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Microwave-assisted synthesis of carboxymethylcellulose – based polymeric surfactants

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Summary

Carboxymethylcellulose (CMC, $DS_{CM} = 1$) was partially hydrophobized in order to prepare polymeric surfactants by the transesterification reaction using the methyl ester of the fatty acid complex of rapeseed oil (MERO). The chemical modification was performed in different reaction media (i) DMF/TSA and (ii) H_2O/DMF with and without K_2CO_3 as catalyst, at various reaction conditions and using microwave radiation with controlled power as heating source. The obtained MERO-hydrophobized CMC (MH-CMC) comprising mixed fatty acyl esters were characterized by FT-IR and NMR spectroscopic techniques, which indicated a very low degree of esterification ($DS < 0.1$). The derivatives showed, in spite of moderate surface tension-lowering effects, excellent emulsifying activity for 'oil in water' type emulsions as well as good performance properties including washing power and antiredeposition efficiency. The results suggested that surface-active MH-CMC derivatives can be prepared under microwave heating at reaction times in the range of several minutes, what is a great advantage in comparison to transesterification reactions lasting up to 6 h at conventional heating. The novel CMC esters represent biodegradable polymeric surfactants with potential applications in manufacture of consumer products and in industrial processes.

Keywords

carboxymethylcellulose, transesterification, microwave irradiation, biopolymers, polymeric surfactants, rapeseed oil methyl esters

Introduction

During the last decades, a fast growing interest in natural, biodegradable and renewable materials has been noticed. As the current use of non-biodegradable surfactants is a drawback, there is a need to develop new families of 'green' surfactant molecules derived from plant resources. This has led to increasing research activities in the field of amphiphilic polysaccharide derivatives. The anionic cellulose derivative carboxymethylcellulose (CMC) is commercially available in large quantities and known to act as water binder, thickener, suspending agent, emulsion stabilizer and antiredeposition agent in detergents [1]. Moreover, it represents also a potential biopolymer for further modification aimed to create new advanced cellulosic products. A large variety of CMC derivatives was prepared by modification of the hydroxyl groups of CMC using acyl chlorides, anhydrides, isocyanates as well as sulphation, phosphation, and silylation agents [2, 3], and by partial amidation of the carboxyl groups [4]. Etherification of the free hydroxyl groups with C_{12}-C_{18} alkyl halides yielded partially hydrophobized CMC derivatives, which at very low degree of substitution (DS) showed excellent emulsifying properties for emulsions of the ‘oil in water’ type and effective antiredeposition efficiency, but a poor washing power [5]. Recently, a novel series of polymeric surfactants based on CMC grafted with macromonomers [6] was reported to exhibit excellent surface activity due to their unique structure.

The most applied hydrophobization methods are based on classical esterification reactions with acyl chlorides or anhydrides and their more recent modifications, such as using fatty acid chlorides [7] and mixed anhydrides [8, 9], even without organic solvents, and carboxylic acid imidazoles in DMSO [10]. As further attempts to substitute the environmentally unfriendly and toxic classical esterification processes, the earlier transesterification reactions with fatty acid methyl esters [11, 12] were reinvestigated and used also under solvent-free conditions [13]. Esterification with vinyl laurate in organic solvents was applied on starch, carboxymethyl starch and glucuronoxylan [14-16]. However, the reaction performed in base-catalyzed aqueous medium [15] yielded starch laurates with very low degree of esterification (DS up to 0.02) after very long reaction times. From CMC, surface-active amphiphilic polymers exhibiting acceptable detergent performance properties were obtained by the unconventional esterification of CMC with mixed anhydrides and vinyl laurate [17].

The reaction temperatures used in the mentioned esterification reactions ranged from 40 up to 190°C. Nowadays attention has been paid to apply the new heating system - microwave irradiation in organic and polymer chemistry [18-20]. Its most important advantage is that microwave-enhanced chemical reactions are very rapid, lasting usually a few minutes, compared to hours with classical heating methods. There are few reports concerning the application of microwave heating in the esterification of cellulose and starch [21-25], some of them performed under solvent-free conditions. Since fatty acid esters are found in nature as triacyl glycerides, attempts have been made to use them as non-expensive acylation reagents [13] or served as raw material for the production of fatty acid chlorides [11, 26].

In continuation of our research on partial hydrophobization of various polysaccharides using transesterification with vinyl laurate and methyl laurate [15-17, 25], this paper is focused on the synthesis of water-soluble amphiphilic CMC derivatives using the methyl ester of rapeseed oil (MERO) as esterifying agent.

Experimental

Materials and Methods

CMC (Na^+ salt; $DS_{CM} = 1$; Mw = 741 kDa, Walsrode, Germany) was a gift from Prof. Thomas Heinze (Centre of Excellence of Polysaccharide Research, Friedrich Schiller

University of Jena). N,N-Dimethylformamide (DMF), 4-toluenesulfonic acid (TSA) and K_2CO_3 were commercial products from Sigma-Aldrich Chemie (Schnelldorf, Germany). The methyl ester of rapeseed oil (MERO) was from VÚTCH-Chemitex s.r.o. (Žilina, Slovakia). It contains oleic acid (58 %), linoleyl acid (17 %), linolenyl acid (17 %) and saturated $C_{14\text{-}20}$ fatty acids (8 %). Tween 20 was from Aldrich Chemical Co. (Steinheim, Germany).

Fourier-transform infrared (FT-IR) spectra were obtained on the NICOLET Magna 750 spectrometer with DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of 4 cm^{-1}. The samples (2.0 mg) were pressed into pellets of KBr (200 mg). ^1H and ^{13}C NMR spectra (in D_2O) in the inverse gated decoupling mode were recorded at 40ºC on a Bruker DPX AVANCE-300 spectrometer operating at 300 MHz for ^1H and 75,46 MHz for ^{13}C. The sample for NMR measurements were dissolved in water (0.1 g in 50 mL) and subjected to ultrasonication for 2×5 min at 100 W sonic power using the Ultragen system PERSON (Nitra, Slovakia, 20 kHz) as previously desribed [27].

High-pressure gel-permeation chromatography (HPGPC) was performed using a commercial instrument (Laboratorní přístroje, Prague, Czech Republic) equipped with two Labio Prague Biospher GM 300 and 1000 exclusion columns (8 x 250 mm) and using aqueous 0.1 M $NaNO_3$ as solvent (0.4 $mL{\cdot}min^{-1}$) and differential refractometry for detection. The columns were calibrated with pullulan standards P10 - P 800 (Shodex Standard P-82, Macherey-Nagel, Germany).

Synthesis of MERO-hydropobized CMC derivatives (MH-CMC)

(i) CMC (1.0 g) was activated in 22 mL DMF containing TSA (0.6 g) by stirring at 60°C for 30 min to yield the 'gel suspension' consistence [2]. MERO (1.0-2.0 g) was added to the 'gel suspension', which was under permanent stirring exposed to microwave heating in two stages, using the microwave reactor ‘Milestone’ (maximum 1000 W power) equipped with a magnetic stirrer (Sorisole, Italy). In the first stage lasting 5 min the power was increased from 0-300 W and the temperature increased from room to reaction temperatures (90-120°C). In the second stage (300 W power) the reaction continued at the selected reaction temperature and measuring of the reaction time started. After reaction, the product was poured into 4-6 volumes of acetone and the precipitated derivative was separated by filtration, thoroughly washed with acetone, and extracted in a Soxhlet apparatus with acetone for 8 h to remove the unreacted acylation agent and degradation products. For FT-IR measurements, the carboxymethyl substituent of the derivatives was transformed into its carboxylate form. The derivative (1.0 g) was stirred in distilled water (50 mL) at room temperature for 6 h, then the pH was adjusted to 7 by slow addition of 0.1 M NaOH, and the MH-CMC product was recovered by lyophilization. Eventually, occurring non-dissolved particles were separated by centrifugation before lyophilization.

(ii) CMC (1.0 g) was solubilized in 25 mL H_2O under stirring at room temperature for 1 h. Subsequently, MERO (1.0-3.0 g) in 25 mL DMF was added to the CMC solution. The reaction mixture, with and without addition of K_2CO_3 (0.07 g in 5 mL water) as catalyst, was under permanent stirring exposed to the above-mentioned two-stage microwave heating. The recovery and purification of the MH-CMC derivatives were the same as described in method (i).

The dry mass of the starting CMC was determined by oven drying at 105°C for 8 h. The MH-CMC derivatives were dried at 60°C for 6 h and stored over P_2O_5. The yield of the derivatives was expressed in g per g CMC on dry mass basis.

Characterization of the surface-active properties of MH-CMC derivatives

The emulsifying efficiency was tested on emulsion of the ‘oil in water’ (O/W) type. The emulsion was prepared by mixing 9 mL water containing 0.05 g of the CMC derivative and 1 mL of paraffinic oil dyed with SUDAN IV in the laboratory mixer (Heidolph DIAX 600) at 20 500 rpm for 1 min. 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 surface tension of aqueous polysaccharide solution in the concentration range 0.015-5.0 $g\cdot L^{-1}$ was determined at 25°C using the Du Nouy ring apparatus. Surface tension data were plotted against the logarithm of polysaccharide concentration in order to obtain the critical micelle concentration (c.m.c.) and minimum surface tension (γ_{min}), as described in previous papers [5, 28].

Performance testing methods

The washing power (WP) was assessed by determining the reflectance of an artificially soiled cotton fabric (SK-standard 800101) after washing in an alkaline surfactants solutions (concentration of the tested derivatives were 0.5 and 3.0 $g\cdot L^{-1}$) [28]. The cotton fabric was immersed for 5 min in the model soil consisting of 40 g dry milk, 20 g CCl_4 (tetrachloromethane), 3.0 g gelatine, 40 g sunflower oil, 20 g black ink, and 350 mL water. The excess of soil was removed by a squeezing mangle and the fabric was dried on air. Samples of the soiled fabric (6.0 x 6.0 cm) were washed in a Koltest apparatus. The volume of the alkaline bath containing 2.0 $g\cdot L^{-1}$ of Na_2CO_3 and 0.05 or 0.3 g of tested derivatives was 100 mL. Washing temperature were 40 and 80°C and washing time 10 min.

The antiredeposition efficiency (ARE) was determined by the method of Stüpel [29] using the above mentioned standard cotton fabric. The model soil consisted of 1.0 g carbon black, 0.5 g Spolion 8 (wetting agent) and 100 mL water. The fabric samples (6.0 x 6.0 cm) were washed at 60°C for 60 min using a bath containing 89 mL of water, 1 mL of the tested derivative solution with a concentration of 5.0 $g\cdot L^{-1}$ and 10 mL of soil. ARE was calculated by the relation $ARE = (R_2 - R_1)/(R_0 - R_1)$, where R_0 is the reflectance of the unsoiled cotton fabric, R_1 is the reflectance of the cotton fabric after scouring in a bath of soil, and R_2 is the reflectance of the cotton fabric after scouring in a bath containing the derivative.

Results and discussions

The transesterification reaction was performed using the methyl ester of vegetable rapeseed oil (MERO), which represents a mixture of fatty acid methyl esters, under microwave irradiation with controlled power in two different reaction media: (i) DMF/TSA and (ii) H_2O/DMF. Variations of the CMC/MERO mass ratio, reaction time and temperature, and power profiles of the microwave reactor served to prepare water-soluble MH-CMC derivatives. By activation of CMC in the DMF/TSA system, the carboxylate groups were protonated and CMC transformed into suspension of highly swollen particles, what increased the accessibility of CMC hydroxyl groups, thus enabling homogeneous reaction conditions. A disadvantage is that the derivatives

I-IV (Table 1) were obtained in the H^+ form, in which they are only partially soluble in water. Therefore, they were transformed into the Na^+ salt form. In this way the vibration of the COO^- groups at ~ 1600 cm^{-1} is well separated from that of the protonated and ester forms absorbing at ~ 1730-1740 cm^{-1}. As illustrated in Fig. 1a, the FT-IR spectra of the MH-CMC derivatives III and IV provided a qualitative proof of the introduced ester function, which gave the characteristic absorption at ~ 1740 cm^{-1}. Deconvolution of the spectra in this region confirmed the predominating presence of the ester vibration. It is to be mentioned that the starting commercial CMC showed a weak absorption band at ~ 1730 cm^{-1}, what indicates that a part of the carboxyl groups are protonated. As seen in Table 1, under the used reaction conditions and very short reaction time, the yields of the MH-CMC derivatives varied between 0.90 and 1.02 g per g CMC. A drawback of this esterification method is the need of subsequent transformation of the derivative into the salt form, representing an additional time-consuming step in a technological process.

Table 1. Reaction conditions and yield of MH-CMC derivatives prepared in the DMF/TSA medium at controlled power 300 W.

Sample	CMC:MERO (Mass ratio)	Reaction time[a] (min)	Temperature (°C)	Yield (g/g)[b]
I	1 : 1	1	90	1.00
II	1 : 1	1	110	1.02
III[c]	1 : 2	5	90	0.90
IV	1 : 2	5	120	0.92

[a] Measured after the 1st stage of microwave heating; [b] Expressed as g of the recovered derivative per g CMC (on dry mass basis); [c] Controlled power of 500 W was used.

In order to avoid the usage of TSA we investigated the esterification of CMC with MERO in the heterogeneous reaction system (ii) H_2O/DMF without (Table 2) and with addition of K_2CO_3 as catalyst (Table 3). All the MH-CMC derivatives were obtained in the carboxylate form and were water-soluble. The yields of the derivatives V-XIII (Table 2) varied between 0.87 to 1.05 g per g CMC. The FT-IR spectra of the HM-CMC derivatives prepared without the catalyst (Fig. 1a, samples V-VIII) showed, in contrast to those prepared under the homogenous conditions (samples III and IV) only weak shoulders at ~ 1740 cm^{-1}, indicating a low extent of esterification. Using the differential FT-IR spectra (shown for samples V, VII and VIII in Fig. 1b), the presence of ester groups was confirmed by the intensity increase of the absorption bands at ~ 2924 cm^{-1} and 2856 cm^{-1}, respectively, attributed to the $\nu_{as}CH_2$ and ν_sCH_2 vibrations of the fatty acyl substitutent. Slightly higher yields (up to 1.12 g/g) were achieved by the K_2CO_3-catalyzed esterification performed at temperatures between 90-105°C (Table 3), which resulted in a higher extent of esterification, documented by the distinct ester absorption bands in the FT-IR spectra (Fig. 1a, samples XV, XVI).

No correlation was observed between the yield and the amount of the reactant - MERO for the reaction temperatures ranging between 90 and 120°C. In comparison to method (i), in the case of the heterogeneous transesterification (method ii) resulting in a non-uniform distribution of the ester substituents, the yields of the derivatives might be more affected by the precipitation conditions due to possible losses of higher substituted and/or low molar mass derivatives being less precipitable.

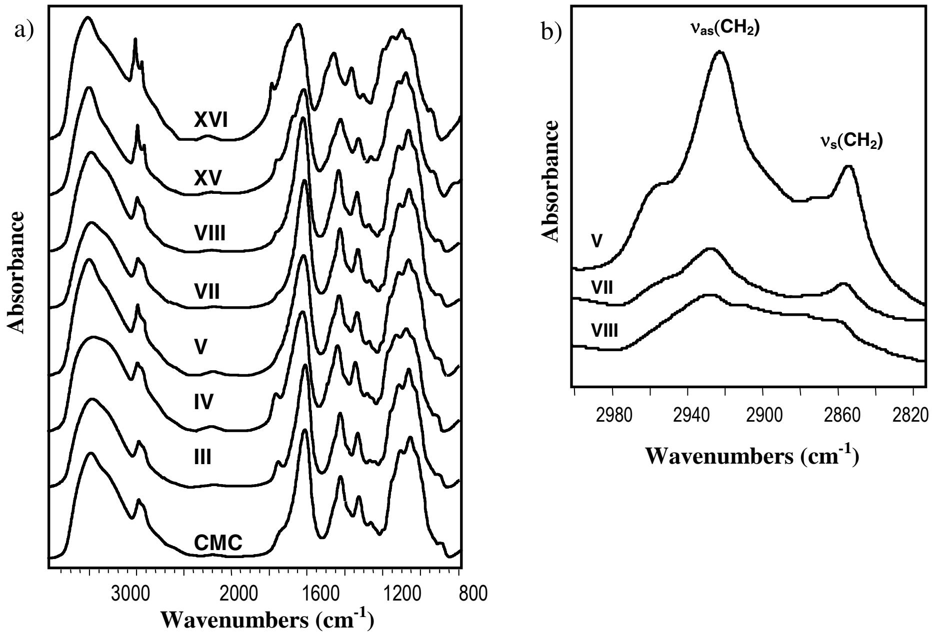

Figure 1. (**a**) FT-IR spectra of CMC and MH-CMC derivatives prepared by transesterification of MERO in the DMF/TSA medium (III and IV), and in the H_2O/DMF medium without (V, VII, and VIII) and with K_2CO_3 as catalyst (XV and XVI); (**b**) Differential FT-IR spectra between the MH-CMC derivatives V, VII and VIII and the starting CMC.

Table 2. Reaction conditions and yield of MH-CMC derivatives prepared in the H_2O/DMF medium at controlled power 300 W.

Sample	CMC:MERO (Mass ratio)	Reaction time[a] (min)	Temperature (°C)	Yield (g/g)[b]
V	1:1	1	90	1.03
VI	1:1	2	90	1.03
VII	1:2	1	90	1.03
VIII	1:2	2	90	0.87
IX[c]	1:1	2	90	1.03
X	1:2	3	105	1.02
XI	1:2	7	105	1.05
XII[d]	1:1	1	110	1.02
XIII[d]	1:3	2	110	1.05

[a] Measured after the 1st stage of microwave heating; b) See footnote to Table 1; [c] The 1st stage lasted only 3 min; [d] Controlled power of 500 W was used.

The ^{13}C NMR and ^{1}H NMR spectra of the MH-CMC derivatives, shown for sample XVI in Fig. 2a and 2b, respectively, were measured after a short ultrasonic treatment in water used to reduce the viscosity of the solution. The low extent of esterification was evidenced by the very weak resonances in the high field region at δ 0.8-2.5, where the protons of the acyl moieties resonate. The ^{13}C NMR spectrum (Fig. 2a) was poorly-resolved and, therefore, resonances of the acyl chain carbons

Table 3. Reaction conditions and yield of MH-CMC derivatives prepared in the H_2O/DMF medium at controlled power 300 W in presence of catalyst K_2CO_3.

Sample	CMC:MERO (Mass ratio)	Reaction time[a] (min)	Temperature (°C)	Yield (g/g)[b]
XIV	1 : 1	1	90	1.11
XV	1 : 2	1	90	0.99
XVI	1 : 2	3	90	1.02
XVII	1 : 2	5	90	1.12
XVIII	1 : 2	3	105	1.11
XIX	1 : 1	2	90	0.92

[a] Measured after the 1st stage of microwave heating; [b] See footnote to Table 1.

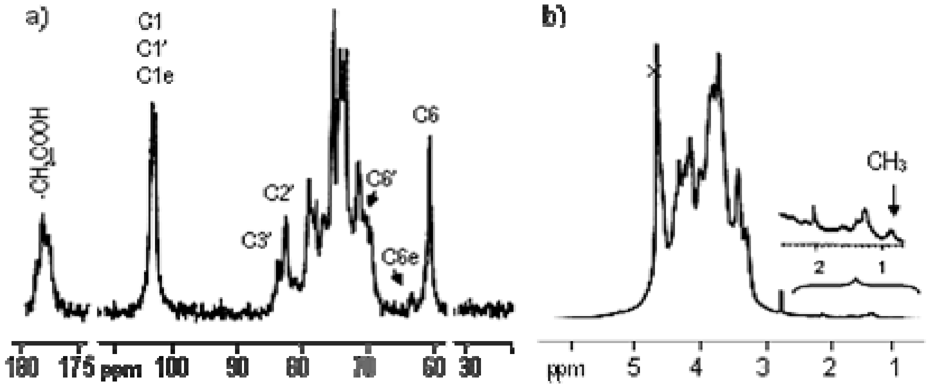

Figure 2. (**a**) ^{13}C NMR spectrum (in D_2O) of MH-CMC derivative XVI. The primed carbons correspond to glucopyranose units carboxymethylated at positions 2, 3 and/or 6, and C6e to that esterified at position 6. (**b**) ^1H NMR spectrum of MH-CMC derivative XVI.

were not distinguishable from the noise. The spectrum showed the typical pattern of CMC [30] with carboxylmethyl groups located mainly at position 2, followed by positions 6 and 3. In addition, a distinct small peak was observed at δ 63.1, which can be attributed to C-6 substituted by the acyl groups [31]. The degree of esterification (DS_e) of XVI at position 6 of the glucose residue (C-6e) was roughly estimated by the signal area ratio of C-6e to the anomeric carbon signals at δ 102.6-103.2, yielding the value of ~ 0.06. It can be assumed that this position is preferred, based on former cellulose acetylation studies [32], which revealed a 3-4 times higher reactivity of hydroxyl groups at position 6 compared to those at positions 2 and 3. Very low DS_e (up to 0.02) was reported also for starch laureates prepared by the base-catalyzed esterification with vinyl laurate [14], performed under classical heating at temperatures 100°C for 24 and 48 h.

The data in Tables 1-3 indicate that under the used esterification conditions, the application of higher microwave power (500 W) had no significant effect on the yield and/or extent of esterification, as evidenced by FT-IR spectroscopy. The effect of microwave heating on the molecular properties of CMC is shown in Table 4. The mean molecular mass (M_r) of the MH-CMC, varying between 352 and 298 kDA, was considerably lower in comparison to that of the starting CMC (M_r = 740 kDa), and even decreased to 305 kDa, when the sample was subjected to microwave radiation

Table 4. Molecular properties (M_r, relative mean molar mass and D, polydispersity index)[a] of CMC and selected MH-CMC derivatives.

Sample	M_r (kDa)	D M_w/M_n	MW-treatment conditions
CMC	740	1.98	No
CMC[b]	305	1.68	90°C - 5’
III	352[c]	2.40	90°C - 5’
XIII	317	1.70	110°C - 2’
XV	339	1.75	90°C - 1’
XVII	298	1.72	90°C - 5’

[a] Measured on pullulan-calibrated Biospher columns; [b] Microwave-treated CMC without acylation (300 W); [c] The value corresponds to the main molecular population (~ 70 %), the M_r of the second population (~ 30 %) was 10.6 kDa.

for 5 min at 90°C without addition of the acylation agent. Recently, such depolymerization effect of microwave irradiation was reported for seed polysaccharides within 2 min in absence of anorganic acid [33]. The M_r drop was the most pronounced after acylation in the H_2O/DMF/K_2CO_3 system (sample XVII, M_r = 298 kDa). At the same microwave heating conditions, the degradation was somewhat lower in the DMF/TSA system. The corresponding derivative III showed a high polydispersity index (D = 2.40) and contained about 30% of a molecular population with M_r = 10.6 kDa, in contrast to derivative XVII exhibiting a very narrow molecular mass distribution (D = 1.72).

The tensioactive properties of the derivatives were first tested by studying the emulsifying efficiency in an ‘oil in water’ system (Table 5). As seen, high emulsifying activities were observed with samples I, III, IV which gave emulsions stable even after 24h. The achieved hydrophobization effect of the derivative II was too low resulting in unstable O/W emulsions.

Most of the tested derivatives prepared in the H_2O/DMF system without and with catalyst showed considerable emulsifying properties comparable to that of the control-Tween 20, although they had no pronounced suppressing effect on the surface tension of water (γ_{min}). The γ_{min} values ranged between 54 and 63 $mN\cdot m^{-1}$. Exceptions are derivatives VII and XIV, which lowered the surface tension of water from 72.8 to ~ 46 $mN\cdot m^{-1}$. The other samples formed less stable emulsions, with oil drops in the cream layer observed after 24 h.

The usage of certain water-soluble polysaccharides (hydrocolloids), such as some galactomannans, pectins and gums, as emulsifiers and/or stabilizers in food industry [34] is well known. These effects were attributed mainly to the viscosity-increasing effect of the polysaccharides. In a recent review [35] the authors demonstrated that polysaccharides, even when they are free of protein, can exhibit surface and emulsification properties inspite of their rigid and hydrophilic nature. They form thick birefringent gel-like mechanical barriers at the oil-water interface of emulsion oil droplets and reduce the surface tension, which is time-dependent, to 48-55 $mN\cdot m^{-1}$ at polymer concentration up to 0.5 %. The presented results on partially MERO-hydrophibized CMC as well as studies on other amphiphilic polysaccharide derivatives [35] indicated that, although not obligatory for the active adsorption, the presence of native or introduced hydrophobic moieties enhances the surface-active and emulsifying activities.

Table 5. Surface-active properties (surface tension, γ_{min}, critical micelle concentration, c.m.c., emulsifying efficiency) of selected MH-CMC derivatives and controls.

Sample	γ_{min} (mN·m^{-1})	c.m.c. (g·L^{-1})	Oil / Cream layers[a] (mm/mm)		
			h_1	h_2	h_3
I	56.8	2.06	0/13	0/12	0/12
II	-	-	0/0	0.5/9	8/5
III	57.6	2.88	0/16	0/14	0/11
IV	-	-	0/0	0/6	0/9
V	55	0.32	0/0	0/10	0/9
VI	-	-	0/0	0/0	0/7
VII	46.6	2.45	0/0	0/0	0/6
VIII	62.9	1.77	0/0	0/0	0/6
IX	54.1	0.79	0/0	0/0	0/7
X	-	-	0/0	0/2	0/7
XI	-	-	0/0	0/1	0/8
XII	53.6	0.56	0/0	0/0	0/7
XIII	-	-	0/0	0/0	0/6
XIV	45.6	No	0/0	0/1	0/4
XV	58.1	1.25	0/0	0/11	1/9
XVI	49.9	0.74	0/0	0/0	0/5
XVII	50.4	2.04	0/0	0/0	1/7
XVIII	46.5	No	0/0	0/0	0.5/9
XIX	47.5	1.78	0/0	0/10	8/2
CMC	65.8	0.75	0/0	0/0	0/3
Tween 20	-	-	0/0	0/0	0/8

[a] Height of oil and cream layers formed on the surface of the emulsion after 5 min (h_1), 1 h (h_2) and 24 h (h_3); (-) Not determined.

Table 6. Washing power (WP) and antiredeposition efficiency (ARE) of selected MH-CMC derivatives and controls.

Sample	WP (%)			ARE (%)
	c = 0.5 g·L^{-1}		c = 3.0 g·L^{-1}	
	80°C	40°C	80°C	
III	91.6	58.2	94. 7	43
VII	82.1	-	-	41
IX	95.4	51.6	-	63
XV	-	51.2	-	34
XVI	94.2	65.1	96.4	84
XVII	98.8	63.7	-	38
XIX	96.7	45	91.0	84
CMC	94.6	55	90.0	70
SDS	96.0	35.0	-	-

SDS, Sodium dodecyl sulphate; (-) Not determined.

The detergents performance of some of the hydrophobized CMC derivatives were tested by the washing power (WP) at two polymer concentrations using sodium dodecyl sulfate (SDS) and CMC as standards and by the antiredepositive efficiency (ARE). The results summarized in Table 6 indicated that the WP of some samples was higher when compared to the standard, even if tested at lower polymer concentration and washing temperature. Excellent ARE, higher than that of the unmodified CMC, was exhibited by the partially esterified CMC derivatives prepared in the H_2O/DMF medium with addition of K_2CO_3 as catalyst, whereas other samples gave results comparable to those of the control CMC, used as co-builder in detergents [36].

Conclusions

The presented result confirmed that the application of microwave heating substantially reduces the reaction time down to several min also in the case of the transesterification reaction and, in some cases, lower reaction temperatures can be used, when compared to the conditions of transesterification methods performed under classical heating [11-13, 16]. Promising results were obtained by esterification of CMC with MERO in the DMF/TSA medium as well as in the H_2O/DMF medium in presence of K_2CO_3 as catalyst. The water – soluble polysaccharide esters with low degree of esterification were achieved under mild reaction conditions such as short reaction time, low amount of esterification agent, using appropriate reaction media. In spite of the low degree of esterification, most of the CMC esters exhibited very positive surface-active properties such as excellent emulsification properties, which are comparable to that of the commercial synthetic emulsifier Tween 20. Although the derivatives do not substantially lower the surface tension of water, they form micelles in the concentration range 0.3 to 2.9 $g \cdot L^{-1}$. Vaca-Garcia et al. [9] by measuring the contact angle suggested that grafting of fatty acid chains to cellulose increases the hydrophobicity of the ester derivatives even at a low degree of esterification. The detergent performance properties are documented by excellent WP and acceptable ARE values.

The results suggested that the hydrophobized CMC derivatives containing a very low amount of mixed fatty acyl substituents represent potential polymeric surfactants, which are due to their low degree of esterification still biodegradable. The presented microwave-assisted transesterification method might substitute the toxic, hazardous and time-consuming classical esterification processes in preparing polysaccharide-based surfactants. The proved applicability of MERO as acylation agent contributes to a further valorisation of the rapeseed biomass.

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