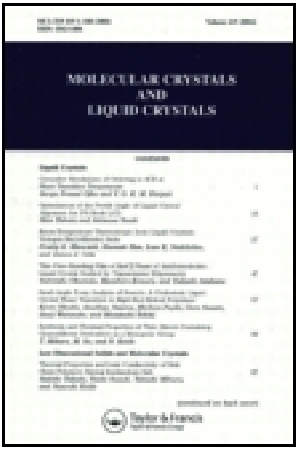

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Surface-Active and Viscous Behavior of HM-CMC in Aqueous Solutions

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Water-soluble, partially hydrophobized derivatives of carboxymethylcellulose (CMC) were prepared by the transesterification reaction using the methyl ester of rapeseed oil (MERO). The chemical modification was performed in reaction media 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 hydrophobically modified carboxymethylcellulose (HM-CMC) derivatives were characterized by FT-IR spectroscopy. The surface-active and viscometric properties of aqueous solutions of unmodified CMC and its HM-CMC derivatives were investigated. The surface-active properties were studied by surface tension, critical micelle concentration and emulsifying efficiency. The complexation of CMC or some HM-CMC derivatives with cationic surfactants – tetraalkylammonium bromides (C_nTAB) in aqueous medium was studied by measuring the surface tension. The studied derivatives showed, in spite of moderate surface tension-lowering effects, excellent emulsifying activity for 'oil in water' type emulsions comparable to that of the commercial emulsifier Tween 20. The viscometric properties were investigated in the dilute domain. For all HM-CMC solutions the intrinsic viscosities were distinctly lower than for CMC, probably due to molecular degradation. The increased Huggins constant of some of the derivatives are indicative of intramolecular hydrophobic interactions. The results suggested that the HM-CMC derivatives and their complexes with C_nTAB surfactants can be exploited as potential biosurfactants in various industrial applications.

Keywords: hydrophobically modified carboxymethylcellulose; hydrophobic interaction; polymeric surfactants; surface-active properties; viscosity

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INTRODUCTION

Hydrophobically modified (or associative) water-soluble polysaccharides from natural, biodegradable and renewable materials have captured the attention of macromolecular chemists. As the current use of non- biodegradable surfactants is a drawback, there is the need to develop new families of green surfactants molecules derived from plant resources. This has led to increasing research activities in the field of amphiphilic polysaccharide derivatives. Water-soluble amphiphilic cellulose derivatives containing hydrophobic chains grafted to a hydrophilic polymer backbone have been extensively investigated as polymeric surfactants [1–3]. Due to the both hydrophilic and hydrophobic character these polysaccharides have interesting solution properties which enable their application as polymeric surfactants (O/W emulsifier), surface-active agents, associative thickeners in oil recovery, latex paint or as support for enzyme immobilization [4].

CMC is the most important water-soluble anionic cellulose derivative of significant technical importance. It is commercially available in large quantities and known to act as water binder, thickener, emulsion stabilizer, suspending agent and antiredeposition agent in detergents [5]. Moreover, it represents also a potential biopolymer for further modification aimed to create new advanced cellulosic materials.

A large variety of CMC derivatives were prepared by modification of the hydroxyl groups of CMC using acyl chlorides, anhydrides, isocyanates as well as sulphation, phosphation, and silylation agents [6,7], and by partial amidation of the carboxyl groups [8].

In our previous works surface-active and performance properties of partially hydrophobized CMC ethers and esters were studied [9,10]. 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 showed excellent emulsifying properties for emulsions of the ‘oil in water’ type and effective antiredeposition efficiency, but a poor washing power [9]. From CMC esters, surface-active amphiphilic polymers obtained by the unconventional esterification of CMC with mixed anhydrides and vinyl laurate exhibited acceptable detergent performance properties [10].

In continuation of our research on partial hydrophobized CMC derivatives prepared by transesterification with methyl ester of rapeseed oil (MERO) under microwave irradiation with controlled power [11], this article is focused on the characterization of dilute HM-CMC solutions by surface-activity and viscometric measurements.

EXPERIMENTAL PART

Materials and Methods

CMC (Na^+ salt; $DS_{CM} = 1$; $Mw = 741\,kDa$) was from Walsrode (Germany). Tween 20 was from Aldrich Chemical Co. (Steinheim, Germany). The cationic surfactants tetraalkylammonium bromides (C_nTAB, n = 12, 14, 16) from Sigma, Aldrich were used without further purification. The methyl ester of rapeseed oil (MERO) used as esterification agent was from VÚTCH-Chemitex s.r.o. (Žilina, Slovakia).

Hydrophobically modified carboxymethylcellulose (HM-CMC) was prepared by chemical modification of CMC with MERO in the H_2O/DMF system using microwave irradiation with controlled power as heating source, as previously described in detail [11]. The reaction conditions of selected derivatives used for the presented solution characterization are summarized in Table 1.

Fourier-transform infrared (FT-IR) spectra were obtained on the NICOLET Magna 750 spectrometer with DTGS detector and OMNIC

TABLE 1 Reaction Conditions and Yield of Selected HM-CMC Derivatives prepared in H_2O/DMF Medium at Controlled Power of 300 W [11]

Sample	CMC:MERO (Mass ratio)	Reaction time[b] (Min)	Temperature (°C)	Yield[c] (g/g)
I[d]	1:1	1	110	1.02
II	1:1	1	90	1.03
III	1:2	1	90	1.03
IV	1:2	2	90	0.87
V	1:2	7	105	1.05
VI[a]	1:1	1	90	1.11
VII[a]	1:2	1	90	0.99
VIII[a]	1:2	3	90	1.02
IX[a]	1:2	5	90	1.12
X[a]	1:1	2	90	0.92

[a] K_2CO_3 was used as catalyst.

[b] Reaction time were measured after 1st stage of microwave heating.

[c] Expressed as g of the recovered derivative/g CMC.

[d] Controlled power of 500 W was used.

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).

Characterization of the Surface-Active Properties of MH-CMC Derivatives

All derivatives were characterized by emulsifying efficiency and surface tension. 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 measurements of samples dissolved in distilled water in the concentration range 0.039–5.0 g · L^{-1} were performed 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 corresponding surface tension ($\gamma_{\min}$), as described in previous articles [9,10].

The surface-active properties of complexes of the water-soluble HM-CMC derivatives with oppositely charged cationic surfactants (C_nTAB, n = 12, 14, 16) were studied by surface tension measurements. All solutions were prepared at least 24 hours before measurements. The concentration range of CMC samples used was 0.0196–5.0 g · L^{-1}, while C_nTAB concentration was kept at (0.01%, 0.001%).

Viscosity Properties of HM-CMC Derivatives

The dilute solution properties of the derivatives were examined by viscometry of HM-CMC solutions in aqueous 0.1 M NaCl using the Ubbelohde-type capillary viscometer (0.64 mm, diameter). The temperature was regulated by a circulating bath at 25°C. The concentration of HM-CMC solutions ranged between 0.32–0.0886 g · dL^{-1}. Prior to measurements, the polymer solutions were filtered through 0.2 mm quantitative filter.

The concentration dependence of the reduced viscosity [η_{red}] of the solutions is described by the Huggins equation (1):

$$\eta_{red} = \eta_{sp}/c = [\eta] + k_{\mathrm{H}}\cdot[\eta]^2 \cdot c, \qquad (1)$$

where k_H is the Huggins constant depending on the nature of the polymer-solvent and polymer-polymer interaction in solution. This equation allows the determination of k_H and intrinsic viscosity $[\eta]$ by plotting the reduced viscosity ($\eta_{red} = \eta_{sp}/c$) as a function of polymer concentration.

RESULTS AND DISCUSSIONS

Characterization of HM-CMC Derivatives by FT-IR Spectroscopy

The partial hydrophobization of CMC was carried out by transesterification reaction with MERO under microwave irradiation with controlled power in H_2O/DMF system at various reaction conditions (Table 1) described in our previous article [11]. The obtained series of water-soluble HM-CMC derivatives were characterized by FT-IR spectroscopy, because elemental analysis (not shown) revealed non-significant differences from the data obtained with the starting CMC. The FT-IR spectra provided a qualitative proof of the extent of esterification.

The FT-IR spectra of the HM-CMC derivatives prepared without the catalyst, illustrated for samples II-IV in Figure 1, showed only weak shoulders at $\sim$1740 cm^{-1}, indicating a low extent of esterification. Using the differential FT-IR spectra (not shown), the presence of ester groups was confirmed by the intensity increase of the absorption bands at $\sim$2924 cm^{-1} and 2856 cm^{-1}, respectively, attributed to the $\nu_{as}CH_2$ and $\nu_{s}CH_2$ vibrations of the fatty acyl substitutent.

Slightly higher yields (up to 1.12 g/g) were achieved by the K_2CO_3-catalyzed esterification, which resulted in a higher extent of esterification, documented by the distinct ester absorption bands in the FT-IR spectra (Figure 1, samples VII, VIII).

Surface-Active Properties of HM-CMC Derivatives

The tensioactive properties of the HM-CMC derivatives were first tested by studying the emulsifying efficiency in an ‘oil in water’ system (Table 2). As seen, high emulsifying activities were observed with samples I to VI, which gave emulsions stable even after 24 h. Derivatives VII to IX yielded less stable O/W emulsions with oil drops in the cream layer observed after 24 h. The sample X showed no surface-activity and formed unstable emulsion with an oil layer separated after 24 h. It can be caused by the too low extent of esterification resulting in a very low hydrophobization effect.

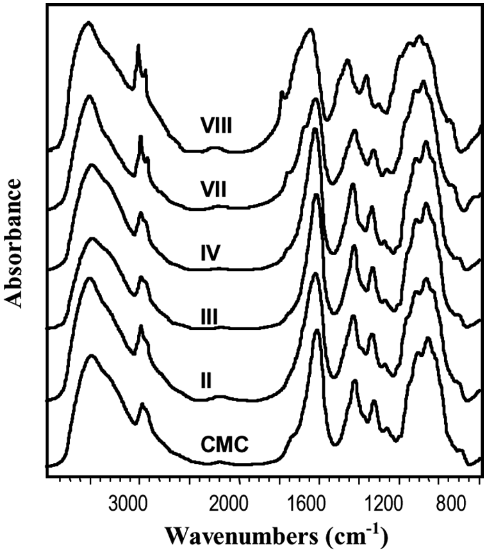

FIGURE 1 FT-IR spectra of CMC and HM-CMC derivatives prepared by transesterification of MERO in the H_2O/DMF medium without (II, III, and IV) and with K_2CO_3 as catalyst (VII and VIII).

TABLE 2 Surface-Active Properties (Surface Tension, $\gamma_{\min}$, Critical Micelle Concentration, c.m.c., Emulsifying Efficiency) of Selected HM-CMC Derivatives and Controls

Sample	$\gamma_{\min}$ ($mN \cdot m^{-1}$)	c.m.c. ($g \cdot L^{-1}$)	Oil/Cream layers[a] (mm/mm)		
			h_1	h_2	h_3
I	53.6	0.56	0/0	0/0	0/7
II	55	0.32	0/0	0/10	0/9
III	46.6	2.45	0/0	0/0	0/6
IV	62.9	1.77	0/0	0/0	0/6
V	50.2	2.45	0/0	0/1	0/8
VI	45.6	No	0/0	0/1	0/4
VII	58.1	1.25	0/0	0/11	1/9
VIII	49.9	0.74	0/0	0/0	0.5/5
IX	50.4	2.04	0/0	0/0	1/7
X	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).

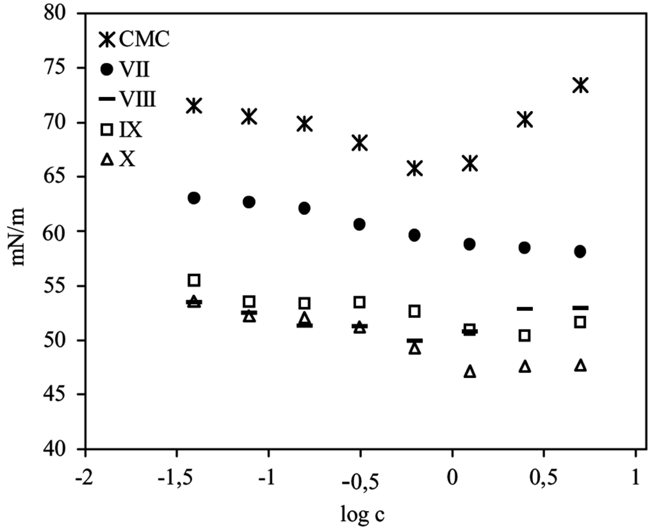

FIGURE 2 Surface tension versus log of polymer concentration of CMC and HM-CMC derivatives.

Anyway, most of the tested derivatives prepared in the H_2O/DMF system without and with catalyst K_2CO_3 showed considerable emulsifying properties comparable to that of the control-Tween 20. Although they had no pronounced depressing effect on the surface tension of water (γ_{min} values ranged between 63 to $50\,mN \cdot m^{-1}$), they form micelles in the concentration range 0.5 to $2.45\,g \cdot L^{-1}$ (Figure 2, Table 2). A similar low surface tension depressing effect was report also for C_n-alkylated CMC [9] and C_n-acylated CMC [10] both exhibiting significant emulsifying efficiency as well as for carboxymethylstarch [12]. Exceptions are derivatives III, VI and X, which lowered the surface tension of water from 72.8 to $\sim 46\,mN \cdot m^{-1}$.

The usage of water-soluble polysaccharides (hydrocolloids), such as some pectins, gums and galactomannans as emulsifiers and/or stabilizers in food industry [13] is well known. These effects were attributed to the viscosity effect that they impart to the system. In a recent review [14] the authors demonstrated that certain hydrophilic (anionic or non-ionic) 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. The presented results on partially MERO-hydrophibized CMC as well as studies on other amphiphilic polysaccharide derivatives [14] indicated that, although not obligatory for the active adsorption, the presence of native or introduced hydrophobic moieties enhances the surface-active and emulsifying activities.

Effect of Oppositely Charged Surfactants on Surface Tension

In order to increase the surface tension effect of CMC and selected HM-CMC derivatives, the influence of small amounts of added oppositely charged surfactants was studied. Recently, it has been shown that low surface-active polyelectrolytes, such as the cationic [15] and anionic [17,18] cellulose derivatives, chitosan [16], and carboxymethylchitin [19] are transformed in presence of extremely small amounts of oppositely charged surfactants (sodium dodecylsulphate, SDS, or tetraalkylammonium bromides) into much more surface-active complexes by virtue of the hydrocarbon chains of the bound surfactants. The values of surface tension and c.m.c. of CMC, C_nTAB and HM-CMC solutions, and mixed solutions of CMC and HM-CMC with C_nTAB are shown in Table 3. It can be seen that the addition of the oppositely charged surfactant significantly lowers the surface tension of CMC and HM-CMC solutions. The C_nTAB surfactants alone lowered the surface tension of water from 72.8 to $\sim 35\,\mathrm{mN \cdot m^{-1}}$. The surface tension of mixed CMC/C_nTAB solutions decreased in the order CMC/0.01% C_{16}TAB - CMC/0.01% C_{14}TAB - CMC/0.01% C_{12}TAB. This is in accord with the Duclaux – Traube's rule that every $-CH_2-$ group of the hydrocarbon chain increases the surface-activity of the

TABLE 3 Surface-Active Properties (Surface Tension, $\gamma_{\min}$, Critical Micelle Concentration, c.m.c.) of CMC/C_nTAB and HM-CMC/C_nTAB complex

Sample	$\gamma_{\min}$ ($\mathrm{mN \cdot m^{-1}}$)	c.m.c. ($\mathrm{g \cdot L^{-1}}$)
C_{12}TAB	36.9	2.50
C_{14}TAB	34.3	1.24
C_{16}TAB	33.2	0.62
CMC	65.8	0.75
IV	62.9	1.77
X	47.5	1.78
IV/0.01% C_{14}TAB	35.4	0.31
CMC/0.01% C_{12}TAB	49.0	0.15
CMC/0.01% C_{14}TAB	42.9	0.15
CMC/0.01% C_{16}TAB	41.2	0.31
X/0.01% C_{14}TAB	31.7	0.62
X/0.001% C_{14}TAB	29.2	2.45
X/0.01% C_{16}TAB	31.9	2.34

surfactants 3 to 3.5 times. By adding surfactants with a sufficiently long hydrocarbon chain [20], the surface tension of water was shown to decrease to 30–35 $mN \cdot m^{-1}$. As shown in Table 3, the complexes of C_nTAB with HM-CMC exhibit higher surface activity (γ_{min} ranged between 35 and 31 $mN \cdot m^{-1}$) than those with CMC (γ_{min} ranged between 49 and 41 $mN \cdot m^{-1}$).

Dilute Solution Properties of HM-CMC Derivatives

The parent CMC and HM-CMC derivatives were analyzed by viscometry of solutions in aqueous 0.1 M NaCl and the data evaluated using the Huggins equation (1). The plots of reduced viscosity as a function of the polymer concentration are illustrated in Figure 3. The derived intrinsic viscosity, $[\eta]$ and Huggins constant, k_H data are summarized in Table 4. In general, these quantities provide insight to molecular structure and interactions of the polymers in solution. The Huggins constant is generally around 0.4 for non-interacting macromolecules in good solvents and can reach values above 5 for highly interacting macromolecules, what is typical of associative amphiphilic polymers. The k_H of the unmodified CMC (DS = 0.9) in 0.1 M NaCl [8] has been

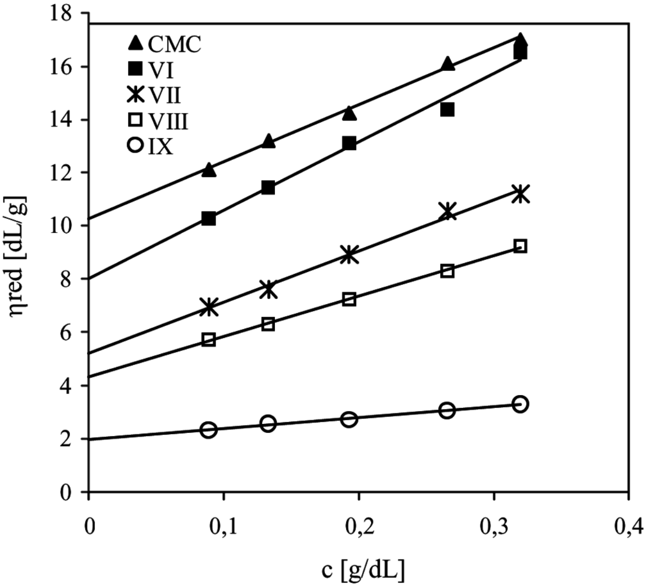

FIGURE 3 Reduced viscosities as a function of the polymer concentration in 0.1 M NaCl for CMC and HM–CMC derivatives.

TABLE 4 Viscometric Results Obtained with HM-CMC Derivatives, in Aqueous Sodium Chloride Medium at 25°C

Sample	k_H	$[\eta]$ (dL/g)
I	0.34	3.66
II	0.23	6.86
III	0.35	6.82
IV	0.32	5.34
V	0.95	1.99
VI	0.31	8.46
VII	0.71	5.19
VIII	0.81	4.32
IX	1.06	1.97
X	0.48	5.15
CMC	0.20	10.26
CMC_{mw}	0.23	8.53

reported to be close to 0.5. A similar value has been found for chitosan in water [21] and for dextran in water [22].

As seen in Table 4, the Huggins constant and intrinsic viscosity for the unmodified CMC (DS = 1) are about 0.2 and $10.26\,\mathrm{dL\cdot g^{-1}}$, respectively. For all HM-CMC derivatives, the intrinsic viscosities are distinctly lower than for the unmodified CMC and k_H remains relatively small. Only for derivatives V and IX the Huggins constant is 4–5 times higher (k_H close to 1.0). These results suggest the existence of intra- and/or intermolecular associates formed, the most probably, due to intramolecular interactions of the hydrophobic substituents. The decrease of intrinsic viscosities of HM-CMC derivatives could be ascribed to a coil contraction of the mentioned hydrophobic interactions resulting in decrease of the hydrodynamic volume, which is directly related to viscosity or to degradation of CMC during the esterification under microwave irradiation [11], or to a combination of both effects. The mean molecular mass (M_r) of the HM-CMC derivatives, varied between 339 and 298 kDA, and was considerably lower in comparison to that of the starting CMC ($M_r = 740$ kDa).

CONCLUSIONS

The surface-active and viscous properties of unmodified CMC and its low esterified HM-CMC derivatives were investigated. The results of the surface-activity testing revealed that some of the HM-CMC derivatives show excellent emulsifying activity for ‘oil in water’ type emulsions comparable to that of the commercial synthetic emulsifier

Tween 20. In spite that they had surface tensions, which were not significantly lower than that of water, they form micelles in the concentration range 0.5 to 2.45 $g \cdot L^{-1}$, except of derivative VI.

The surface tension effect of CMC and selected HM-CMC derivatives was improved by addition of small amount of oppositely charged surfactants. In dependence on the concentration of the surfactant and the length of its alkyl chain, the complexes HM-CMC/C_nTAB are able to reduce the surface tension of water from 72.8 to $\sim 31\,mN \cdot m^{-1}$.

The Huggins constant derived from the viscometric measurements of the HM-CMC derivatives in the dilute sodium chloride solution indicated the existence of hydrophobic interactions. The decrease of intrinsic viscosity of the HM-CMC derivatives can be explained mainly by molecular degradation of CMC during the microwave-assisted esterification reaction [11]. However, the intramolecular associations induced by the hydrophobic substituents of the macromolecular chains might contribute to the observed effect as well. As expected, the tensioactive properties of the HM−CMC derivatives were not affected by the molecular degradation.

The results suggest that the HM-CMC esters and HM-CMC/surfactant systems are potentially applicable in various branches such as personal care, cosmetics and pharmaceuticals, paints and inks, detergents, and flotation.

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