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A Study of the Viscosity of Cellulose Derivatives in Aqueous Solutions

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SUMMARY

The flow behaviour of two types of cellulose derivatives (carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC)) in aqueous solution was investigated at 25°C, pH 7·0 and 0·1 M *(NaCl) ionic strength, within a wide concentration range (0·05–20 g litre*$^{-1}$*) using two coaxial cylinder viscometers covering shear rate range 0·01–700 s*$^{-1}$*.*

Each flow curve was characterized by the limiting viscosity at zero shear rate (η_0) *and, above a critical concentration* c_s*, by a relaxation time* (τ) *corresponding to the shear rate above which the apparent viscosity became shear rate dependent (shear-thinning behaviour).*

Variations of the specific viscosity at zero shear rate, η_{sp0}*, as a function of* $c[\eta]$ *led to typical curves as for other polysaccharides. The curves for two CMC samples differing in their molecular weights closely superimposed and were in agreement with the relationships previously found for alginate and* λ*-carrageenan, while data for HEC gave a different curve. Each of these curves exhibited two critical concentrations,* c^* *and* c^{**}*, the significance of which is discussed.*

A master flow curve could be obtained for each polysaccharide using the reduced coordinates $\eta_r = \eta/\eta_0$ *and* $\dot{\gamma}_r = \tau \times \dot{\gamma}$ *and described by a reduced Soong and Shen model with two parameters.*

The relaxation time τ *was shown to vary as* $c^{4\cdot3-4\cdot4}$ *for* $c > c_e$*,* c_e *being intermediate between* c^* *and* c^{**}*.*

INTRODUCTION

Polysaccharides are natural components of many food systems or are added in processed foods to play an important role due to their thickening or gelling properties. When compared with synthetic polymers,

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solutions of these polysaccharides give high viscosities at relatively low concentrations (0·1–1·0%). Such thickening properties of these natural polymers or their derivatives are very useful in controlling the texture of foodstuffs, and rheological studies of polysaccharide solutions are of importance for estimating and understanding on a molecular basis the function of these components in food systems. Moreover, such characteristic rheological properties are of interest in many other industrial areas and a further development of the utilization of these polymers may be expected from these studies.

For a wide range of polysaccharides in random coil conformation, with the exception of galactomannans, low shear viscosity data can be superimposed on a single log η_{sp0}–log $c[\eta]$ relationship (Morris *et al.*, 1981): below and above a critical concentration ($c^* \sim 4/[\eta]$), the specific viscosity at zero shear rate η_{sp0} is generally found to be linearly related to $c[\eta]$, the slopes of the two linear segments being about 1·4 and 3·3, respectively. For galactomannan solutions, the critical concentration (c^*) was $2{\cdot}6/[\eta]$ and the slopes were 1·4 and 4, respectively. Furthermore, almost all concentrated polysaccharide solutions are shear-thinning, and Morris *et al.* (1981) observed the same shear-thinning profile for different polysaccharides, irrespective of concentration, molecular weight, solvent environment and chemical type. This is interpreted as reflecting the existence of non-specific physical entanglements in the polysaccharide solutions, the rearrangement of the entangled structure due to the applied deformation being similar for all the polysaccharides. The authors noted that the similar non-Newtonian behaviour would probably be partly due to the polydispersity of commercial polysaccharides, as has been suggested by Graessley (1974) for polymer solutions and melts.

The aim of the present investigation is to examine the role, if any, of the substituent groups on the flow behaviour of two types of cellulose derivatives: an anionic derivative (carboxymethylcellulose, CMC) and a neutral one (hydroxyethylcellulose, HEC). Studies were made in aqueous solutions at neutral pH (pH 7·0) and 0·1 M NaCl ionic strength.

EXPERIMENTAL

Materials

Two CMC samples were supplied by Hercules SA, France (CMC 7LXF and CMC 9M65). Their degrees of substitution (*DS*) as determined by the I-acid colorimetric method (Roushdi *et al.*, 1982) were 0·71 and 0·80, respectively.

An HEC sample ('medium viscosity' lot 128-8) was obtained from Polysciences, UK.

Molecular characteristics determined for these polysaccharides are collected in Table 1 (Castelain, 1985). The viscosity average molecular weights ($\bar{M}_v$) were determined by using the Mark-Houwink relationships proposed by Gelman (1982) for CMC:

$$[\eta] = 2{\cdot}0(\bar{M}_v/\bar{M}_0)^{0{\cdot}78} \text{ at } 25°\text{C in } 0{\cdot}1 \text{ M NaCl}$$

and by Kamide and Miyazaki (1978) for HEC:

$$[\eta] = 7{\cdot}4 \times 10^{-3}(\bar{M}_v)^{0{\cdot}89} \text{ at } 25°\text{C in water (for } MS \sim 1)$$

where $\bar{M}_0$ is the average molecular weight of the monomer unit and MS is the molar substitution degree of the HEC, the intrinsic viscosity being expressed in ml g^{-1}.

Methods

Preparation of polysaccharide solution

In order to control exactly the sodium content of CMC solutions, they were first converted into the acidic form: the CMC powder was added to

TABLE 1

Molecular Characteristics of CMC and HEC and Experimental Values of the Different Critical Concentrations

	CMC 7LXF	*CMC 9M65*	*HEC*
Intrinsic viscosity, $[\eta]$	288·6 ml g^{-1}	1 212·95 ml g^{-1}	807·1 ml g^{-1}
Viscometric average molecular weight, $\bar{M}_v$	119 200	771 000	457 400
Substitution degree:			
DS	0·71	0·80	
MS			1·61
Average molecular weight of the monomer unit:			
$M_0 = 162 + DS \times 58$	203·3 g	208·6 g	
$M_0 = 162 + MS \times 44$			232·6 g
Experimental critical concentrations:			
c_s	—[a]	0·7–0·9 g litre^{-1}	about 1 g litre^{-1}
c^*	4·85 g litre^{-1}	1·15 g litre^{-1}	0·70 g litre^{-1}
c^{**}	18·02 g litre^{-1}	4·29 g litre^{-1}	6·44 g litre^{-1}
c_e	—[a]	2·80 g litre^{-1}	4·09 g litre^{-1}

[a] Values cannot be determined as CMC 7LXF solutions are Newtonian.

distilled water at 20°C with vigorous stirring and the cations were removed with an acidic resin (Amberlite IRN 177). The pH was then adjusted to 7·0 by addition of 1 M NaOH, and the ionic strength to 0·1 M with NaCl solution, taking into account the ionic strength of CMC. The ionic strength 0·1 M was chosen in order to screen the intramolecular electrostatic repulsions, and thus to limit the chain expansion due to polyelectrolyte effects in CMC solutions; further dilutions were performed with NaCl solutions according to the isoionic dilution principle (Pals & Hermans, 1952).

HEC solutions were prepared by adding HEC to 0·1 M NaCl solution at 20°C with vigorous stirring.

Viscometry

Viscosity measurements were performed at 25 ± 0·02°C using two coaxial cylinder viscometers: Rheomat 30 and Low Shear 30 (Contraves). The Low Shear 30 was used with standard coaxial cylinders ($r_1 = 5{\cdot}5$ mm, $r_2 = 6{\cdot}0$ mm, $h = 8{\cdot}0$ mm) over the shear rate range of 0·017–128 s^{-1}. The Rheomat 30 was used with the A measuring system ($r_1 = 22{\cdot}9$ mm, $r_2 = 24{\cdot}2$ mm, $h = 56{\cdot}5$ mm) within the shear rate range 0·09–662 s^{-1}. Due to the small gap between the two cylinders ($r_1/r_2 = 0{\cdot}92$ and 0·95, respectively), shear rate corrections for non-Newtonian behaviour were neglected.

The flow behaviour was investigated over a wide range of concentrations (0·05–20 g $litre^{-1}$). Measurements were performed stepwise: the solution was initially sheared at the highest shear rate ($\dot{\gamma}$), then the shear rate was decreased stepwise and the shear stress (σ) was measured at each of these steps. Whatever the shear rate and the concentration of the solutions, no thixotropic behaviour was observed.

RESULTS AND DISCUSSION

Description of flow curves

A typical set of flow curves (log η_{ap} plotted against log $\dot{\gamma}$) obtained for HEC solutions at different concentrations is shown in Fig. 1. For the more concentrated solutions ($c > 2{\cdot}8$ g $litre^{-1}$), these curves are the result of a combination of data obtained with the Low Shear 30 and the Rheomat 30 instruments: the Low Shear 30 apparatus only can be employed for the less concentrated solutions.

At low polysaccharide concentrations, Newtonian behaviour is observed. For higher concentrations ($c > c_s$, $c_s = 1{\cdot}0$ g $litre^{-1}$ for HEC), the behaviour becomes shear-thinning with a Newtonian region in the low shear rate range. A comparable set of flow curves was obtained with CMC 9M65 ($c_s = 0{\cdot}7$–$0{\cdot}9$ g litre^{-1}), while CMC 7LF displayed Newtonian behaviour over the whole range of concentrations investigated (0·5–20 g litre^{-1}), probably due to its too low molecular weight.

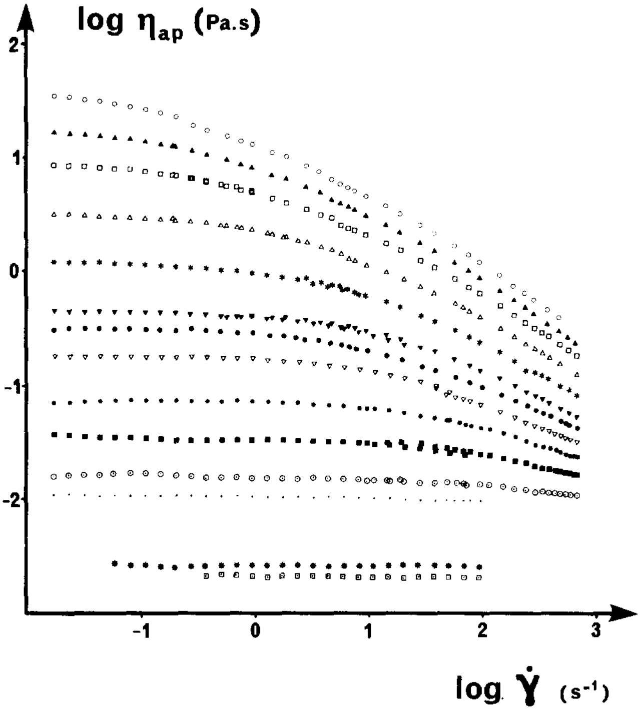

Fig. 1. Flow curves of HEC solutions (from top to bottom) at pH 7·0, 0·1 M ionic strength, $t = 25$°C at different concentrations (g litre^{-1}): (○) 20·6, (▲) 18·0, (□) 15·5, (△) 12·8, (★) 10·3, (▼) 8·25, (●) 7·20, (▽) 6·17, (★) 5·20, (■) 4·11, (⊙) 3·11, (·) 2·54, (★) 1·08, (⊡) 0·83.

The flow curves were characterized by the initial Newtonian viscosity, η_0, and, above the concentration c_s, by a relaxation time τ, $\tau = 1/\dot{\gamma}_c$, $\dot{\gamma}_c$ being the shear rate at which the apparent viscosity becomes shear rate dependent. The influence of the polysaccharide concentration on these parameters has been studied.

Concentration dependence of zero shear rate viscosity

The concentration dependence of the specific viscosity at zero shear rate (η_{sp0}) is shown in Figs 2 and 3 for the three cellulose derivatives and

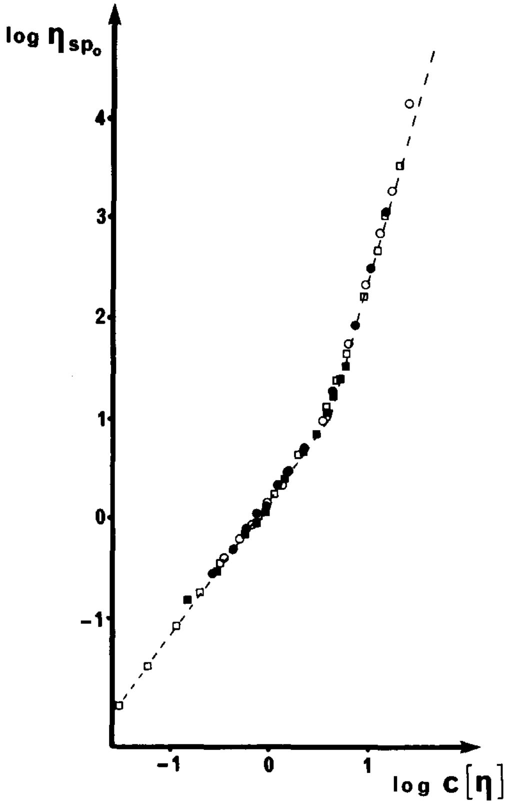

Fig. 2. Specific viscosity at zero shear rate (η_{sp0}) as a function of $c[\eta]$: ■, CMC 7LXF; □, CMC 9M65; (●) sodium alginate and (○) λ-carrageenan from Goncalves (1984); ---, Morris *et al.* (1981) for dextran, carboxymethylamylose, alginates, λ-carrageenan and hyaluronate (pH 7·0, 0·015 M NaCl).

compared with data from other polysaccharides, the concentration being expressed by the dimensionless parameter $c[\eta]$.

In Fig. 2, data obtained for the two CMC samples are reported as well as those obtained by Goncalves (1984) for sodium alginate and λ-carrageenan. The general curve obtained by Morris *et al.* (1981) for dextran, carboxymethyl amylose, a 'high mannuronate' and a 'high guluronate' alginate, λ-carrageenan and hyaluronate (0·015 M NaCl, pH 7·0) is also plotted (dashed lines). It can be seen that the data for the solutions of the two CMC samples are in close agreement with each other and with the data reported by Goncalves (1984). The master curve we obtain by fitting two straight lines to all these superimposed data gives a critical concentration $c^* = 3{\cdot}4/[\eta]$ and two slopes a_1 and a_2 of 1·3 and 3·5, respectively. Experimental values of the reduced critical

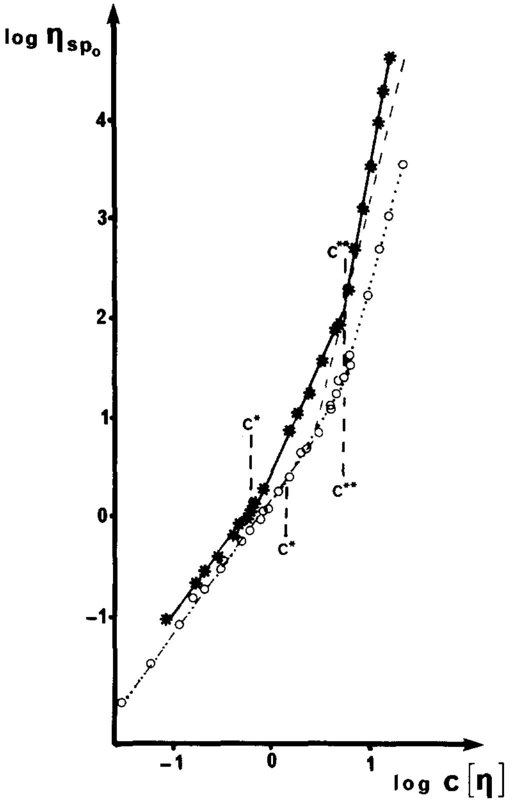

Fig. 3. Specific viscosity at zero shear rate (η_{sp0}) as a function of $c[\eta]$: ○ · · · ○, CMC; ★—★, HEC; - - -, Morris *et al.* (1981) for galactomannans (locust bean and guar gum) and hyaluronate (pH 2·5, 0·15 M NaCl).

concentration $c^*[\eta]$ are generally found to be in the range 2·5–4 (Launay *et al.*, 1986). So, as a first approximation, the present data on anionic polysaccharides seem to conform to the general behaviour of most randomly coiled hydrocolloids with respect to the η_{sp0}–$c[\eta]$ representation.

On close examination of the data from the two CMC samples, an intermediate zone, limited by two critical concentrations, $c^* = 1{\cdot}4/[\eta]$ and $c^{**} = 5{\cdot}2/[\eta]$, can be seen, the three slopes being then $a_1 = 1{\cdot}3$, $a_2 = 1{\cdot}8$ and $a_3 = 3{\cdot}9$, respectively, as shown in Fig. 3. In the same way, an intermediate zone could be found for the data of Morris *et al.* (1981), where c^* and c^{**} would be about $1{\cdot}2/[\eta]$ and $7{\cdot}5/[\eta]$ (Launay *et al.*, 1986).

The existence of three domains appears much more clearly in the case of HEC solutions, as shown in Fig. 3. For this polysaccharide, the critical concentrations are $c^* = 0{\cdot}6/[\eta]$ and $c^{**} = 5{\cdot}2/[\eta]$ and the slopes are $a_1 = 1{\cdot}3$, $a_2 = 2{\cdot}0$ and $a_3 = 5{\cdot}0$. The HEC data do not superimpose with CMC data and are rather closer to the results obtained by Morris *et al.* (1981) for galactomannans (dashed line in Fig. 3). Our experimental values for c^* and c^{**} are reported in Table 1.

Three domains were also reported by Cuvelier & Launay (1986) and Launay *et al.* (1984) in the case of xanthan solutions and, as shown in Table 2, the slopes were roughly similar to our results on CMC: $a_1 = 1{\cdot}3$, $a_2 \simeq 2$ and $a_3 \simeq 4$. For HEC the slope in the third domain is clearly higher (~ 5) than found for the other polysaccharides.

The significance of the two critical concentrations needs to be discussed; it is worth noting that c^* and c^{**} are determined by the intercept of two linear segments corresponding to different regimes of concentration, but the crossing from one domain to the next must be progressive. Let the three domains be called the dilute, the semi-dilute and the concentrated domains.

The existence of two critical concentrations, c^* and c^{**}, is consistent with the concept of progressive compression of the coils with increasing concentration, and one may assume that the first critical concentration, c^*, is related to the onset of significant coil overlap: it would represent the upper limit of the dilute regime. Above c^*, the contraction of the coils progressively brings the chains to their unperturbed dimensions, and beyond the second critical concentration, c^{**}, a concentrated region is defined as the region where the chain dimensions become independent of concentration. Moreover, the shear-thinning behaviour which appears above c^* is related to the interpretation of the coils and the two phenomena, contraction and interpenetration of the coils, would be more or

TABLE 2

Reduced Critical Concentrations and Slopes of the Regression Lines log η_{sp0} versus log $c[\eta]$ in the Three Flow Regimes for CMC, HEC and Xanthan Gum

	CMC	*HEC*	*Xanthan*[a]	*Xanthan*[b]
$c^*[\eta]$	1·4	0·56	1·4	1·1
$c^{**}[\eta]$	5·2	5·2	5·5	4·3
Slopes				
$c < c^*$	1·3	1·3	1·3	1·3
$c^* < c < c^{**}$	1·8	2·0	2·1	1·9
$c > c^{**}$	3·9	5·0	4·2	3·9

[a] From Cuvelier & Launay (1986).
[b] From Launay *et al.* (1984).

less simultaneous within the intermediate concentration domain. This semi-dilute domain can be divided into semi-dilute non-entangled and semi-dilute entangled regions (Graessley, 1980).

Several definitions of the overlap concentration have been proposed. Graessley (1980) defines the overlap concentration as the concentration at which the average chain spacing is twice the radius of gyration at zero concentration: then $c^* \sim 0{\cdot}77/[\eta]$. Assuming hexagonal packing of the encompassed average spherical coil volumes gives $c^* \sim 1{\cdot}1/[\eta]$ (Simha & Zakin, 1960), whereas a total occupancy of the available volume by coils results in $c^* \sim 1{\cdot}5/[\eta]$ (Morris *et al.*, 1980).

For each polysaccharide, the first critical concentration, c^*, is of the same order of magnitude as the theoretical overlap concentration (see Table 2); the HEC macromolecule appears more extended in the solvent than the CMC since the coil overlapping occurs at lower reduced concentrations.

According to Graessley (1980), the concentration c^{**} is the limit between the semi-dilute and the concentrated regions and c^* and c^{**} are related by

$$c^{**} \sim c^*[\alpha(0)]^8$$

where $\alpha(0)$ is the expansion factor of the chains at infinite dilution, in the case of a Mark–Houwink exponent of 0·8. In other cases, this expression can be extended (Lefebvre, 1982) to

$$c^{**} \sim c^*[\alpha(0)]^{3a/(a-0{\cdot}5)} = c^* \left(\frac{[\eta]}{[\eta]_\theta}\right)^{a/(a-0{\cdot}5)} \qquad (1)$$

where a is the Mark–Houwink exponent and $[\eta]_\theta$ the intrinsic viscosity under theta conditions. Thus, depending upon the compression possibilities of the coils in the present solvent, the semi-dilute region ($c^* < c < c^{**}$) would be more or less broad. For CMC, the intrinsic viscosity at 0·1 M ionic strength is rather close to the intrinsic viscosity at infinite ionic strength, which is in turn not very much higher than $[\eta]_\theta$; this could partly explain why c^{**}/c^* is not very large ($c^{**}/c^* \sim 3{\cdot}8$) and also why it is difficult to observe the semi-dilute domain. In contrast, for HEC the semi-dilute region is broader ($c^{**}/c^* \sim 9{\cdot}3$). The better the solvent for a polymer, the broader the semi-dilute domain; the present results would imply that at neutral pH, 0·1 M NaCl solution is a better solvent for HEC than for CMC as could be foreseen from the value of the Mark–Houwink exponent a.

If one defines c^{**} as the overlap concentration of the coils in theta conditions, it would be given by $c^{**} \sim 0{\cdot}77/[\eta]_\theta$, $c^{**} \sim 1{\cdot}1/[\eta]_\theta$ or $c^{**} \sim 1{\cdot}5/[\eta]_\theta$ by analogy to the definitions of Graessley (1980), Simha &

Zakin (1960) and Morris *et al.* (1980), respectively. Kok & Rudin (1981) defined c^{**} as the concentration at which the dimension of the equivalent hydrodynamic sphere has shrunk to its theta value, and gave

$$c^{**}[\eta]_\theta = \frac{9{\cdot}4 \times 10^{24}}{4\pi N_A} \sim 1{\cdot}23 \tag{2}$$

where N_A is the Avogadro's constant.

Since the intrinsic viscosity in theta conditions was not available, its value was estimated from the theoretical treatment of Hsu & Schummer (1983), who showed for most neutral polymers that

$$\log \frac{K_\theta}{K} = 4(a - 0{\cdot}5) \tag{3}$$

where K, a and K_θ, 0·5 are the parameters of the Mark–Houwink equations in non-theta solvents and theta solvents, respectively. Then $[\eta]_\theta$ can be determined by the relation

$$[\eta]_\theta = K_\theta \bar{M}_v^{0{\cdot}5} \tag{4}$$

As shown in the first column of Table 3, the use of eqn (1) leads to higher values than the experiment whereas the Kok & Rudin (1981) expression and the criterion of Simha & Zakin (1960) are the best predictions of the second critical concentration c^{**} for HEC.

TABLE 3

Second Reduced Critical Concentrations and Different Theoretical Predictions for CMC 9M65 and HEC

	HEC[a]	*CMC with* $[\eta]_\infty$[b]	*CMC with* $[\eta]_\theta$[c]
Experimental data, $c^{**}[\eta]$	5·2	5·2	5·2
$c^{**}[\eta]$ from eqn (1)	16·9	9·0	35·7
Graessley criterion $c^{**}[\eta] \sim 0{\cdot}77[\eta]/[\eta]_\theta$	3·4	1·5	2·5
Simha & Zakin criterion $c^{**}[\eta] \sim 1{\cdot}1[\eta]/[\eta]_\theta$	4·9	2·1	3·5
Total occupancy $c^{**}[\eta] \sim 1{\cdot}5[\eta]/[\eta]_\theta$	6·7	2·9	4·8
Kok & Rudin criterion $c^{**}[\eta] \sim 1{\cdot}23[\eta]/[\eta]_\theta$	5·5	2·4	3·9

[a] $[\eta]_\theta = 181{\cdot}7$ ml/g from a combination of eqn (3) and eqn (4).
[b] $[\eta]_\infty = 621{\cdot}7$ ml/g from eqn (5).
[c] $[\eta]_\theta = 395{\cdot}6$ ml/g from a combination of eqn (3) and eqn (4).

For CMC solutions, it was not clear whether $[\eta]_\theta$ or $[\eta]_\infty$, the intrinsic viscosity at infinite ionic strength, must be used to calculate the theoretical critical concentrations. The intrinsic viscosity in theta conditions was estimated in the same way as for HEC, whereas the intrinsic viscosity at infinite ionic strength was determined for CMC 9M65 from the Mark–Houwink relationship given by Kamide and Miyazaki (1978):

$$[\eta]_\infty = 0{\cdot}173(\bar{M}_v)^{0{\cdot}604} \text{at } 25°\text{C (for } DS \sim 0{\cdot}8) \tag{5}$$

Values calculated from each definition of critical concentration c^{**} are shown in column 2 (calculated with $[\eta]_\infty$) and in column 3 (calculated with $[\eta]_\theta$) of Table 3. It may be seen that the best agreement is obtained using the total occupancy criterion of Morris *et al.* (1980) with $[\eta]_\theta$. However, it is noteworthy that, except for eqn (1), each of the overlap criteria in theta conditions yields theoretical c^{**} values of the order of magnitude of the experimental ones. Since all of these predictions assume that, within the semi-dilute domain, the coils are reaching their unperturbed dimensions, the present data are consistent with such interpretations.

Interpretation of the shear-thinning behaviour

The shear-thinning behaviour has been reported in the section 'Description of Flow Curves' to occur above a concentration c_s ($c_s = 0{\cdot}7\text{–}0{\cdot}9$ g litre^{-1} for CMC 9M65 and approximately 1 g litre^{-1} for HEC). These values are close to the experimental c^* values (defined in the section 'Concentration Dependence of Zero Shear Rate Viscosity') corresponding to the overlap of the coils (see Table 1).

For flow curves displaying non-Newtonian behaviour ($c > c_s$), a critical shear rate $\dot{\gamma}_c$ (the shear rate above which the shear-thinning behaviour appears) and a characteristic relaxation time τ, $\tau = 1/\dot{\gamma}_c$, can be determined. Other definitions of critical shear rate or relaxation time have been employed, thus Morris *et al.* (1981) have taken the shear rate $\dot{\gamma}_{0{\cdot}1}$ required to reduce the viscosity to $\eta_0/10$.

The two parameters (η_0 and τ) allow master flow curves to be constructed in reduced coordinates ($\eta_r = \eta/\eta_0$ and $\dot{\gamma}_r = \tau \times \dot{\gamma}$) for these two cellulose derivatives as shown in Fig. 4. A difference between the two cellulose derivatives can be seen in the high reduced shear rates region, in contrast with the results of Morris *et al.* (1981) who found the same master flow curve for various polysaccharides even at high shear rates.

The characteristic relaxation time τ corresponds to the slower molecular movements influencing the viscosity. According to the inter-

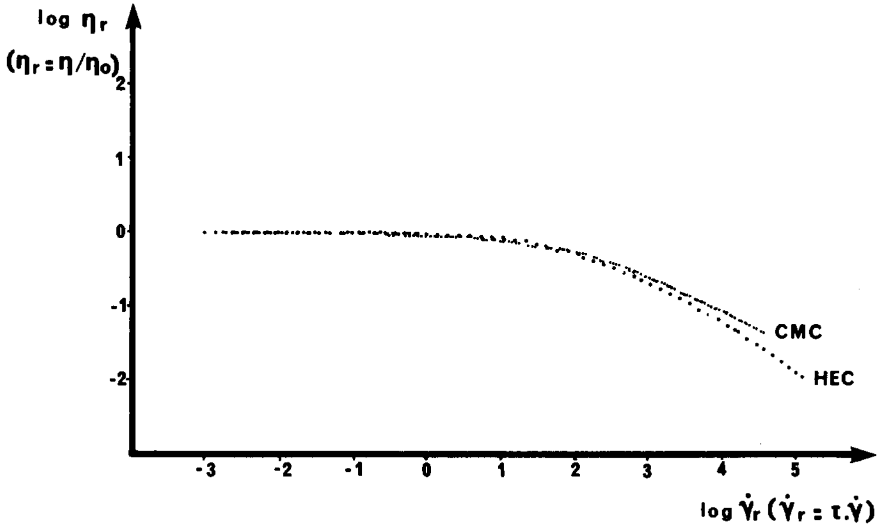

Fig. 4. Master flow curves of CMC 9M65 (■) and HEC (○) at pH 7·0, 0·1 M NaCl ionic strength, $t = 25°C$.

pretation of Graessley (1974), the polymer coil interpenetration results in an entangled structure above the coil overlap concentration. At low shear rates, some of these entanglements are disrupted by shearing but are immediately replaced by new ones so that no net change in entanglement occurs: it is the range of the Newtonian 'plateau'. For higher shear rates, the rate of disruption becomes greater than the rate of the formation of new entanglements and the apparent viscosity decreases with shear rate.

Variations of the characteristic relaxation time τ as a function of the polysaccharide concentration are shown in Fig. 5 for CMC 9M65 and HEC: two linear segments intercepting at a concentration c_e are observed. In the more concentrated region ($c > c_e$), both cellulose derivatives exhibit in logarithmic coordinates a linear dependence upon concentration with slopes of 4·4 (CMC) and 4·3 (HEC) very close to one another. In the less concentrated region ($c < c_e$), slopes are about 1·5 for CMC and 1·8 for HEC; however, it must be pointed out that in the low concentration range only a few points of the flow curves belong to the shear-thinning behaviour region so that the characteristic relaxation time τ cannot be determined with high precision. The reduced concentration $c_e[\eta]$ is rather similar for the two cellulose derivatives: 3·4 for CMC 9M65 and 3·3 for HEC, but it is not clear whether this coincidence is significant. In Fig. 5, the critical concentrations (c^* and c^{**}), previously

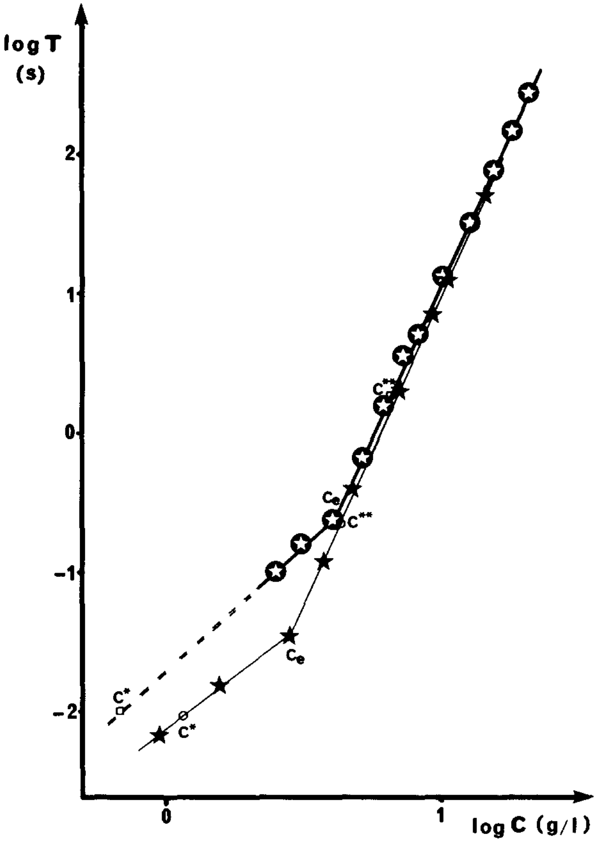

Fig. 5. Characteristic relaxation time (τ) as a function of polysaccharide concentration at pH 7·0, 0·1 M NaCl ionic strength: ★, CMC 9M65; ✪, HEC; critical concentrations c^* and c^{**} being pointed for CMC (○) and HEC (□).

defined, are also shown and in both cases c_e is found to be intermediate between c^* and c^{**}.

These results can be compared with the data on xanthan gum reported by Launay *et al.* (1984) and by Cuvelier & Launay (1986) in which the relaxation time τ_r was calculated by fitting eqn (6) to experimental data:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\tau_r \dot{\gamma})^m} \qquad (6)$$

This equation has been first derived for suspensions by Cross (1965) and more recently by Soong & Shen (1980) for polymer solutions and melts using a kinetic network model.

In that case, the relaxation time τ_r corresponds to the shear rate at which the apparent viscosity is the average of the two Newtonian viscosities (at zero shear rate, η_0, and at high shear rates, η_∞). Such a definition could not be used here since the high shear rate Newtonian viscosity was never approached. However, eqn (6) can be simplified to eqn (7), assuming $\eta_0 \gg \eta_\infty$:

$$\eta = \frac{\eta_0}{1 + (\tau_r \dot{\gamma})^m} \tag{7}$$

which can be also written

$$\eta_r = \eta / \eta_0 = \frac{1}{1 + C\dot{\gamma}_r^m} \tag{8}$$

with $\dot{\gamma}_r = \dot{\gamma}/\dot{\gamma}_c$ and $\tau_r = C^{1/m}/\dot{\gamma}_c = \tau C^{1/m}$. C and m are adjustable parameters and can be obtained by fitting eqn (8) to the points of the master flow curves: C and m were 0·0680 and 0·521, respectively, for CMC 9M65 and 0·0431 and 0·646, respectively, for HEC. Since τ_r and τ are linearly related, the variations of τ and τ_r (determined from eqn (6) by other authors) as a function of concentration can be compared, especially in the more concentrated domain where η_∞ can be neglected ($\eta_0 \gg \eta_\infty$).

According to the interpretation of Launay *et al.* (1984) and Cuvelier & Launay (1986) of two sets of data for xanthan solutions, relaxation time was shown not to vary much with concentration in the dilute domain ($c < c^*$) and was shown to vary as $c^{1\cdot4}$ or $c^{2\cdot1}$ in the semi-dilute domain ($c^* < c < c^{**}$), which they say agrees with Doi's theoretical prediction ($\tau \propto c^2$) for rigid rods in the concentration region where the collision effect dominates their molecular motion (Doi, 1975), and to vary as $c^{3\cdot55}$ or $c^{3\cdot7}$ in the concentrated domain ($c > c^{**}$) — c^* and c^{**} have the same significance as previously described. In fact, if their results are considered in detail, one can see that critical concentrations c^* and c^{**} are not the real limits of the three domains for the variation of the relaxation time τ_r with concentration.

Compared with the zero shear rate viscosity, the characteristic relaxation time τ is the result of a dynamic phenomenon. Therefore it is reasonable to find $c^* < c_e < c^{**}$.

It can be seen that in the case of HEC the reduced $c_e[\eta]$ concentration corresponds to the overlap concentration of the coils under theta conditions, according to the Graessley criterion, and that c_e is closer to c^{**} than in the case of CMC where the contraction possibilities of the coils are more limited.

Between c^* and c_e, one may assume that the compression of the coils would limit the increase with concentration of the average number of entanglements per molecule: whereas between c_e and c^{**}, the contraction of the coils would be less and the interpenetration of the chains would increase until the concentrated domain was reached ($c > c^{**}$). Furthermore, Cuvelier & Launay (1986) found from dynamic measurements on xanthan solutions that for $c > c^{**}$ the density of junction zones of the elastic network seemed not to increase with concentration, which they explained by a parallel packing of chain segments. Such an interpretation would be consistent with the higher dependence of η_{sp0} upon the concentration for $c > c^{**}$ than observed for a simple entangled structure and the high dependence of relaxation time τ on the concentration.

CONCLUSION

From this study of the flow behaviour of two cellulose derivatives, it can be seen that the viscous behaviour is roughly similar with two critical concentrations, c^* and c^{**}, delimiting three flow regimes on the log η_{sp0}–log $c[\eta]$ representation, and a third critical concentration, c_e, intermediate between c^* and c^{**} determined from the variations of τ with concentration.

For HEC, the different regimes are rather clearly defined, and critical concentrations are in good agreement with theory. But for CMC the semi-dilute domain is less broad and c_e is closer to c^*, which would correspond to a limited compression of the coils with concentration.

These differences between the two cellulose derivatives could be ascribed to a direct or an indirect effect of the substituents on the polyglucosyl backbone. The direct effect would be due to differences in steric hindrance which would result in differences in rigidity between the two cellulose derivatives. The indirect effect would occur through differences in substituents–solvent interactions. It seems that, at neutral pH, 0·1 M NaCl solution is a better solvent for HEC than for CMC whose carboxylic groups are dissociated but the electrostatic repulsions screened.

From the study of the relaxation time τ, one can see that the response of the structure to flow seems very similar for these two cellulose derivatives with equivalent $c_e[\eta]$ reduced concentrations and a τ value which varies as $c^{4\cdot3-4\cdot4}$ for $c > c_e$ in both cases. A study of cellulose derivatives of different molecular weights and substituents under various solvent conditions would be needed to distinguish the effects of substituents, solvent and backbone.

REFERENCES

Castelain, C. (1985). Thesis (Food Sciences), ENSIA, Universities of Paris VII and Paris XI, Paris.

Cross, M. M. (1965). *J. Colloid Sci.* **20**, 417.

Cuvelier, G. & Launay, B. (1986). *Carbohydr. Polym.* **6**, 5.

Doi, M. (1975). *J. Phys.* **36**, 607.

Gelman, R. A. (1982). *J. Appl. Polym. Sci.* **27**, 2957.

Goncalves, M. P. (1984). Doctor Engineer Thesis, University of Clermont Ferrand II, France.

Graessley, W. W. (1974). *Adv. Polym. Sci.* **16**, 1.

Graessley, W. W. (1980). *Polymer* **21**, 258.

Hsu, Y. T. & Schummer, P. (1983). *Rheol. Acta* **22**, 12.

Kamide, K. & Miyazaki, Y. (1978). *Polym. J.* **10**, 409.

Kok, C. M. & Rudin, A. (1981). *J. Appl. Polym. Sci.* **26**, 3583.

Launay, B., Cuvelier, G. & Martinez-Reyes, S. (1984). In *Gums and stabilisers for the food industry 2*, eds G. O. Phillips, D. J. Weedlock & P. A. Williams, Pergamon Press, Oxford, p. 79.

Launay, B., Doublier, J. L. & Cuvelier, G. (1986). In *Functional properties of food macromolecules*, eds J. R. Mitchell & D. A. Ledward, Elsevier Applied Science Publishers, London, p. 1.

Lefebvre, J. (1982). *Rheol. Acta* **21**, 620.

Morris, E. R., Rees, D. A. & Welsh, E. J. (1980). *J. Mol. Biol.* **138**, 383.

Morris, E. R., Cutler, A. N., Ross-Murphy, S. D., Rees, D. A. & Price, J. (1981). *Carbohydr. Polym.* **1**, 5.

Pals, D. T. F. & Hermans, J. J. (1952). *Rec. Trav. Chim.* **71**, 433.

Roushdi, M., Abdel-Akher, M., Ismail, F. A. & Attia, E. (1982). *Stärke* **34**, 410.

Simha, R. & Zakin, J. L. (1960). *J. Chem. Phys.* **33**, 1791.

Soong, D. & Shen, M. (1980). *Polym. Engin. Sci.* **20**, 1177.