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Physical properties of methylcelluloses in relation with the conditions for cellulose modification

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Water-soluble methylcellulose (MC) samples were synthesized by a new homogeneous reaction using DMAc/LiCl as solvent, a dimsyl sodium solution as activator and $CH_3\cdot$ as alkylating reagent. Different degrees of substitution were obtained ($0.9 < \overline{DS} < 2.2$). A commercial MC ($\overline{DS} = 1.7$) was also studied. The structural characterization of the samples was carried out using ^{13}C-NMR and h.p.l.c. measurements. Rheological and steric exclusion chromatography studies in the dilute regime were performed as a function of the temperature and the properties of the samples were compared. According to the $\overline{DS}$ value, two different behaviours were observed. For $\overline{DS} > 1.5$, interactions occur for $T > 45°C$. If $\overline{DS} < 1.5$ there is no clear evidence for aggregation. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Cellulose is the most important natural polymer from renewable sources, so it is important to develop its use as an alternative to natural polymers. This polysaccharide is insoluble in most organic and inorganic solvents which reduces its range of applications. To overcome this problem of low solubility and, therefore, to extend its application, a large number of cellulosic derivatives have been investigated.

Due to the initial insolubility of cellulose, the chemical modifications are generally conducted under heterogeneous conditions. This results in a heterogeneous distribution of substituents along the polymeric chain. A blockwise distribution of the substituents and corresponding irregular properties are obtained, for example, the formation of a fraction of gel-like material on dissolution.

For these reasons, we are investigating different methods of preparing cellulosic derivatives under homogeneous conditions in order to obtain products with homogeneous chemical structures, which have properties that are independent of the origin of the initial cellulose (morphology and chain packing). For such homogeneous derivatives, the physical properties should be predicted more directly and related only to the nature of substituent, average degree of substitution ($\overline{DS}$) and molecular weight distribution.

Cellulose ethers are widely used as thickeners within the food and other industries. Aqueous solutions of methylcellulose are known to form a gel, upon heating. The mechanism of gelation is discussed in the literature, but no definitive interpretation has yet been proposed. The more recent published studies proposing a mechanism suggest a partial dissociation and subsequent aggregation of cellulosic bundles present in the dispersion state at low temperature (Haque & Morris, 1993). The kinetics of thermal gelation and hydration properties of methylcellulose were also reported (Sarkar, 1995).

Our purpose is to underline the role of the chemical structure on the physical properties of MC (to lead to a better understanding of the gelation mechanism). This paper concerns the preparation of methylcellulose (MC) with different $\overline{DS}$ using cellulosic solution in the direct solvent DMAc/LiCl (McCormick & Lichatowich, 1979) for alkylation. The characteristics and physical properties of these derivatives, in aqueous dilute solution, are compared with that of commercial samples.

MATERIALS AND METHODS

Methylcellulose samples used in this study were either commercial samples (Methocel A4C from the Dow Chemical Company) or samples prepared in our laboratory according to an original procedure based on a method for methylation previously proposed (Hakomori, 1964). The characteristics of these samples will be discussed later. All the MC samples obtained and studied are soluble in water at room temperature.

We used two different cellulose samples: a dissolving wood pulp with $\overline{DP}_v = 1300$ (called cellulose A) and a cellulose Avicel PH-101 provided by Fluka with $\overline{DP}_v = 130$ (called cellulose B).

The solvents used for the synthesis (*N,N*-dimethylacetamide (DMAc) from Aldrich; dimethylsulfoxide (DMSO) from Fluka) were dried over a dessicant (respectively, BaO and CaH_2) and distilled before use. Lithium chloride (Sigma) was dried at 100°C for 24 h before use. Iodomethane (Fluka) was used without further purification.

Synthesis

The cellulose dissolution consists of a swelling procedure followed by solvent exchange. All the quantities given in these paragraphs are examples and the exact conditions for each methylcellulose prepared are given in Table 1. Cellulose (6 g) was stirred with water (200 ml) for 30 min and centrifuged at 9000 *g* for 15 min. The supernatant was then discarded. The same procedure was repeated twice with DMAc. The cellulose after the last solvent-exchange was dissolved in a solution of DMAc (600 ml) containing 6 wt.% LiCl. The mixture was stirred overnight at room temperature until a clear solution was obtained.

The preparation of the dimsyl sodium solution was conducted as follows: the sodium hydride (NaH) was cleaned, i.e. the powder (20 g) was washed thorougly with hexane under a nitrogen atmosphere. After 15 min, the stirred suspension was allowed to settle and the supernatant was discarded. The same operation was conducted at least five times. Then, distilled DMSO (100 ml) was added and the solution was stirred at 50–60°C until the end of gaseous emission.

The dimsyl sodium solution was added to the cellulose solution and the mixture was stirred at ambient temperature for one night. The solution became white in colour. This cannot be considered to be a precipitation of the cellulose. The polymer was so swollen and dispersed that its state was similar to a homogeneous cellulose solution. After cooling the cellulose solution to 10°C, iodomethane (30 ml) was added and the mixture was stirred at room temperature for different times (from 8 h to 5 days) to reach different substitution degrees. Then, we added a small quantity of acetic acid to neutralize and a small quantity of water to decrease the ionic strength. The mixture was dialysed against water (using a cellulose membrane Spectra/Por from Bioblock with a molecular weight cut-off of 12–14 000) and ultrafiltered (membrane Minitan 4/PK 10 000 NMWL, low binding regenerated cellulose from Millipore) to get a salt-free solution. A colourless solution was obtained and freeze dried. Methylcellulose (MC) samples were recovered with a yield of about 70% based on the initial dried weight of cellulose.

Determination of the degree of substitution ($\overline{DS}$) of the MC

^{13}C-NMR measurements were performed on a Brucker AC 300 spectrometer at 353 K using DMSO-d_6 as solvent. The peak signals (Fig. 1) were attributed based on the assignments by Parfondy & Perlin (1977) and studies of Takahashi *et al.* (1986). The relative DS value at an invidual hydroxyl group was estimated from the ratio between peak areas.

Total hydrolysis of MC was carried out with 2 N trifluoroacetic acid for 4 h at 120°C. After evaporation of the acid *in vacuo*, water was distilled from the samples 10 times to remove traces of the acid before h.p.l.c. chromatography.

H.p.l.c. analysis was performed with a Waters-Millipore chromatograph equipped with a differential refractometer detector (Waters 410). A reversed-phase column Nucleosil C18 5 μm (250*4.6 mm), with water as eluent, at ambient temperature was used. The elution profile (Fig. 2) allows the separation and quantification of the methylated sugars produced by hydrolysis (unsubstituted, mono-, di- or tri-substituted sugars). The determination of both the average degree of substitution and the substitution pattern of MC are possible, according to the assignments given in the

Table 1. Experimental conditions for the synthesis of methylcellulose samples using the homogeneous procedure

Samples	Cellulose	Ratio[a] cell:DMAc	Anion[a] NaH:DMSO	Duration of the synthesis	$\overline{DS}$[b]
M10	A	6:700	20:100	8 h	0.9
M12	A	7.5:720	20:100	18 h	1.5
M14	A	6:550	15:50	7 h	1.2
M18	A	6:700[c]	10:50	7 days	2.2
M20	A	6:600	20:100	5 days	1.4
M22	B	10:600	20:100	24 h	1.0
M23	B	10:600	20:100	7 days	1.2

[a] Quantity of product in gram.
[b] Determination by ^{13}C-NMR measurements.
[c] Cellulose in DMAc/LiCl kept 1 month at 5°C.

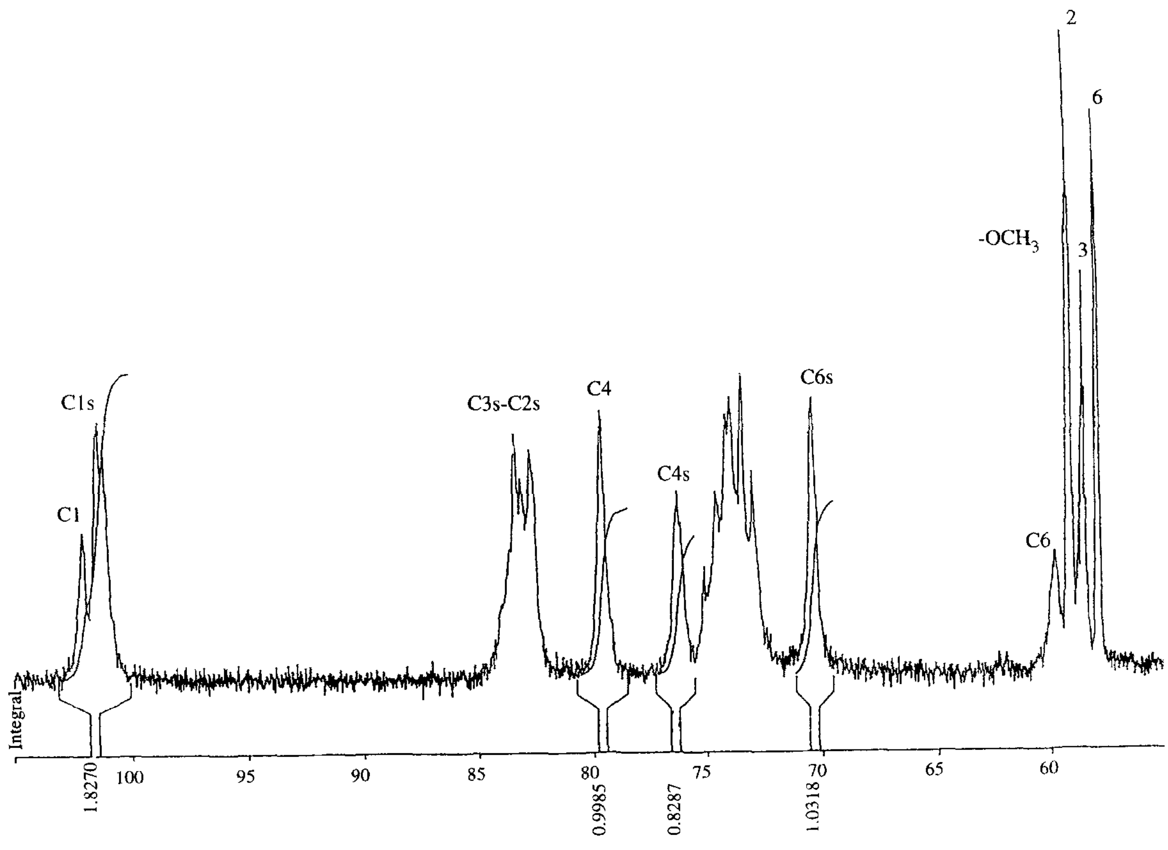

Fig. 1. ^{13}C-NMR spectrum recorded at 80°C of a 3% w/v solution of A4C in DMSO-d_6.

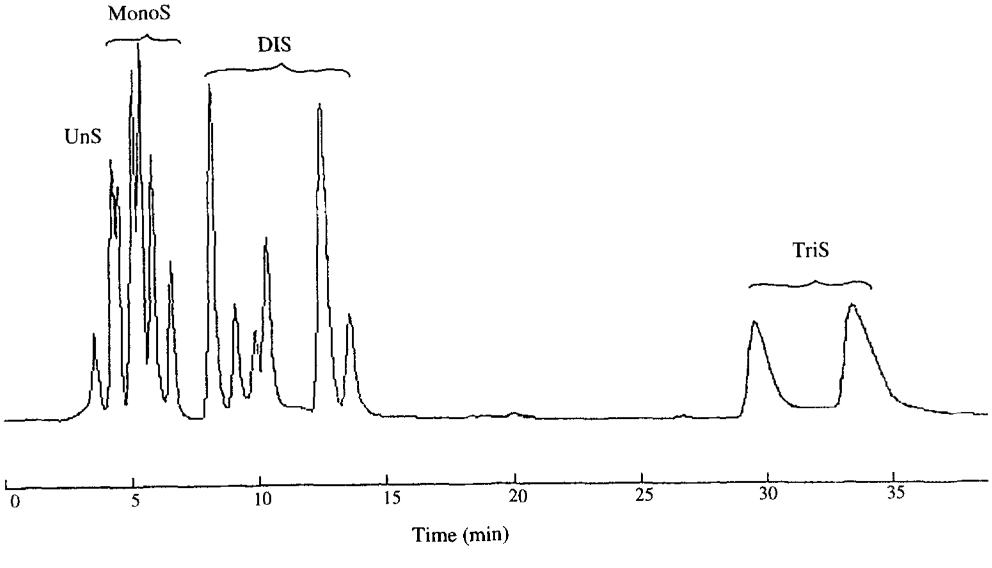

Fig. 2. H.p.l.c. analysis of a methylcellulose sample (A4C) after total hydrolysis on a reversed-phase column. Eluent: water; flow gradient: 0.6 ml/min.

literature (Heyraud & Salemis, 1982; Erler *et al.*, 1992).

Solubilization of methylcelluloses

MC used in the freeze-dried form is dissolved in water at 5°C for 24 h to assure complete solubilization.

Steric exclusion chromatography (SEC) studies

The determination of the molecular weight distribution, the average molecular weights and the intrinsic viscosity were carried out at controlled temperatures (between 30 and 55°C) on MC solutions in free water by SEC using the multidetection equipment described previously

(Tinland *et al.*, 1988). For each temperature, the calibration of the detector and the diode normalization of the apparatus were made using toluene and a solution of polyethyleneglycol as a standard polymer. The refractive index increment d*n*/d*c* for the MC was measured using a differential refractometer and was found to be equal to 0.136 ml/g in water. This value is consistent with the value recently given in the literature (Nilsson *et al.*, 1995). Water is the eluent used and the experiments were performed on grafted silica gel columns (Shodex OHpak B-804, B-805). Our equipment allows the determination of the molecular weight distribution without any calibration.

Rheological studies

Viscosity measurements were performed at different temperatures (from 20 to 50°C) using a Contraves Low Shear 30 viscometer, a capillary viscometer Fica Viscomatic MS or a CS 50 rheometer (Carri-Med) equipped with a Rheo 1000 C system. The choice of the viscometer depends on the solution concentration. In the semi-dilute regime, where the polymeric concentration is higher than the overlap concentration, rheological measurements as a function of shear rate and temperature were made using cone-and-plate geometry (4 or 6 cm diameters, 4° cone angle).

The specific viscosity η_{sp} is taken over on the Newtonian plateau and $[\eta]$ (in ml/g) is the intrinsic viscosity obtained by extrapolation of the reduced viscosity for zero concentration and zero shear rate.

RESULTS AND DISCUSSION

Synthesis

Usually the preparation of cellulose derivatives involves a heterogeneous reaction in which the cellulose remains insoluble in the reaction mixture. The obvious advantage of a solvent such as DMAc/LiCl for the synthesis of cellulose derivatives lies in the ability to conduct a variety of reactions under mild conditions (McCormick & Callais, 1987). Moreover, such a homogeneous procedure ensures a more uniform distribution of the substituents due to greater accessibility of the –OH sites.

Etherification needs to be conducted under basic conditions. As sodium or potassium hydroxide, which are typically used in the industrial process of methylation, were not very soluble in DMAc/LiCl solutions, we used highly reactive dimsyl sodium (sodium methylsulfinylmethylide). Recently a homogeneous alkylation process was proposed using DMSO/LiCl solvent and dimsyl sodium activation (Petrus *et al.*, 1995). The solvent used in our work has the advantage of dissolving cellulose in a better way and affords solutions with much higher cellulose concentrations.

Several samples of MC (all soluble in water) were obtained using different parameters: liquor ratio (ratio of the cellulose to DMAc, w/w), quantity of activator (dimsyl sodium) or alkylating agent (methyliodide) and duration of reaction (Table 1). We did not systematically study the influence of these parameters on the methylcellulose finally obtained.

As the alkylating agent was always in excess, the effect of time on the value of the degree of substitution was underlined. Indeed, $\overline{DS}$ increases when time increases. For example, in the same synthesis, a sample of MC with $\overline{DS} = 1.1$ is achieved within a period of 8 h and a sample of MC with $\overline{DS} = 1.6$ after 24 h.

We refer to our samples by the code Mi, where i is the reaction reference in the synthesis series. The commercial one is called A4C according to the supplier.

Structural characterization of the samples

The characteristics of the MC are compared to that of the commercial sample A4C in Table 2. Concerning the distribution of the substituted sugars (glucose units, mono-, di- or tri-substituted units), a large number of samples, including the commercial ones, have the same proportion of unsubstituted sugars (10%). The hydrolysis conditions are suitable for methylcelluloses and we verified that it was complete. For the moment, we cannot interpret this result. In our products the yield of the monosubstituted sugars widely predominate (60–70%). The distribution of the sugars along the chain will, therefore, be more homogeneous.

With increasing degrees of substitution, the solubility

Table 2. Some characteristics of methylcellulose samples

Samples	%UnS[a]	%MonoS[b]	%DiS[c]	%TriS[d]	$\overline{DS}$[e]	$[\eta]$[f]	$\overline{Mv}$[g]
A4C	10	29	39	22	1.7	509*	149 000
M12	5	51	29	15	1.5	250**	—
M18	9	12	36	43	2.2	339**	—
M22	9	6	19**	4	1.0	153**	

[a–d] Number fraction (%) of unsubstituted, mono-, di- or tri-substituted sugars, respectively (as determined by h.p.l.c.).

[e] Determination by ^{13}C-NMR measurements.

[f] In ml/g in water at 20°C (*) or 30°C (**).

[g] Calculated from the Mark–Houwink relation in water at 20°C.

of the cellulose ethers passes through various stages depending on the polarity of substituents. In the case of commercial methylcellulose, the solubility in cold water is generally obtained for $\overline{DS}$ varying from 1.3 to 2.6. It is well-known that the range of $\overline{DS}$ values of water-soluble methylcelluloses depends strongly on the preparation conditions (Bock, 1937; Abe *et al.*, 1955). We have here some more evidence for this. We obtained a sample perfectly soluble in water with a $\overline{DS}$ as low as 0.9, which is not possible under heterogeneous reaction conditions.

Other characteristic data were reported in Table 2. Using the Mark–Houwink relation for MC in water at 20°C (Uda & Meyerhoff, 1961), the viscometric average molecular weight can be estimated according to the relation:

$$[\eta](\text{ml/g}) = 0.28\,\overline{M_v}^{\,0.63} \qquad (1)$$

Physico–chemical properties

It is well-known that methylcelluloses possess unusual solubility properties in aqueous media. The polymer is insoluble in water when the solution is heated above a particular temperature. Below this temperature, the solvation and the solubility of the polymer increase as the temperature is lowered. Then, semi-dilute solutions of MC will thermally gel when heated to a specific temperature. This gelation phenomenon is reversible on cooling. Some reports (Neely, 1963; Sarkar, 1979) indicate that an aggregation of the polymer takes place in solution. Here, we have further and more precise evidence of this fact. Our studies on MC synthesized in our laboratory reveal that a sol–gel transition can be shown even by MC samples prepared by homogeneous reaction (Vigouret *et al.*, 1996), in disagreement with other authors (Takahashi *et al.*, 1987; Savage, 1957).

For a polymeric solution, it is possible to define three domains of concentration (c): dilute, semi-dilute or concentrated solution. The concentration c^* separates the dilute and the semi-dilute regimes. It corresponds to the limit for overlapping of the polymeric chains.

Using viscosity measurements, we can approximate the value of c^* as the critical concentration above which the reduced viscosity deviates from the Huggins relationship.

Generally, it is assumed that a direct relation between the specific viscosity η_{sp} and the overlap parameter $c[\eta]$ exists (Kulicke & Kniewske, 1984) as:

$$\eta_{sp} = C[\eta] + k'(C[\eta])^2 + B(c[\eta])^n \qquad (2)$$

when the viscosities at zero shear rate are considered. In this relation, k' is the Huggins constant.

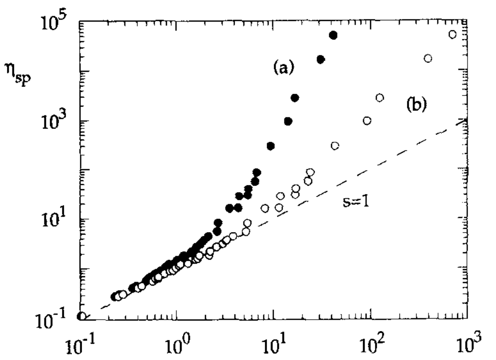

Fig. 3. Specific viscosity as a function of the overlap parameter (a) ●: $c[\eta]$ and (b) ○: $c[\eta]+k'(c[\eta])^2$ for A4C at 20°C in water.

For the commercial methylcellulose A4C in water at 20°C, the graphs η_{sp} vs $c[\eta]$ and η_{sp} vs $c[\eta]+k'(c[\eta])^2$, respectively, are reported in Fig. 3. The Huggins relation is followed by A4C up to $c[\eta]$ around 2.1 as a limit of the dilute domain (linear part of curve (b), with a slope equal to 1). This value is in the same range as those usually found for other polysaccharides with relatively low persistence lengths (Ganter *et al.*, 1992). The constants B and n are found equal to $B=0.05$ and $n=3.7$ allowing the viscosity of a solution with given polymer concentration and molecular weight to be predicted. A similar value of n is also usually found for other water-soluble polymers in the absence of intermolecular interactions (Morris *et al.*, 1981).

We studied the evolution of $[\eta]$ and k' as a function of temperature for the different samples—A4C, M18, M12 and M22 (Table 3). For these samples, the intrinsic viscosity decreases as the temperature increases. k' remains almost constant for the MC having the lowest $\overline{DS}$ (M12, M22) while it increases with temperature for the others. Moreover, k' increases as $\overline{DS}$ increases. As mentioned by many authors (Dort, 1988; Flory, 1953) and confirmed by experimental works (Chee, 1979; Seefried *et al.*, 1980), the Huggins constant is independent of the molecular weight of the macromolecule. Its value is influenced by the quality of the solvent (Howard *et al.*, 1972) or interactions between polymeric chains (Sakurai *et al.*, 1993; McCormick *et al.*, 1988; Magny *et al.*, 1991). In particular it is very sensitive to

Table 3. The intrinsic viscosity $[\eta]$ and the Huggins constant k' of aqueous MC solutions as a function of temperature T

MC	M22$\overline{DS}=1.0$			M12$\overline{DS}=1.5$			A4C$\overline{DS}=1.7$			M18$\overline{DS}=2.2$		
T(°C)	30	40	50	30	40	50	30	40	50	30	40	50
$[\eta]$ (ml/g)	153	140	131	250	23	209	448	386	338	339	285	—
k'	0.45	0.51	0.45	0.54	0.56	0.54	0.58	0.66	0.75	0.61	0.77	—

the presence of supermolecular structures. The decrease in intrinsic viscosity means a decrease of the hydrodynamic volume of the macromolecular chain and the increase in k' indicates the formation of aggregates. A method was proposed to evaluate the polymer associations able to exist from the Huggins viscosity constant (Dort, 1988). In associating systems the Huggins constant k' is the sum of a 'natural' value and an 'additional' k_a value. k_a is considered as a contribution expressing the extent of association in a given polymer–solvent system. To determine the extent of association, it is proposed to relate the Huggins constant calculated from the Martin–Staudinger–Heuer relationship (MSH)

$$\ln\frac{\eta-\eta_0}{\eta_0 c} = \ln[\eta]_{\mathrm{MSH}} + k_{\mathrm{MSH}}[\eta]_{\mathrm{MSH}}C \qquad (3)$$

and the value K'_{HE} from Heller's viscosity equation (HE):

$$0.5\left[\left(\frac{\eta-\eta_0}{\eta_0 c}\right)^{-1}+\left(\frac{1}{c}\ln\frac{\eta}{\eta_0}\right)^{-1}\right]=\frac{1}{[\eta]_{\mathrm{HE}}}-K'_{\mathrm{HE}}c \qquad (4)$$

According to theoretical conclusions (Sakai, 1968), k_{MSH} is in good agreement with k' determined in poor solvents and is equally applicable for good solvents. Non-associating systems will be described by the equation:

$$k_{\mathrm{MSH}} = \alpha + \beta K'_{\mathrm{HE}} \qquad (5)$$

and associating systems by a quadratic function;

$$k_{\mathrm{MSH}} = \alpha + \beta K'_{\mathrm{HE}} + \gamma (K'_{\mathrm{HE}})^2 \qquad (6)$$

Values of the constants α and β are not molecular-weight-dependent. The value of γ is the measure of the ability of a polymer to associate in solution.

When the experimental data are considered, it is found for methylcelluloses (Fig. 4): $\alpha=0.26$, $\beta=1.14$, $\gamma=0.20$, in good agreement with data obtained with polystyrene and polyurethane samples (Dort, 1988).

For low K'_{HE}, a straight line may be assumed meaning the absence of strong interactions, but as the temperature is equal to 50°C the experimental data is not linear and fits the quadratic function. This indicates the presence of interactions above a certain temperature even for low concentration solutions, as will be confirmed later.

We reported the specific viscosities values for the four samples at 20, 30, 40 and 50°C as a function of the overlap parameter (Fig. 5). The polymer concentration varies from 0.5 to 60 g/l. In the dilute regime, no dependence on methylcellulose type or temperature was found. A unique curve seems to be obtained for all the samples and all temperatures due to the small influence of k'. Some deviations appeared above 40°C for the more concentrated solutions, more especially for the sample M18 (which has the highest $\overline{\mathrm{DS}}$ and is the more aggregated polymer). These deviations suggest the presence of interactions reflected by the variation of k' as previously discussed.

SEC studies

Aqueous solutions of methylcelluloses (commercial and synthesized) in dilute regime have been studied by SEC at different temperatures, from 30 to 55°C. The polymer concentration injected was around 1.5 g/l. All samples were subjected to SEC, only certain results are displayed in Fig. 6 because they are the most representative (other samples gave the same type of result).

The refractive index curve, which is proportional to the concentration, exhibits, for all samples, several peaks. This reflects the presence of different populations of molecules in solution. In general, there are four

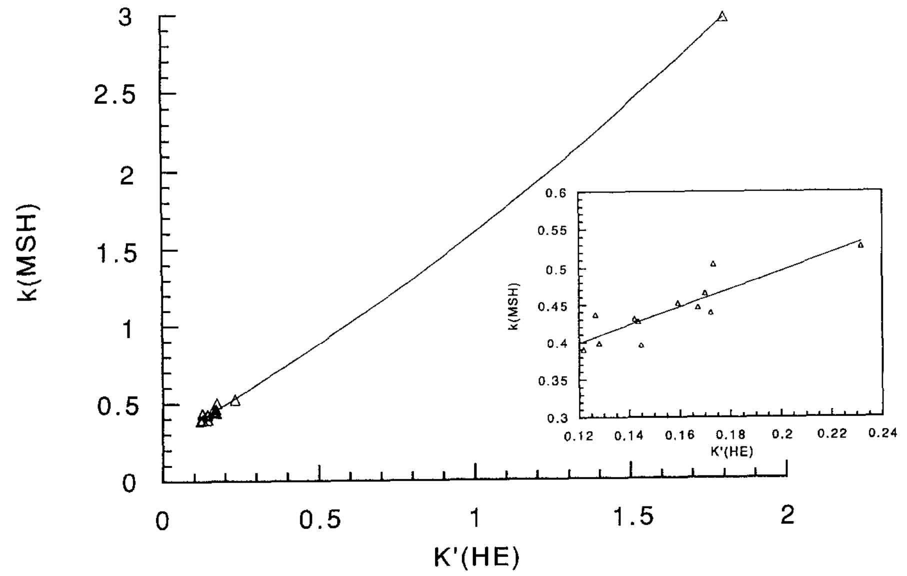

Fig. 4. Evolution of k_{MSH} as a function of K'_{HE} for MC samples at different temperatures.

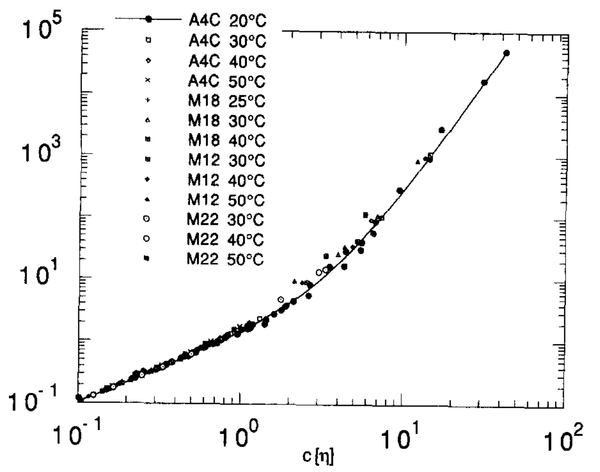

Fig. 5. Specific viscosity as a function of $c[\eta]$ for A4C (DS = 1.7), M18 ($\overline{DS}$ = 2.2), M12 ($\overline{DS}$ = 1.5) and M22 ($\overline{DS}$ = 1) in water for different temperatures (from 20 to 50°C).

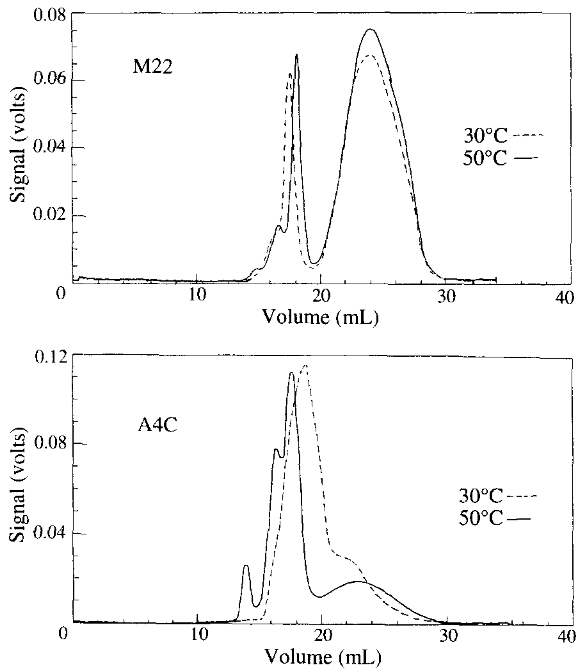

Fig. 6. Evolution of the elution refractive index signal at 30 and 50°C for M22 ($\overline{DS}$ = 1) and A4C ($\overline{DS}$ = 1.7).

peaks, but in certain cases some additional peaks can be observed (Fig. 6). Peak **1**, at the largest elution volume (around 23 ml), is present whatever the samples considered and seems to correspond to isolated chains.

We studied the evolution of these peaks as a function of the temperature. In Fig. 7, the elution volume corresponding to each peak is plotted as a function of the temperature. Two different behaviours depending on the $\overline{DS}$ range can be observed. For the samples with $\overline{DS} < 1.5$ (Fig. 7a–c), firstly the molecules corresponding to peak **1** are always present, whatever the temperature is. The position of the other peaks is slightly temperature-dependent (in general, the elution volume decreases as the temperature increases). For the samples with $\overline{DS} > 1.5$ (Fig. 7d–f), the elution volume value of peak **1** (single chains) increases above 45°C (the hydrodynamic volume decreases due to the compaction of single chains). For the other peaks the elution volume value decreases significantly with temperature, corresponding to an increase in the hydrodynamic volume with aggregation.

In Fig. 8, we plotted the weight fraction corresponding to each peak for one temperature (the sum of the values of each column bar for one temperature is equal to 100%). Two samples (M22 and M23) which are not shown, present a really different behaviour from the others. They were synthesized using the cellulose Avicel as a starting material. These methylcelluloses are more homogeneous than the others in terms of the number of populations. The two behaviours mentioned in the previous paragraph are observable. For A4C, for example, the concentration corresponding to peak **a** (larger hydrodynamic volume) increases with temperature. These peaks can consequently be attributed to a population of aggregates that grows above 45°C.

Each sample was filtered before the experiments and maintained at the chosen temperature for one night. The quantity of the polymer eluted through the SEC columns is, indeed, a good indication of the formation (or not) of aggregates retained on the filter when the temperature increases. The mass injected (Mi)/mass calculated (Mc) ratio was calculated and plotted vs temperature (Fig. 9). The mass calculated is obtained from the area of the refractive index peak and the refractive index increment dn/dc.

At a temperature around 40°C, the values of Mi/Mc for some samples pass through a minimum. A similar minimum was observed by other authors in the elastic modulus G', turbidity and detectable high-resolution NMR signal (Haque & Morris, 1993).

Two behaviours were obtained depending on $\overline{DS}$ values. For $\overline{DS} < 1.5$, the Mi/Mc ratio does not vary significantly while for M12, A4C and M18 ($\overline{DS} > 1.5$), the ratio increases in a significant way above 45°C. This confirms clearly the formation of aggregates for these samples ($\overline{DS} > 1.5$) when the temperature reaches 45°C.

CONCLUSION

In this paper, we have presented studies on methylcelluloses with different degree of substitution values synthesized by a heterogeneous method (commercial sample) and in homogeneous way (laboratory-made samples).

The samples were characterized and studied in aqueous solution in the dilute regime at different temperatures.

With the rheological experiments, we observed at 20°C the behaviour of a water-soluble polymer without intermolecular interactions. According to the $\overline{DS}$ value, when $\overline{DS} > 1.5$, interactions occur for $T > 45$°C, but

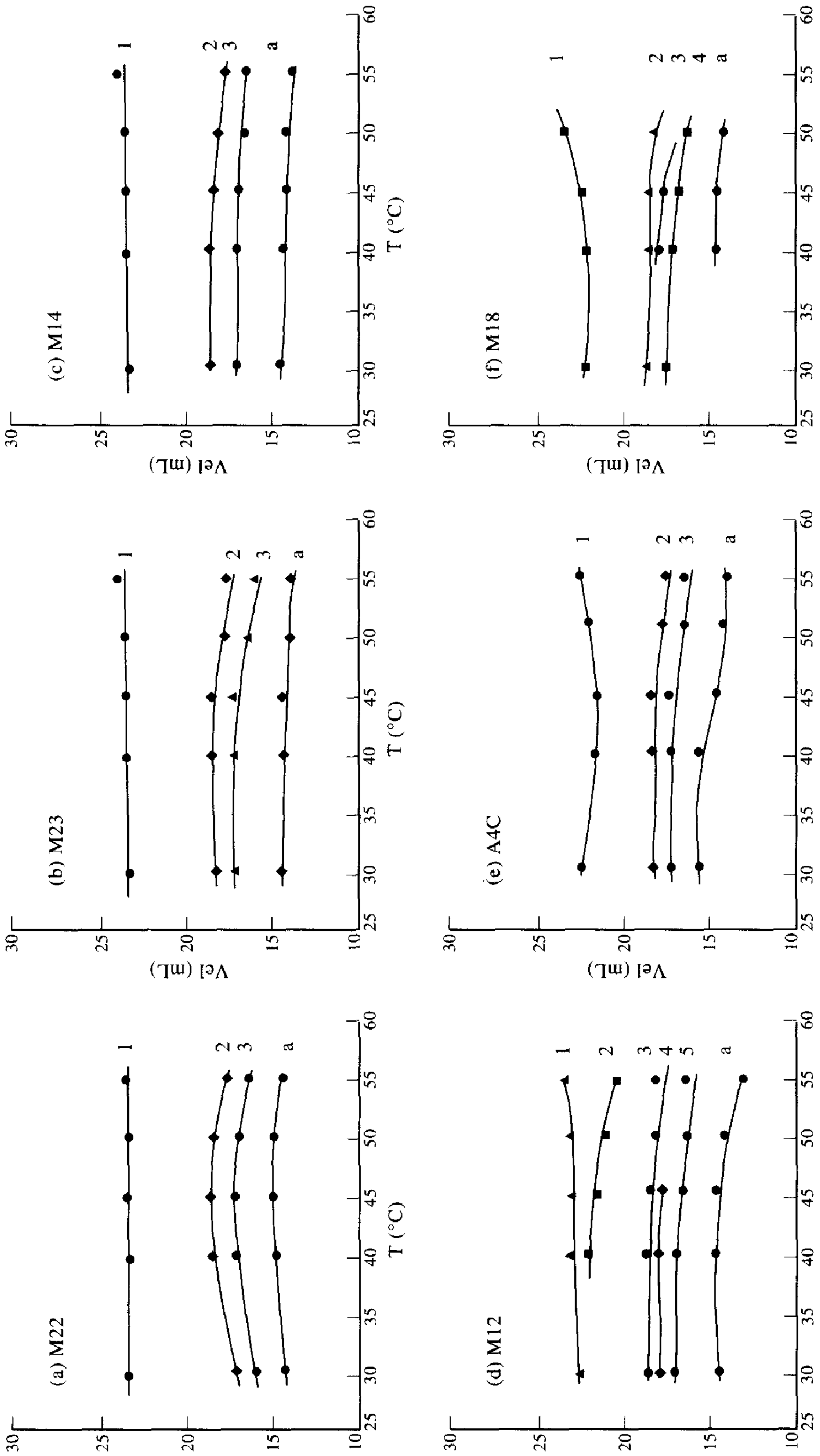

Fig. 7. Evolution of the elution volume value for each peak as a function of temperature for: (a) M22; (b) M23; (c) M14; (d) M12; (e) A4C; and (f) M18.

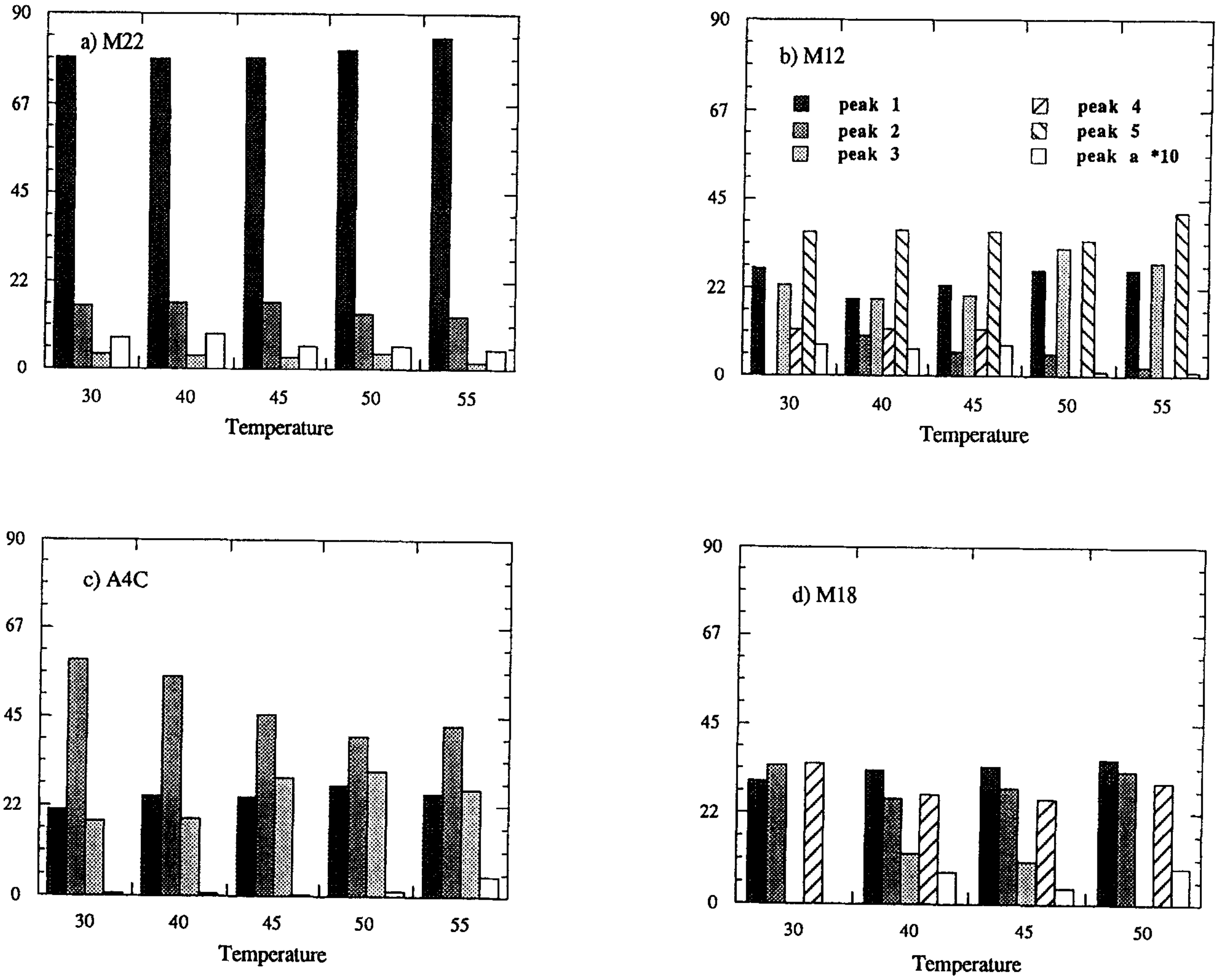

Fig. 8. Evolution of the weight fraction corresponding to each peak as a function of temperature for: (a) M22; (b) M12; (c) A4C; and (d) M18.

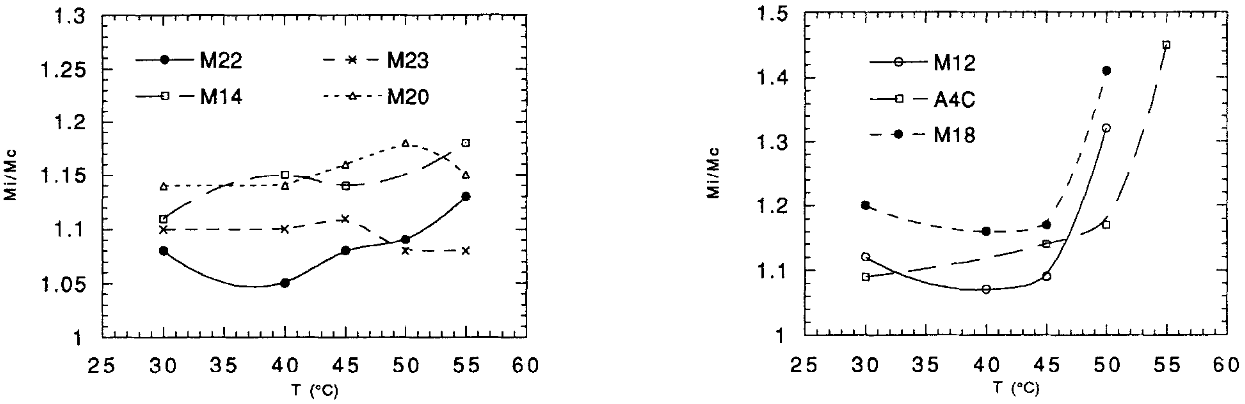

Fig. 9. Evolution of the ratio mass injected (*M*i)/mass calculated (*M*c) as a function of temperature for MC samples.

when $\overline{\mathrm{DS}} < 1.5$, there is no evidence for further association. This aggregation is confirmed from SEC experiments.

From these data, it is clearly demonstrated that the structure of MC, and especially the $\overline{\mathrm{DS}}$ value, has a great influence on its physical properties in aqueous solution, even at low polymeric concentration.

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