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Characterization of aqueous carboxymethylcellulose solutions in terms of their molecular structure and its influence on rheological behaviour[*]

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A set of carboxymethylcellulose (CMC) samples was varied in degree of substitution (DS) from 0.71 to 2.95, with the partial degree of substitution being raised uniformly at positions C2, C3 and C6, so that a homologous series of CMC was made available. A further set of samples varied in molar mass from 200 000 to 2 000 000 g mol^{-1} at a constant DS of ~ 1. The chemical structural parameters were determined by n.m.r. spectroscopy, showing that quantification of the degree of substitution at position C6 may be distorted by impurities of glycolic acid. The mean molar masses, for establishing the $[\eta]$–M relationship, were determined by multiangle laser light scattering preceded by size exclusion chromatography. The influence of concentration on zero-shear viscosity was given by $\eta_0 \propto c^{4.3}$, whereas the influence of the molar mass was determined by $\eta_0 \propto M^{3.9}$. An increasing DS within a homologous series influences the viscosity in different solvents (H_2O 0.01 M NaCl, 0.1 M NaCl) at low polyelectrolytic concentrations. Surprisingly, the viscosity for all the CMC samples can be predicted by the single equation:

$$\eta_0[\mathrm{Pa\ s}] = 8.91 \times 10^{-4} + 1.30 \times 10^{-5}\, cM_W^{0.9} + 5.33 \times 10^{-8} c^2 M_W^{1.8} + 4.60 \times 10^{-15} c^{4.34} M_W^{3.91}$$

at $T = 298$ K in 0.01 M NaCl. Increasing the DS up to a value of ~ 1 improves the solubility characteristics (increases the viscosity), whereas above DS ≈ 1 this effect is overlapped by degradation of the molar mass. It was also possible to quantitatively determine the viscoelasticity as a function of frequency and molecular parameters. Copyright © 1996 Elsevier Science Ltd.

(Keywords: carboxymethylcellulose; molecular structure; rheology)

INTRODUCTION

The biologically degradable, regenerative raw material cellulose can be modified by chemical reaction in many ways[1]. Good film-forming properties of the cellulose derivatives can be achieved by the introduction of hydrophobic alkyl groups, whereas hydroxyalkylation results in good solubility[2]. Faster and better solubility in water is obtained by the introduction of ionic groups. Thus sulfoethylation, even at degrees of substitution around 0.3, produces water-soluble products[3] that exhibit a relatively good salt stability to multivalent cations. By reaction of celluloses with chloroacetic acid, carboxymethylcelluloses (CMC) are obtained, which in contrast to the sulfoethylated products, first start to exhibit good water solubility beyond substitution degrees of about 0.8[4], display a distinct sensitivity to multivalent salts[5], form complexes and are used in aqueous coating systems and ceramic masses. Industrially manufactured CMC is also employed as an additive in aqueous flushing systems for deep drilling and machine cleaning, where the structure-forming properties play an important role[6–8]. Carboxymethylcelluloses have a very high water-bonding capacity, good compatibility with skin and mucous membranes and, because they are physiologically harmless, are used widely in pharmacy, cosmetics and the food industry in order to improve the consistency and flow properties[9–12].

In spite of the great interest in this group of substances it has still not been possible to optimize the properties because chemical and steric characterization of the microstructure for this complex system is extremely difficult. Very often[13,14], in dealing with variation in the chemical microstructure, only the average degree of substitution (DS) is given and not important information such as how the substituents are distributed amongst the

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[*] Dedicated to Professor Dr J. Klein on the occasion of his 60th birthday

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positions C2, C3 and C6. An indication of the molar mass is important if comparisons of the influence of concentration and solvent quality are to be made.

Previous studies[15,16] used structure–property relationships to predict the solution viscosity, and the same will be performed for CMC in this investigation. The aim is to correlate the influence of the parameters molar mass, concentration and chemical structure with rheomechanically determined values, whilst considering other factors such as salt content and temperature.

EXPERIMENTAL

Sample material

For these investigations two sets were compiled from a large pool of samples. The first set comprises carboxymethylcelluloses with differing degrees of substitution (samples 1–12), in which the partial degrees of substitution increase uniformly. To synthesize these polymers, celluloses with identical degrees of polymerization underwent heterogeneous reaction with chloroacetic acid in an isopropanol/sodium hydroxide slurry. In some cases the reaction was repeated several times. *Figure 1* shows a greatly simplified reaction scheme. A further set of eight samples was obtained by a corresponding reaction of celluloses of different degrees of polymerization up to a degree of substitution of approximately 1.0 (samples 13–20).

N.m.r. spectroscopy

The ^{1}H n.m.r. spectra of the first two sample sets were recorded with an MSL 300 NMR Spectrometer (Bruker, Karlsruhe, Germany) at a frequency of 300.13 MHz in a 5 mm probehead at room temperature. Thirty-two scans were accumulated at a pulse angle of approximately 30° and a relaxation delay of 5 s. Sample preparation was carried out according to the method described by Ho and Klosiewicz[17] by hydrolysis of the CMC samples with sulfuric acid. Sodium acetate ($\delta = 2.04$) was added as a reference substance.

The $\{^1H\}$–^{13}C n.m.r. spectra of the hydrolysates synthesized according to Reuben and Conner[18] were recorded with an AM 360 NMR Spectrometer (Bruker, Karlsruhe, Germany) at a frequency of 90.56 MHz in a 10 mm probehead at room temperature. At least 10 000 scans were accumulated at a pulse angle of 60° and a relaxation delay of 3.5 s. Methanol ($\delta = 49.0$) was used as reference substance. The inverse gated decoupling method (IGATED) was employed to suppress NOE, thus allowing correct quantitative evaluation of the spectra.

The $\{^1H\}$–^{13}C n.m.r. spectra of the ultrasonically degraded CMCs were recorded with an MSL 300 NMR Spectrometer (Bruker, Karlsruhe, Germany) at a frequency of 75.47 MHz in a 10 mm probehead at 363 K. Seven thousand scans were accumulated at a pulse angle of 90° and a relaxation delay of 5 s. Trimethylsilylpropionic acid-d4-sodium salt ($\delta = -2.47$) served as the reference substance. The experimental conditions chosen guarantee full relaxation of all the carbon nuclei, with the exception of the carbonyl centres.

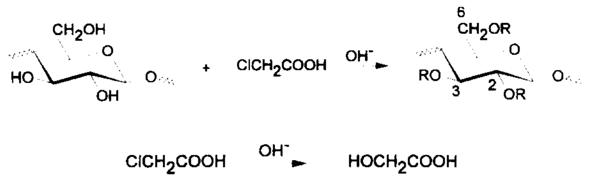

Figure 1 Schematic representation of the etherification of cellulose to carboxymethylcellulose with chloroacetic acid in an alkaline medium (R = carboxymethyl or hydrogen); glycolic acid was formed from chloroacetic acid as a side reaction

In the quantitative evaluation the relevant signals were simulated on a 486 PC using the program Win-NMR (Bruker). The signal intensities obtained (area beneath the resonance signals) were then used to calculate the desired structural information.

Ultrasonic degradation

Ultrasonic reduction of the molar mass was carried out with a Sonifier W-450 (Branson Schallkraft GmbH, Heusenstamm, Germany) with a 19 mm titanium resonator at the medium power setting and at a temperature of ~ 293 K. The abraded metal particles from the resonator were separated by centrifugation.

Determination of molar mass and molar mass distribution

The steric structure was determined by coupling an exclusion chromatography system (SEC, TSK 30/40/50/60 Toyo Soda, Japan) with a multiangle laser light-scattering photometer sensitive to molar mass (Dawn-F and Dawn-DSP-F, Wyatt-Technology Corp., Santa Barbara, USA) and a Shodex RI SE 51 differential refractometer sensitive to concentration (Showa Denko, Tokyo, Japan).

A 0.1 and a 0.5 mol l^{-1} sodium nitrate solution with 0.02% w/w of sodium azide was used as the carrier liquid. The polymers were dissolved in a solvent of the same composition. Before the measurement, the CMC stock solution was centrifuged at 15 000 *g* for 2 h.

Rheology

Rheological measurements were performed at 298 K using an RFS-8500 rotational and oscillating rheometer (Rheometrics Inc., New Jersey, USA) and a CS-50 rheometer (Bohlin Instruments, Mühlacker, Germany); both instruments were equipped with a cone-plate measuring head.

Viscometry

Viscometric measurements were carried out on a Zimm-Crothers rotational viscometer (Krannich, Göttingen, Germany) in 0.01 mol l^{-1} sodium chloride solution at a temperature of 298 K. The small shear rates (0.1–0.3 s^{-1}) ensured that measurement took place within the Newtonian range.

RESULTS AND DISCUSSION

To understand the macroscopic behaviour of carboxymethylcellulose, such as the thickening action and the structure-forming properties, and to correlate these rheological variables with the molecular structure of the polymer, a precise knowledge of both the chemical and steric structure is necessary. The following sections first describe the determination of the chemical structure using ^{1}H and ^{13}C n.m.r. spectroscopy and methods for determining the steric structure by viscometry and size exclusion chromatography coupled with multiangle laser light-scattering and differential refractometry. The flow behaviour is discussed, and an attempt will be made to correlate the chemical and steric structural parameters with the macroscopic behaviour determined from the rheological measurements.

Determination of the chemical structure

Determination of the chemical structure of the carboxymethylcelluloses was performed with n.m.r. spectroscopy, which provides absolute information on the average degree of substitution, (DS) as well as the partial degrees of substitution, x_i, at the positions C2, C3 and C6.

Owing to the relatively short measuring times required, the determination of the structural parameters DS and x_i by acid hydrolysis and ^{1}H n.m.r. spectroscopy is particularly suitable as a standard method for the investigation of CMC. However, contradictory opinions are to be found in the literature on the transferability of the results obtained from hydrolysate measurements for the substitution ratios in undegraded CMC. Some authors[19–21] report major changes in the sample resulting from the hydrolysis; others[22,23] describe acid hydrolysis as a method which exclusively cleaves the acetal bond of the cellulose chain, yielding the ether bonds between substituents and the anhydroglucose unit. A recent comparison of the partial degrees of substitution determined from acid hydrolysates with results from ultrasonically degraded samples was able to show that hydrolysis does not change the substitution ratios[24]. The ultrasonic method has proven its worth in the degradation of high polymers, where comprehensive investigations on both synthetic and biopolymers have established that the structural parameters determined in the degraded sample fully match those in the undegraded sample[25].

Figure 2 shows a comparison of the ^{1}H n.m.r. spectra for the first set of samples, which cover a wide range of the average degree of substitution. The assignment of the resonances given was taken from the literature[17]. Since low molecular mass compounds resulting from the synthetic process, such as glycolic acid, display resonances in the range 4.5–4.1 ppm, it is essential that the samples be purified prior to hydrolysis. In *Figure 2* it can be seen that there is overlap between the resonance signals of the glycolic acid and the substituent at C6. The presence of glycolic acid therefore prevents evaluation of the partial degree of substitution at position C6 and the average degree of substitution.

Figure 3 shows a corresponding comparison of ^{13}C n.m.r. spectra for ultrasonically degraded samples over a range of DS from 0.99 to 2.95. *Table 1* contrasts the results of the two investigative methods. Within the given limits of reproducibility there is good agreement for the degrees of substitution (DS and x_i) of the CMCs investigated here. Thus the two methods described above yield reliable results and are suitable for characterization. Examination by means of hydrolysis and ^{1}H n.m.r. spectroscopy can, as mentioned above, be employed as a rapid and efficient standard method. The chemical structural parameters that were determined are summarized in *Table 1*.

The degrees of substitution (DS) and partial degrees of substitution (x_i) can also be determined from acid hydrolysates by ^{13}C n.m.r. spectroscopy. Results obtained by this method show a similarly good level of agreement with the values determined by the other two methods[26]. In addition, the ^{13}C n.m.r. spectra of the

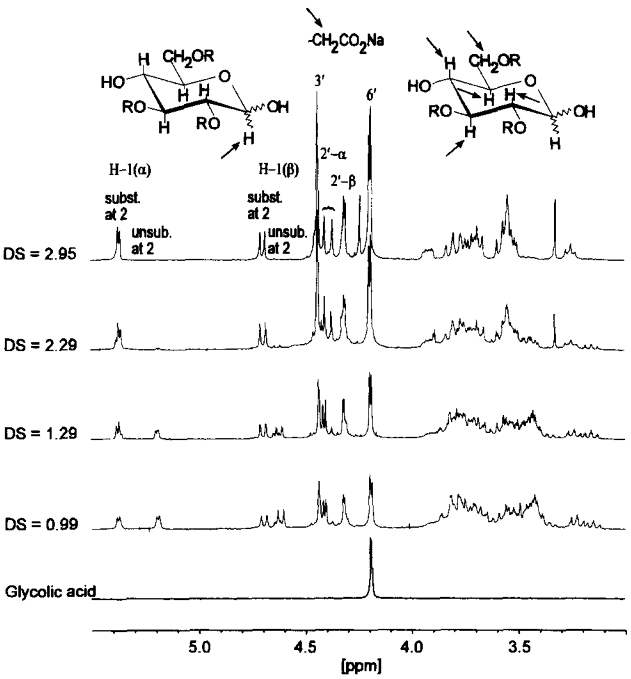

Figure 2 Comparative representation of four ^{1}H n.m.r. spectra for carboxymethylcelluloses degraded by acid hydrolysis with graduated degrees of substitution and signal assignment. The bottom spectrum is that of glycolic acid in 25% v/v D_2SO_4. Sodium acetate ($\delta = 2.04$) was added as the reference substance in each case

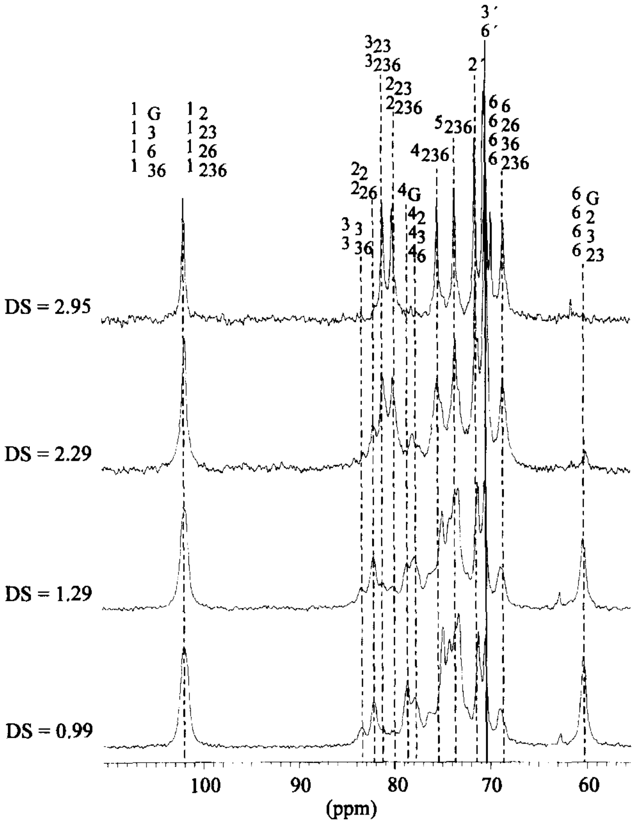

Figure 3 Comparative representation of four ^{13}C n.m.r. spectra for ultrasonically degraded carboxymethylcelluloses with graduated degrees of substitution; the region of the carbonyl carbon atoms is not shown

Table 1 Average and partial degrees of subsitution determined by ^{13}C n.m.r. spectroscopy for ultrasonically degraded carboxymethylcelluloses and by ^{1}H n.m.r. spectroscopy for sulfuric acid hydrolysates

Sample	Method	x_2	x_3	x_6	DS
1	^{1}H-Hy	0.37	0.12	0.22	0.71
2	^{1}H-Hy	0.35	0.19	0.32	0.86
	^{13}C-US	0.49	0.09	0.31	0.89
3	^{1}H-Hy	0.43	0.20	0.32	0.95
4	^{1}H-Hy	0.44	0.21	0.32	0.97
5	^{1}H-Hy	0.43	0.22	0.34	0.99
	^{13}C-US	0.46	0.17	0.31	0.94
6	^{1}H-Hy	0.50	0.22	0.39	1.11
7	^{1}H-Hy	0.54	0.25	0.41	1.20
8	^{1}H-Hy	0.56	0.31	0.44	1.31
	^{13}C-US	0.56	0.30	0.44	1.30
9	^{1}H-Hy	0.64	0.30	0.47	1.41
10	^{1}H-Hy	0.87	0.63	0.79	2.29
	^{13}C-US	0.97	0.67	0.80	2.44
11	^{1}H-Hy	0.97	0.75	0.94	2.66
12	^{1}H-Hy	1.00	0.92	1.05	2.97
	^{13}C-US	0.92	1.02	1.02	2.96
13–20	^{1}H-Hy	0.46 ± 0.03	0.22 ± 0.03	0.34 ± 0.03	1.02 ± 0.04

hydrolysed CMCs also provide information on the mole fractions of the eight possible 'monomeric components'[18], details of which, however, will not be given here.

In a previous study[24] the relative rate constants for the etherification reaction were determined from the partial degrees of substitution obtained by ^{13}C n.m.r. spectroscopy. After standardization to the rate constant for position C3, the ratio of $k_2 : k_6$ was found to be 3.0 : 1.0 : 2.1. The rate constants from the ^{1}H spectra are in good agreement with a corresponding ratio of 2.6 : 1.0 : 1.8. Plots of the partial degrees of substitution determined by ^{1}H n.m.r. spectroscopy against the average degree of substitution are in good agreement with the theoretical values, calculated from a kinetic model by Spurlin[27] using the rate constants given above (*Figure 4*). The assumptions made in the calculation, that the heterogeneous etherification is a first order reaction and that the reactivities of the hydroxyl groups are not influenced by the substituents already introduced, do not result in any substantial error.

For average degrees of substitution in the range from DS $\approx$ 0.7–1.5, which is of interest in terms of technical applications, the partial degrees of substitution, x_i, are almost linear in the average degree of substitution, DS, (*Figure 4*, top). The samples differ only in their degree of substitution and not in the distribution of the substituents amongst the possible positions. They are thus suitable for investigating the influence of the parameter 'degree of substitution' upon the macroscopic behaviour.

The CMCs from the second set of samples form a molar mass series with a uniform chemical structure. Characterization of the acid hydrolysates by ^{1}H n.m.r. spectroscopy demonstrates that samples 13–20 have DS ≈ 1 and partial degrees of substitution of $x_2 \approx 0.46$, $x_3 \approx 0.22$, $x_6 \approx 0.34$.

The steric structure of CMC

Apart from the information obtained by n.m.r. spectroscopy, characterization of the sample sets and an understanding of the properties are also aided by a knowledge of the weight-average molar masses.

As was discussed in the mid 1950s[28–34], sharp

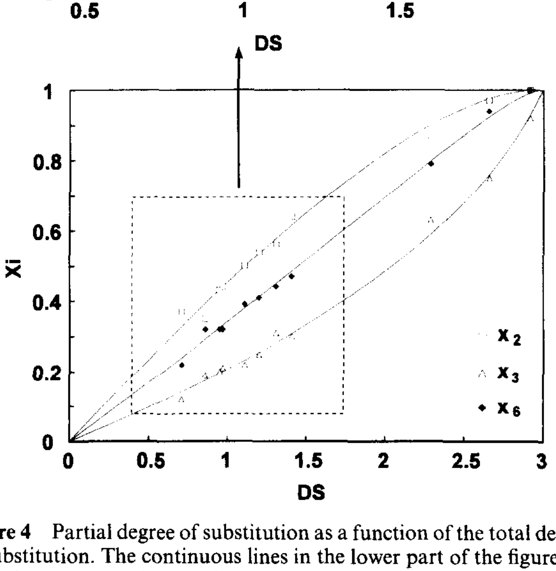

Figure 4 Partial degree of substitution as a function of the total degree of substitution. The continuous lines in the lower part of the figure are the values calculated according to Spurlin's model. The upper part of the figure is an enlargement of the section contained in the dotted box, intended to illustrate the approximately linear relationship that exists between DS and partial degree of substitution in this range

deviations from the molecularly disperse state may occur in solutions of cellulose ethers. A model for the solution state of CMC was developed[35–38] which postulated the presence of microgels (<500 nm) and macrogels (>500 nm) alongside free molecules. The presence of these gel particles makes molar mass determination more difficult. To avoid this interference, attempts are often made to remove the non-molecularly-disperse portion by ultrafiltration or ultracentrifugation. This makes it uncertain, particularly in the case of heterogeneously synthesized samples, whether the portion then used for investigation is completely molecularly disperse. Furthermore, the result obtained is no longer representative of the entire sample[39].

To quickly measure data on the steric structure for rheological characterization, the molar masses were determined by viscometry and an $[\eta]$–M_W relationship. The intrinsic viscosities needed to set up such a relationship were obtained with a low-shear viscometer, the required molar masses by size exclusion chromatography (s.e.c.) coupled with double detection. The latter was performed with a multiangle laser light-scattering photometer (MALLS) and a differential refractometer (DRI). An exact description of the apparatus is given in ref. 40.

The result was the relationship shown in equation (1). This was established using the second set of samples (DS $\approx$ 1, $x_2 \approx 0.46$, $x_3 \approx 0.22$, $x_6 \approx 0.34$, molar masses 200 000–2 000 000 g mol^{-1}, solvent 0.01 mol l^{-1} NaCl, $T = 298$ K).

$$[\eta] = 1.43 \times 10^{-2} M_W^{0.90} (\mathrm{cm^3\,g^{-1}}) \qquad (1)$$

The data employed are compiled in *Table 2*.

Rheological characterization of the CMC solutions

As reported in the Introduction, CMC is used in a wide range of applications; however each individual field of applications is so complex as to rule out a direct correlation with molecular data for optimization purposes. Rheological investigations allow material functions to be directly determined both quantitatively and representatively, with variations in concentration, molar mass, salt content and DS being reflected directly.

For any given polymer–solvent system the molar mass of the dissolved macromolecules and their concentration in the solution are crucial parameters for influencing the rheological properties. In moderately concentrated solution, important for so many applications, in which the thermodynamic solvent quality affects the viscosity, the zero-shear viscosity can be described as a function of the overlap parameter ($c[\eta]$). By including the intrinsic viscosity, this normalization, introduced by Simha and co-workers[41,42] in the 1960s, takes account of the influence of both the molar mass and the solvation power of the solvent on the hydrodynamically effective volume of the polymer coil at very low values of the overlap parameter[43,44]. In 1980 Kulicke showed that if a non-linear function is used, this applies to a very large range, which then makes this method suitable for many polymer–solvent systems[45]. *Figure 5* shows that this is also possible for CMC.

Table 2 Molar masses determined by s.e.c./MALLS/DRI and Staudinger indices determined by viscometry

Sample	Molar mass (g mol^{-1})	$[\eta]$ (cm^3 g^{-1})
13	2 090 000	5852
14	1 000 000	4309
15	930 000	3970
16	1 048 000	3747
17	461 000	1985
18	402 000	1564
19	216 000	1077
20	206 000	675

The calculations performed in this way with a large number of experimental data from viscometry (determination of $[\eta]$ and k_H), light scattering (see equation (1)) and from rheological experiments on concentrated CMC solutions produced the following equation:

$$\eta_{sp} = \frac{\eta_0}{\eta_{LM}} - 1 = c[\eta] + k_H(c[\eta])^2 + B_n(c[\eta])^n \qquad (2)$$

where $k_H = 0.281$, $B_n = 4.80 \times 10^{-4}$, $n = 4.34$ (CMC in 0.01 M NaCl solution, $T = 298$ K).

$$\eta_0[Pa\ s] = 8.91 \times 10^{-4} + 1.30 \times 10^{-5} c M_W^{0.9} + 5.33 \times 10^{-8} c^2 M_W^{1.8} + 4.60 \times 10^{-15} c^{4.34} M_W^{3.91} \qquad (3)$$

The relationships from equation (3) are represented graphically in *Figure 6* in order to clearly illustrate the different influences of concentration and molar mass on the viscosity yield. The curves for $\eta_0 = f(M_W)$ and $\eta_0 = f(c)$ were calculated by maintaining one parameter at a constant value. Both variables have a great effect on the zero-shear viscosity: η_0 increases by several orders of magnitude in the concentration and molar mass ranges illustrated. However, a high viscosity yield is more easily achieved with a higher concentration than by using a product with a higher molar mass.

In the practical applications of sodium carboxymethylcellulose a knowledge of the Newtonian flow

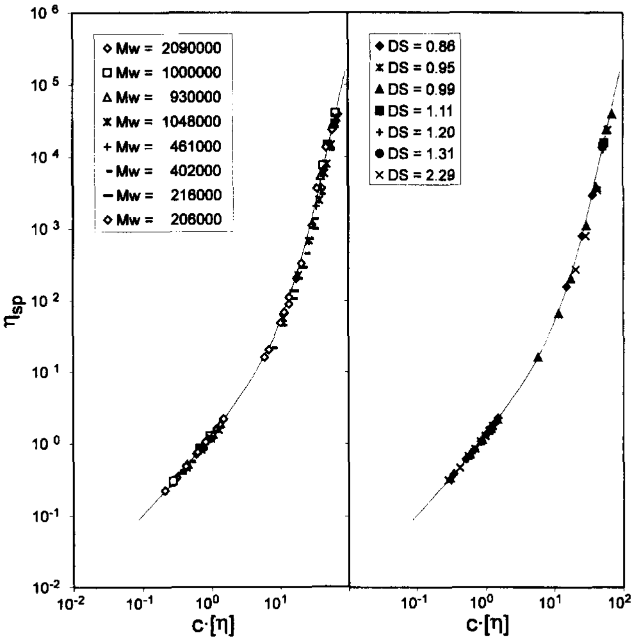

Figure 5 Normalization of the specific viscosity, η_{sp}, against the overlap parameter ($c[\eta]$) for some of the CMC samples with varying DS and samples 13–20 with a variation of the molar mass (in 0.01 mol l^{-1} sodium chloride solution at 298 K)

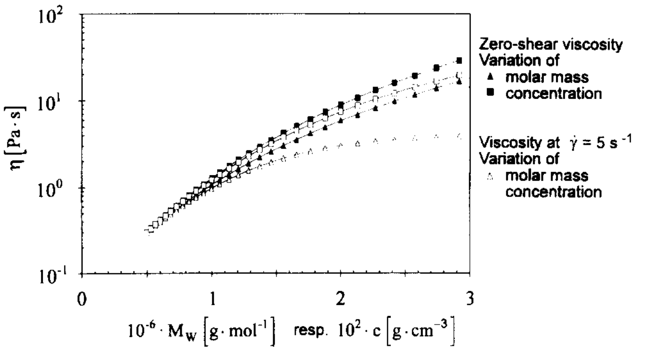

Figure 6 Influence of molar mass and concentration upon the viscosity of CMC solutions. The curves start at $c = 0.005\,\mathrm{g\,cm^{-3}}$ and $M_W = 5 \times 10^5\,\mathrm{g\,mol^{-1}}$; in each case one of the two variables was then increased. Reference temperature = 298 K

behaviour (η_0) alone is not enough since above a critical shear rate, $\dot\gamma_{\mathrm{crit}}$, the viscosity of the solutions decreases sharply with increasing shear rate. In order to predict the rheological properties of CMC solutions under stress, it is necessary to carry out extensive investigations which incorporate a mathematical record of the parameters that influence the entire flow curve in the Newtonian and non-Newtonian ranges. The modified Carreau model[46] has proven to be suitable for the flow curve:

$$\eta(\dot\gamma) = \eta_0\left[1 + (\tau\dot\gamma)^b\right]^{d/b} \tag{4}$$

where η_0 is zero-shear viscosity; τ is relaxation time that describes the transition from Newtonian to non-Newtonian flow, reciprocal of the critical shear rate $\dot\gamma_{\mathrm{crit}}$; d is gradient of the flow curve in the power law region; and b is the transition parameter to adapt the deflection of the viscosity curve in the region between the Newtonian and non-Newtonian range.

The parameters of this empirical model for describing the function $\eta = f(\dot\gamma)$ can be correlated with molecular data such as molar mass, molar mass distribution and concentration of the polymer solutions[47] and are thus open to molecular modelling[48], as shown above for η_0. The steps necessary to calculate the flow curve parameters have already been described[4]; only the results will be presented here. η_0 is described by equations (2) and (3). The following relationships exist for the remaining parameters:

$$\tau = 3.28 \times 10^{-11} c^{-0.25}[\eta]^2 + 9.22 \times 10^{-12} c^{0.75}[\eta]^3 + 1.57 \times 10^{-14} c^{3.09}[\eta]^{5.34} \tag{5}$$

$$d = 0.818 - 0.818 e^{-0.0449 c[\eta]} \tag{6}$$

$$b = 0.73 \tag{7}$$

The relaxation time, τ (equations (5) and (1)), is thus more strongly dependent upon the molar mass than upon the concentration. The limiting value for the gradient of the viscosity curve, d (equation (6)), matches the theoretical value derived by Graessley[49]. The transition parameter, b, with a value of 0.73 is significantly smaller than the value of 2 from the original Carreau model, as expected for industrial polymer samples with a broad spread of molar mass. Since b exhibited no systematic dependence upon the molar mass in the moderate concentration solution range, the mean from a large number of flow curve adjustments was used (10% simple standard deviation).

Equations (1) and (2)–(7) together give a structure–property relationship that enables the viscosity of CMC solutions to be predicted as functions of molar mass or intrinsic viscosity and concentration in a large range of shear rates. This is illustrated in *Figure 6* in order to clearly demonstrate the different influences of concentration and molar mass on the viscosity yield under strain. A value of $5\,\mathrm{s^{-1}}$ was chosen as the shear rate. The curves for $\eta(\dot\gamma = 5\,\mathrm{s^{-1}}) = f(M_w)$ and $\eta(\dot\gamma = 5\,\mathrm{s^{-1}}) = f(c)$ were calculated with the structure–property relationship presented here, with one of the two parameters being held constant in each case.

As can be seen from *Figure 6*, the possibilities of producing CMC solutions that have a high viscosity under strain are significantly restricted. Although the viscosity continues to rise, albeit to a lesser extent than η_0, owing to an increase in concentration, above a certain limit, which depends on the shear rate, the viscosity-raising effect of larger molar masses is largely compensated for by the earlier onset of pseudoplastic behaviour (larger τ, smaller $\dot\gamma_{\mathrm{crit}}$).

It is well known that in addition to their viscous properties, polymers also display elastic characteristics, e.g. as manifested in normal stresses and in stabilizing, structure-forming and viscoelastic effects. The viscoelastic properties of polymer systems can be determined by mechanical oscillatory measurements which are carried out with variable frequency and very low amplitude (in the linear viscoelastic region) and can be employed as a more or less non-destructive measuring method even for investigating sensitive superstructures. The elastic reaction of the material is described by the storage modulus G' and the viscous properties by the loss modulus G''.

To gain better understanding of the influence of molar mass and concentration on viscoelasticity of the CMC solutions and hence to be able to adjust these properties, oscillatory measurements were carried out on a molar mass series and for solutions with differing concentrations. The results are presented in *Figures 7* and *8*. For greater clarity only a few selected measurements are shown; in each case the broken lines link the intersections of the modulus curves, which also take into account the data that have not been depicted. At low frequency the storage modulus, G', is smaller than the loss modulus, G'', in all cases; this means that viscosity is the dominant property of the CMC solutions under low strain. As the

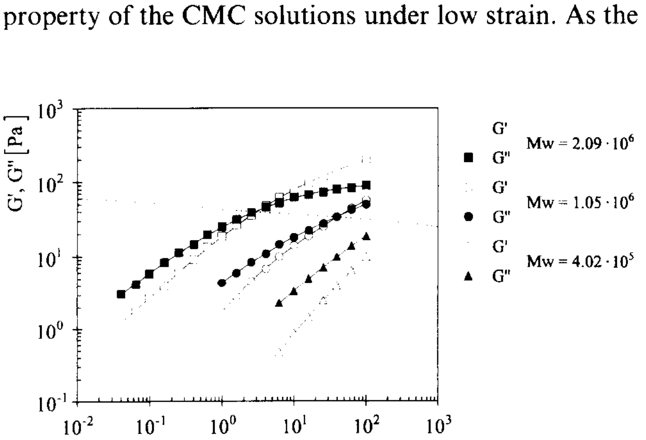

Figure 7 Storage and loss moduli as a function of the angular frequency, ω, for sodium carboxymethylcelluloses of differing molar mass in $0.01\,\mathrm{mol\,l^{-1}}$ sodium chloride solution; $c = 1.5\%$, DS = 1.0, $T = 298\,\mathrm{K}$

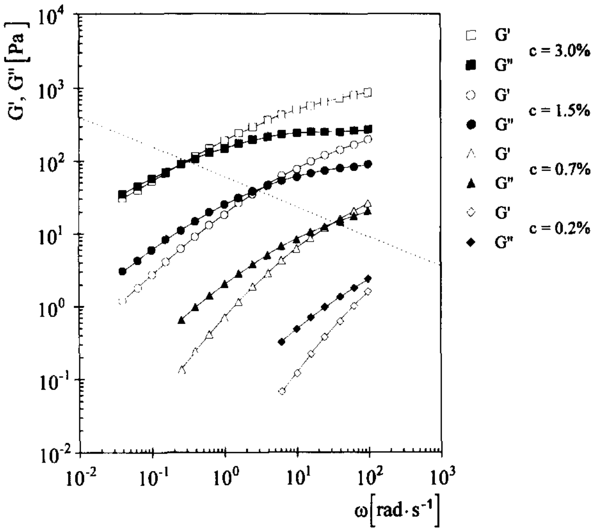

Figure 8 Storage and loss moduli as a function of the angular frequency, ω, for sodium carboxymethylcelluloses of differing concentration in 0.01 mol l^{-1} sodium chloride solution; $M_W = 2.09 \times 10^{-6}$, DS = 0.99, $T = 298$ K

frequency increases, the elastic component becomes more important until the modulus curves eventually intersect and above this characteristic frequency, ω $(G' - G'')$, the storage modulus predominates.

Variation of the molar mass (*Figure 7*) causes a shift of the intersection $G' = G''$ along the frequency axis at an almost constant level. This fact is quite understandable because the reciprocal of the frequency ω $(G' = G'')$ can be regarded as a relaxation time of the entanglement network in the solution. The large influence of the molar mass has already been seen in the transition from Newtonian to pseudoplastic flow (equation (6)). In contrast to this, the number of entanglements is more strongly dependent upon the total number of polymer segments in the solution (i.e. the polymer concentration), which is why there is little change in the level of the moduli in the intersection. A possible explanation for the slight decrease may be that as the mean molar mass declines, the CMCs have a higher proportion of particles with chains that are too short to form entanglements.

A change in concentration (*Figure 8*) affects both the frequency at which the modulus curves intersect and the level. As the concentration increases, the number of entanglements (density of the entanglement network) increases, which causes the value of the moduli to rise; at the same time the mobility of the particles in the more highly concentrated solution decreases, they are no longer able to avoid the strain even at low frequency, and ω $(G' = G'')$ becomes smaller and the relaxation time larger.

The parameter 'concentration' can only be used to a limited extent for adjusting the viscoelasticity of CMC solutions to meet the requirements of various applications. This is because a change in concentration not only influences the relaxation behaviour but also affects the material functions. To selectively set specific property profiles it is necessary to choose a product with the 'correct' molar mass in conjunction with the optimal concentration.

The relationships between chemical structure and macroscopic properties are investigated with a homologous series of CMC, with a DS rising from 0.71 to 2.29 and a constant ratio between the partial degrees of substitution. As shown in *Figure 9*, the viscosity curves of these samples follow a similar pattern, with the greater differences occurring mainly in the low shear-rate region. In order to show this more clearly, *Figure 10* is a plot of the zero-shear viscosity or the value measured at 0.1 s^{-1} against the degree of substitution. Starting from the lowest degree of substitution (DS = 0.71), at first a sharp rise in the viscosity of the solutions can be observed as DS increases. After passing through a maximum around DS $\approx$ 0.95, the viscosity drops significantly towards higher DS values. An analogous pattern is obtained when the storage modulus, G' (measured at 1 rad s^{-1}), is plotted against DS (see *Figure 10*).

This peak behaviour can be explained by two overlapping effects. Firstly, the increase in the material functions with increasing DS in the lower DS range (see *Figure 10*) may be accounted for by a transition from largely insoluble, compact, cellulose-like structures with microcrystalline portions to more readily soluble particles with microgel character. This agrees with the

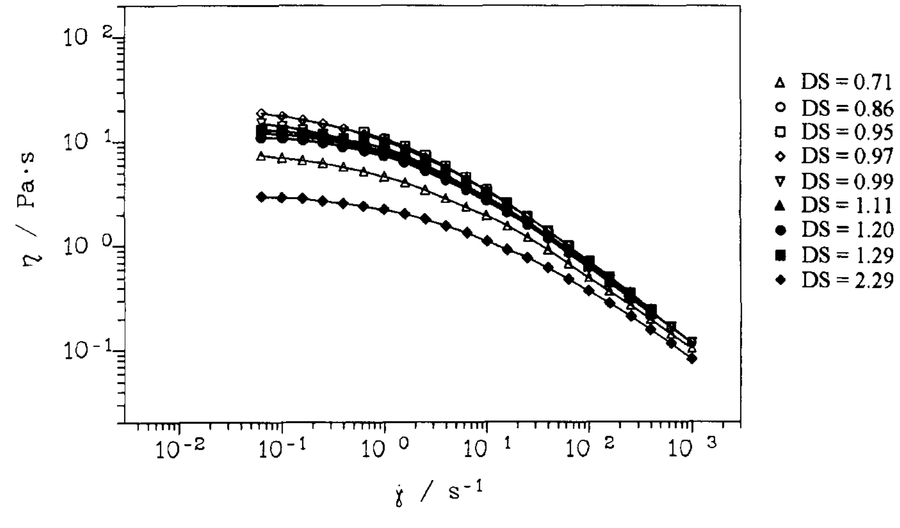

Figure 9 Viscosity functions of a series of sodium carboxymethylcelluloses with degrees of substitution from 0.71 to 2.29 and uniformly statistical substitution pattern (samples 1–10); $c = 1.0\%$ in 0.01 mol l^{-1} sodium chloride solution at 298 K

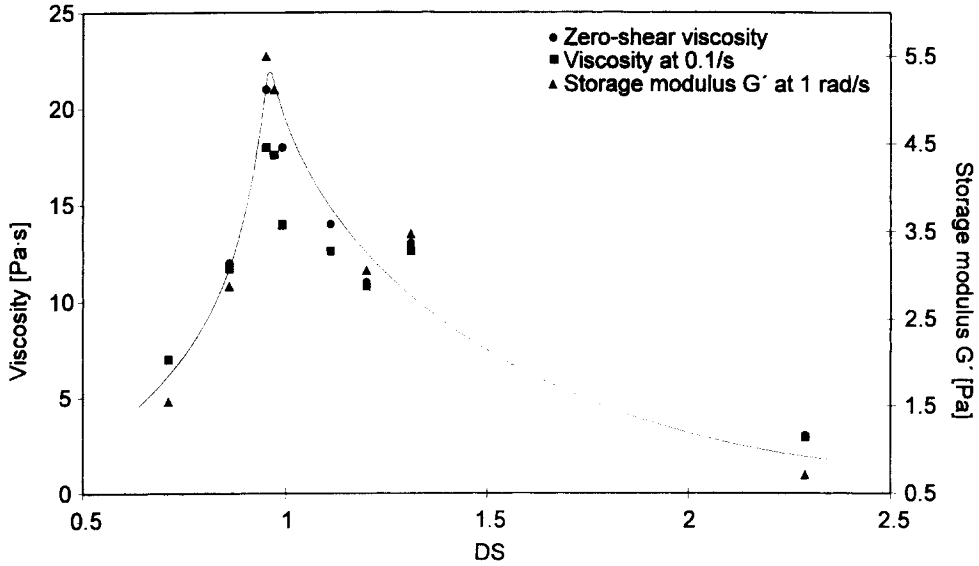

Figure 10 Shear viscosity in the Newtonian region (η_0) and at a shear rate of 0.1 s^{-1} as well as the storage modulus, G', at a frequency of 1.0 rad s^{-1} as a function of DS for the same samples and conditions as in *Figure 9*

Table 3 Compilation of the mean molar masses for some of the first set of samples, calculated by means of equation (1)

DS	Molar mass (g mol^{-1})
0.86	1 440 000
0.95	1 740 000
0.97	1 710 000
0.99	1 680 000
1.11	1 530 000
1.20	1 460 000
1.31	1 470 000
1.41	1 360 000
2.29	1 170 000

observable transition from turbid (suspension) to clear solution in the region around DS = 0.85. Chemical structure can thus be seen to have a clear influence on the macroscopic behaviour for degrees of substitution below 1.

The drop in viscosity and elasticity yield observed on further increase of the DS can be interpreted as a consequence of the corresponding decline in the mean molar mass, as can be seen in *Table 3*. This does not clarify whether the lower molar masses are a result of polymer chain degradation with increasing duration of the etherification reaction or of an inferior tendency for the more highly substituted CMCs to form aggregates. Both effects may play a role.

In order to estimate the influence of the solvent on the viscosity, CMC solutions with differing polymer concentrations were analysed rheologically in deionized water and in 0.01 and 1.0 mol l^{-1} sodium chloride solutions. Some representative results are given in *Figure 11*.

At low polymer concentration the viscosity of the solution falls sharply as the salt content rises, particularly in the low shear-rate range. As the concentration of the CMC solutions increases, this effect becomes significantly weaker. Under the influence of salt ions or

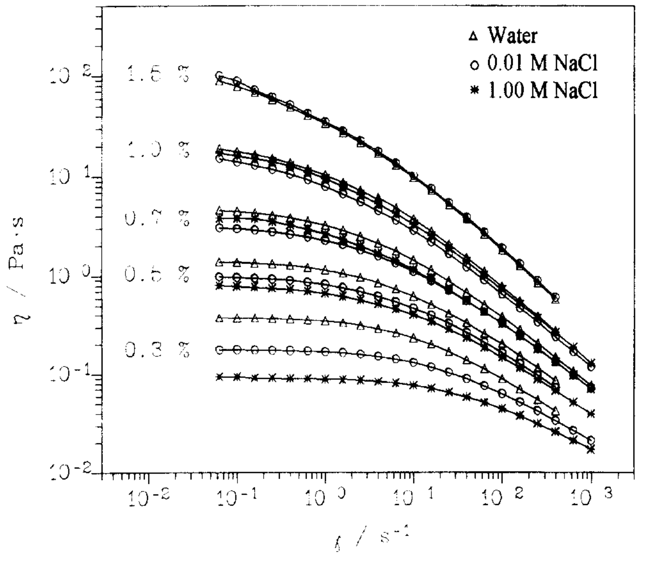

Figure 11 Influence of various salt concentrations upon the viscosity of CMC solutions; $M_w = 2.09 \times 10^6$ g mol^{-1}, DS = 0.99, T = 298 K

a high CMC concentration, coil expansion due to the polyelectrolytic effect is reduced, since, on the one hand, the charges are screened and, on the other hand, there is a reduction in the degree of dissociation of the sodium carboxymethylcellulose groups. With higher polymer concentration the polymer–polymer interactions (entanglements) become the main factor influencing the viscosity of the CMC solutions.

CONCLUSION

In this paper two sets of samples were investigated. One set of samples was varied in molar mass, the other in the DS, with the partial degree of substitution being raised uniformly at positions C2, C3 and C6. It was found that the rheological behaviour of an aqueous CMC solution is mainly influenced by the molar mass of the dissolved CMC and its concentration. The degree of substitution only has a substantial effect in terms of increasing solubility, with the DS being raised in the region DS < 1. The samples investigated did not show any improvement in viscosity yield when the DS was further elevated to DS > 2. The stiffness of the polymer chain is due to the cellulose backbone and is not really influenced by the introduction of more ionic groups, especially in the salt solutions that are technically relevant. Furthermore, the opposite case of decreasing viscosity and viscoelastic material functions with growing DS is observed for solutions containing 1% w/w of CMC. This effect is correlated with the molar mass decreasing in the same direction.

Costly preparation of highly substituted NaCMC is therefore not necessary to obtain a good product for thickening purposes. In this field the best results are achieved with DS ≈ 1. Interactions between NaCMC and electrolytes with higher charges than NaCl are likely to exhibit stronger dependencies on the DS. The investigations of such systems with high DS is therefore considered to be an area worthy of discussion in the future.

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