH and stirred under room temperature for 12 h. Then, 5 - 10 mg DMAP was added as catalyst. Subsequently a solution of alkylamine in chloroform was added using CMS/alkylamine mass ratios ranging between 1:3 - 1:10. The reaction continued at room temperature for 21 - 31 h. From the reaction mixture, the derivative was separated by an addition of 100 ml of acetone and the precipitate filtered off.

**Reaction in DMSO and DCCI.** 0.5 g of CMS in H<sup>+</sup> form (3 mmol for DS = 0.1 and 2.8 mmol for 0.3) was dispersed into 10 ml DMSO under stirring over night. To the gel suspension, 5 - 10 mg of DMAP and one equivalent of DCCI per mol CMS in 2 ml DMSO were added under stirring. After 30 min, one equivalent of DDA per mol CMS in chloroform was added and reaction continued at room temperature for 21 h. From the reaction mixture, the derivative was separated by an addition of 100 ml acetone and the precipitate filtered off.

## Introduction

Hydrophobically modified associative water-soluble polymers exhibit characteristic viscosity-concentration relationships in aqueous solution in comparison to their precursors in the same solvent; they therefore form an important class of thickeners [1]. Their properties are attributed to attractive interactions between long-chain hydrophobic moieties grafted in small quantities onto the hydrophilic polymer backbone. The interactions can be intra and/or intermolecular. The balance depends on the structural parameters of the polymer, such as the nature, lengths and content of hydrophobic groups, their distribution along the backbone, the hydration capacity, the degree of polymerization and polymer concentration, and on other parameters such as salinity, pH, and organic cosolvents [2, 3]. Among the associative polymers, amphiphilic polysaccharides with a natural, non-toxic and biodegradable backbone are of particular interest. They were prepared by the hydrophobic modification of a variety of polysaccharides, such as cellulose [4], hydroxyethylcellulose (HEC) [1], carboxymethyl

The products obtained from both methods were further purified. After introducing 20 ml of water, the derivative was transformed into salt form by adjusting the pH to 7.5 with 0.1 M NaOH, and after dialysis against distilled water the retentate was lyophilized.

### Testing methods

The testing methods applied are described in more detail in our previous paper [11]. The stability of the emulsion was estimated at three different time intervals after the emulsions had been prepared, i.e. 5 min ( $h_1$ ), 1 h ( $h_2$ ) and 24 h ( $h_3$ ), and expressed in terms of the height (mm) of the oil and cream layers formed on the surface of the emulsion. The washing power (WP) of some of the derivatives at a concentration of 0.5 kg m<sup>-3</sup> and the antiredeposition efficiency (ARE) at 5.0 kg m<sup>-3</sup> were determined using cotton fabric (SK-standard 800 101) and model soil. The washing time for the WP test was 10 min at 60 °C and 60 min at 50 °C for the ARE test.

**Table 1.** Amidation of carboxymethyl starch with alkylamines at various conditions; <sup>a</sup>) Room temperature; <sup>b</sup>) DCCI, <sup>c</sup>) Microwave irradiation; DDA- dodecylamine; DA- decylamine; HA- hexylamine; S- soluble; PS- partially soluble.

Derivative	DS <sub>CM</sub>	Medium	CMS:alkylamine (mass ratio)	Time, h	Solubility in water
CMS-1-DDA	0.3	MeOH/DMAP <sup>a</sup>	1: 5 (DDA)	21	S
CMS-2-DDA	0.3	MeOH/DMAP <sup>a</sup>	1: 5 (DDA)	10	S
CMS-3-DA	0.3	MeOH/DMAP <sup>a</sup>	1: 10 (DA)	21	PS
CMS-4-HA	0.3	MeOH/DMAP <sup>a</sup>	1: 5 (HA)	21	S
CMS-5-DDA	0.3	DMSO/DMAP <sup>a,b</sup>	1 eqv/AGU (DDA)	21	PS
CMS-6-DDA	0.1	MeOH/DMAP <sup>a,b</sup>	1: 3 (DDA)	21	PS
CMS-7-DDA	0.1	DMSO/DMAP <sup>a,b</sup>	1 eqv/AGU (DDA)	21	PS
CMS-8-DA	0.1	MeOH/DMAP <sup>c</sup>	1: 5 (DA)	3 min	S
CMS-9-DDA	0.1	MeOH/DMAP <sup>c</sup>	1: 3 (DDA)	3 min	PS

**Table 3.** Surface-active and functional properties of some of the CMS-alkylamides in comparison to CMS and controls; WP, Washing power; ARE, antiredeposition efficiency; Tween 20 – oxyethylated monolaurate of sorbitol; <sup>a</sup>) Oil / cream layers formed after  $h_1$  - 5 min,  $h_2$  - 1h and  $h_3$  - 24h; <sup>b</sup>) critical micelle concentration; <sup>c</sup>) concentration was 1.3%, \* Oil drops dispersed in the cream layer; nd – not determined; \*\*at 60 °C.

Sample	Oil / Cream layers <sup>a</sup> , mm/mm			$\gamma$ min, mNm <sup>-1</sup>	c.m.c. <sup>a</sup> , kgm <sup>-3</sup>	WP, %	ARE, %
	$h_1$	$h_2$	$h_3$				
CMS-1-DDA	0/0	0/0	0/4	53.3	0.29	nd	nd
CMS-2-DDA	0/0	0/0	0/10	57.8	0.16	79.0	53.8
CMS-3-DA	4/14	5/14	5/14	68.3	-	69.0	43.0
CMS-4-HA	0/0	0/55	0/34	65.1	1.33	47.0	50.0
CMS-5-DDA	0/0	0/10	0/12*	nd	nd	nd	nd
CMS-7-DDA	0/0 <sup>c</sup>	0/8	0/11*	42.9	0.31	nd	nd
CMS-8-DA	0/40	0/35	0/27	43.0	0.62	nd	nd
CMS (DS 0.3)	0/0	0/0	0/0	-	-	38.0	23.9
CMS (DS 0.1)	0/10*	0/9*	0.5/9*	-	-	12.0	34.8
Tween 20	0/0	0/0	0/11	-	-	nd	nd
NaDDS				-	-	37.0	nd
CMC				-	-	32.0	70.0**

## Results and discussion

### Preparation and characterization CMS derivatives

Two different reaction media were compared in order to partially hydrophobise CMS by reaction of the carboxyl groups of CMS (in nonionized – COOH form) with various alkylamines. In the first case the reaction of CMS with dodecyl-, decyl- and hexylamines in CMS weight ratios : alkylamine 1 : 5 or 1 : 10 was performed in methanol in the presence of DMAP as catalyst at room temperature as well as under microwave irradiation (temperature about 55 - 60 °C). In the second case the coupling of dodecylamine on the carboxylic groups of CMS proceeded in DMSO at room temperature for 21 h using DCCI for activation of the carboxyl group. The reaction conditions and results are summarised in Table 1.

As can be seen not all the derivatives were water-soluble. The solubility depends on the hydrophilic/hydrophobic balance of the CMS derivative. It

**Table 2.** Elemental analysis of CMS and CMS alkylamides (%); <sup>a</sup>) MW heating.

Sample	C	H	N
CMS (DS 0.3)	36.58	5.80	0
	36.98	5.96	0
CMS-1-DDA	45.24	7.27	1.32
	45.03	7.15	1.22
CMS-8-DA <sup>a</sup>	37.00	5.95	0.35
	37.11	6.00	0.37
CMS-9-DDA <sup>a</sup>	38.31	6.12	0.48
	38.36	5.90	0.48

changes due to partial substitution of the hydrophilic carboxyl groups, which are responsible for the solubility of CMS with alkylamine chains. For CMS with DS<sub>CM</sub> = 0.3, the derivatives became only partially soluble using a large excess of alkylamine (sample CMS-3-DA) or DCCI for carboxyl group activation (sample CMS-5-DDA); in both case a higher degree of amidation could be expected.

Certainly, changes in the hydrophilic/hydrophobic balance are more pronounced in the case of CMS with DS<sub>CM</sub> = 0.1, where after the introduction of small amounts of alkylamine chains the solubility of the derivatives decreases due to loss of the hydrophilic free carboxyl groups. From this CMS preparation, a water-soluble derivative was only obtained with sample (CMS-8-DA. The other three samples were only partially soluble, probably due to higher degrees of amidation achieved by application of DCCI or by introducing longer alkyl chains (DDA). The results indicate that the solubility of the derivatives depends on several effects.

Under classical heating, the alkylamidation yielded water-soluble derivatives at room temperature, but only after a relatively long reaction time. The application of microwave irradiation, performed on CMS with DS = 0.1, resulted in a significant shortening of the reaction time to 3 min, whereby the temperature only moderately increased.

### Structural characterisation

The results of the elemental analysis (Table 2) and the FTIR spectra in Figure 1 indicated that the reaction of CMS with alkylamines occurred. In agreement with literature [16], the typical amide I ( $\nu_{C=O}$ ) band appeared as a shoulder of different intensity at 1651 cm<sup>-1</sup>, whereas the amide II ( $\delta_{NH}$ ) was seen only as a very weak shoulder at ~ 1550 cm<sup>-1</sup> in derivative CMS-9-DA. Therefore, the Fourier self deconvolution method was

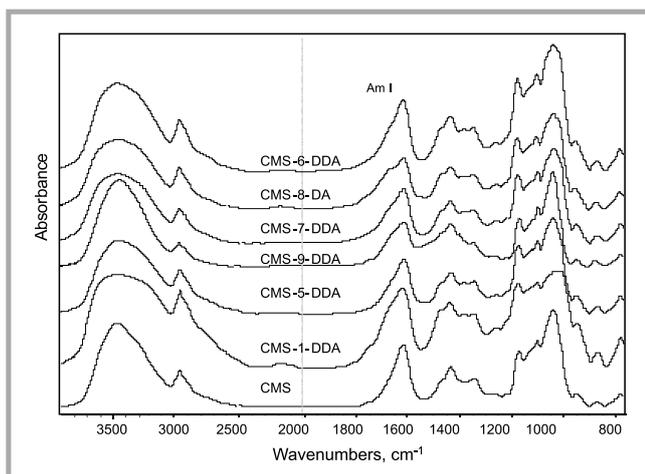


Figure 1. FTIR spectra of CMS and its alkylamide derivatives.

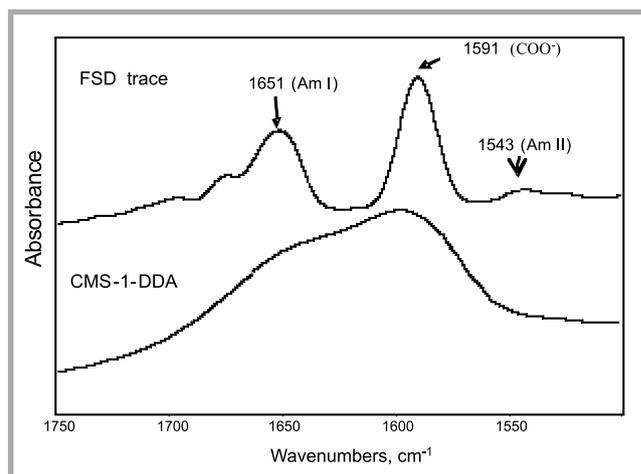


Figure 2. Fourier-SelfDeconvolutionspectrum of derivative CMS-1-DDA.

used to confirm the presence of amide groups, shown for sample CMS-1-DDA in Figure 2. However, it allows no deduction about the degree of amidation of the derivatives obtained.

### Surface- active properties

Some of the prepared CMS alkylamides lowered the surface tension of water, namely at lower concentration of the sample (Table 3). The functional properties of some of the prepared CMS alkylamides were tested for emulsifying efficiency, washing power (WP) and antiredeposition efficiency (ARE). The emulsifying efficiency was characterised by the stability of the parafinic oil/water emulsions. The results summarized in Table 3 show that some of the CMS derivatives made emulsions of the oil/water type stable even after 24 h. Their efficiency was comparable to that of the commercial emulsifier Tween 20. Sample CMS-3-DA gave an unstable emulsion and CMS-5-DDA produced a discreetly separated oil layer after 24 h. As seen from Table 3, the starting CMS with  $DS_{CM} = 0.3$  gave stable emulsions, but the emulsion of CMS with  $DS_{CM} = 0.1$  was unstable, which correlates with the solubility of the respective derivatives. Excellent emulsion stability showed derivatives with a dodecyl chain, whereas the stability of derivatives with shorter alkyl chains (decyl and hexyl) was lower, in accordance with classical surfactants [1].

Some of the tested derivatives showed excellent washing power exceeding that of the anionic detergent NaDDS, namely in the case of sample CMS-2-DDA, containing dodecyl chains. The antiredeposition efficiency was higher than the starting CMS, but moderate in com-

parison to CMC used as a co-builder in detergents [17].

### Conclusions

1. Water-soluble CMS alkylamides can be prepared from both low and high carboxymethylated starch by the economically and environmentally friendly method of using methanol as reaction medium and weight ratio CMS : alkylamine was 1:3 or 1:5.
2. Using DMSO as a solvent, only one equivalent of alkylamine per CMS and DCCI as activator of carboxyl groups was employed. The efficiency of the hydrophobization was comparable to those using higher amounts of alkylamines.
3. The application of microwave irradiation is an effective tool to reduce the reaction time from several hours (at room temperature) to a few minutes, whereby the temperature increased only moderately.
4. Surface-activity and their functional properties related to its application in textile finishing and laundry process, such as washing power and antiredeposition efficiency; some of the tested derivatives were excellent.

### Acknowledgments

This work was financially supported by the Slovak Grant Agency VEGA, grant No. 2/6131/26.

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Received 15.11.2007 Reviewed 15.01.2008