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The Concentration Dependence of the 'Zero-Shear' Specific Viscosity for a Commercial Hydroxyethylmethylcellulose (HEMC) in Water at Several Temperatures

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ABSTRACT

This short paper presents preliminary results on the 'zero-shear' specific viscosity η_{sp_0} of a commercial hydroxyethylmethylcellulose (Tylose MH-4000) in water, at the temperatures 10, 25 and 40·5°C, over a wide range of concentrations. At the two higher temperatures, two regions are found in the plot of log$C[\eta]_0$ against logη_{sp_0} with a $C^*[\eta]_0$ value of about 2·5. This is consistent with the behaviour of other random-coil polymers. At 10°C however, there is an interesting 'upward shift' in this plot in the dilute region. It is suggested that this is related to the different degree of hydration of the oligo(ethyleneoxide) side chains at this temperature.

INTRODUCTION

Hydroxyethylmethylcellulose (HEMC) derivatives are being increasingly used as aqueous thickeners, emulsifiers and stabilisers in various industries (Greminger & Kramel, 1980; Just & Majewicz, 1985).

Recently the temperature dependence of the zero-shear rate intrinsic viscosity ($[\eta]_0$) of a high molecular weight commercial HEMC (MH-4000) in several aqueous systems in the temperature range 10–40°C has been studied (Michaeli & Donbrow, 1988, in preparation). In connection with this, the viscosities were measured over the concentration range of 5×10^{-3} to 3 gdl^{-1} at the temperatures 10, 25 and 40·5°C. In this paper the corresponding 'zero-shear' specific viscosity values (η_{sp_0}) are reported.

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MATERIALS AND METHODS

The hydroxyethylmethylcellulose used was Tylose MH-4000 of narrow polydispersity (Michaeli & Donbrow, 1988, in preparation), with an average molecular weight of about 140 000, obtained from Kalle & Co. AG Hoechst, FRG. The HEMC + water solutions were prepared by a procedure described elsewhere (Touitou & Donbrow, 1982). Recently, Michaeli & Donbrow (1988, in preparation) found that about 22% of the D-glucoside residues of the HEMC polysaccharide chain were substituted with oligo(ethyleneoxide) side chains ($-OCH_2CH_2)_mOH$. These side chains, designated by Claesson *et al.* (1986) as E_m, were estimated by Michaeli & Donbrow (1988, in preparation) to have an average degree of polymerisation m of nearly 2.

The viscosity data were obtained using three different viscometers, according to the concentration regions involved: a Cannon Ubbelhode capillary viscometer with a water flow-time of about 120 s at 25°C was used for the very dilute region $C < 0{\cdot}018$ gdl^{-1}; a Haake Rotovisco RV3 rotational viscometer with its low and medium viscosity range sensors NV and MV respectively, covering the HEMC in water solution medium C-range, between 0·02 and 0·44 gdl^{-1}; and a Ferranti Couette coaxial cylinder portable viscometer was used for HEMC concentrations higher than about 0·45 gdl^{-1}.

For improved estimations of the 'zero-shear' η_{sp_0} values for relatively concentrated ($C > 0{\cdot}22$ gdl^{-1}) solutions, an empirical shear-thinning relationship (1), similar to that introduced by Morris (1984), and recalculated from data presented by Morris *et al.* (1981) was applied. This equation closely describes (as shown in Fig. 1) the shear-thinning behaviour of the concentrated HEMC + water system, in terms of only two fitted parameters η_{sp_0} and $\dot{\gamma}_{0{\cdot}1}$:

$$\frac{\eta_0}{\eta} = (1 + 9(\dot{\gamma}/\dot{\gamma}_{0{\cdot}1})^{0{\cdot}78}) \qquad (1)$$

where η_0 and $\dot{\gamma}_{0{\cdot}1}$ are respectively the 'zero-shear' viscosity and the shear-rate value required to reduce the viscosity of the solution (η) to 0·1 η_0.

RESULTS AND DISCUSSION

The results in terms of $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ for the temperatures 10, 25 and 40·5°C are illustrated in Figs 2 to 4.

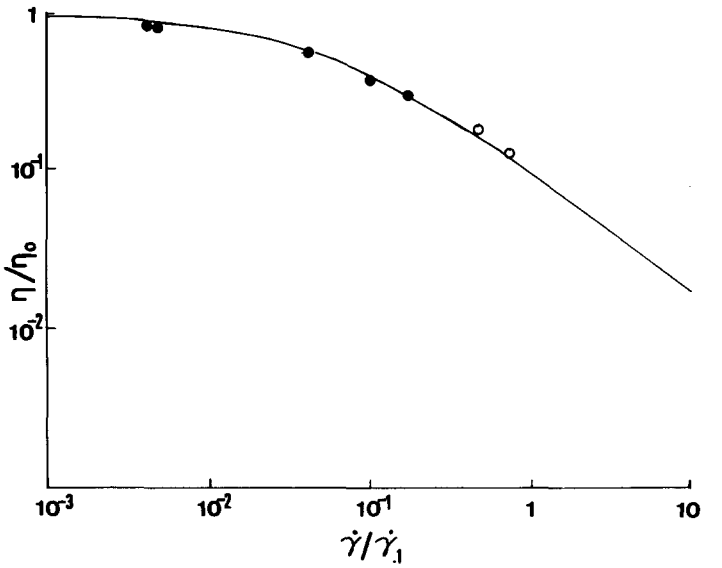

Fig. 1. Examples of the agreement of the behaviour of HEMC solutions at 10°C (○) and 40·5°C (●) with the generalised shear-thinning behaviour of concentrated solutions of disordered polysaccharides. The line is eqn (1) derived from the data presented by Morris *et al.* (1981).

The relevant results, including the regression constants, for the linear relationship $\log \eta_{sp_0} = A + B \log C[\eta]_0$ for all the temperatures and concentration regions measured are presented in Table 1.

The results can be classified into two basic $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ patterns: first, a simple one consisting of two intersecting lines with slopes of about 1·08 and 3·70 for 25°C and similar slopes of nearly 1·3 and 3·5 for 40·5°C, as shown in Figs 3 and 4.

A further, more complicated, pattern of $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ for 10°C, shown in Fig. 2, consists of two nearly parallel lines with very similar slopes of about 1·10 (I) and 1·08 (II), respectively. The second shifts upwards significantly from the first, and is intersected by a third, much steeper, line with a slope of about 3·8 (III).

These two distinctly different concentration-dependent 'zero-shear' specific viscosity patterns (Fig. 2 compared with Figs 3 and 4) indicate that the hydrodynamic properties of the fully-hydrated HEMC at 10°C are very different from those revealed for the same system at 25°C and 40·5°C. The difference is especially significant within the 'semi-dilute' concentration region of 0·03–0·3 gdl^{-1}.

At the two higher temperatures the η_{sp_0} concentration dependence indicates that the system is transformed abruptly at a certain unique

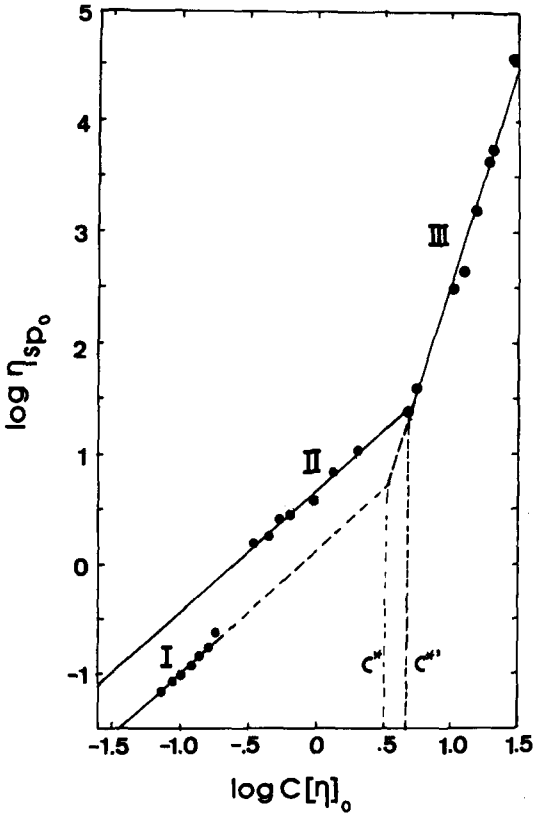

Fig. 2. Plot of $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ obtained for HEMC in water at 10°C, showing the determination of two critical concentrations C* and an extrapolated C*'.

critical concentration C* from its 'dilute' aqueous solution structure to its concentrated solution structure, probably involving 'coil overlap' amongst the polysaccharide chains (see Morris, 1984, 1986; Morris *et al.*, 1981).

At 10°C this $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ transition from dilute to semi-dilute and then to a concentrated region is probably accompanied by more complicated 'structural' changes, possibly similar to those recently mentioned for xanthan-gum solutions by Cuvelier & Launay (1986). In the present system these 'structural' changes are probably related to the temperature- and concentration-dependent hydration properties of the oligo(ethyleneoxide) side chains.

Claesson *et al.* (1986) have shown that at temperatures less than 20°C the important temperature-dependent short-range repulsive part of the inter-layer interactions of $C_{12}E_5$, in water decrease sharply with increasing temperature (> 18°C) ($C_{12}E_5$ stands for $C_{12}H_{25}(OCH_2CH_2)_5OH$).

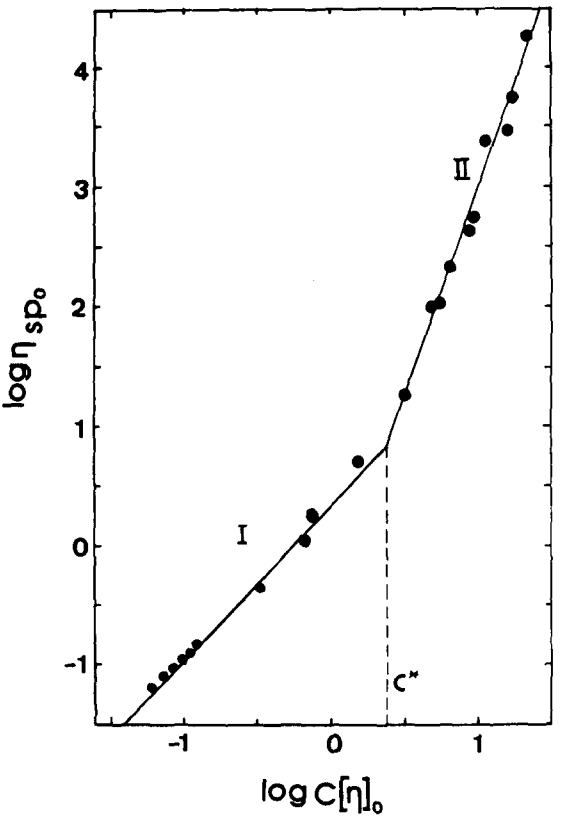

Fig. 3. Plot of $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ at 25°C, showing the determination of the critical concentration C*.

The results in Table 1 strongly indicate that the long-range hydrophobically-active oligo(ethyleneoxide) side chains (Claesson *et al.*, 1986) attached to more than 20% of the polysaccharide's D-glucose monomers (Michaeli & Donbrow, 1988, in preparation) significantly affect the hydrodynamic properties of the aqueous HEMC, probably by 'neighbouring-water structuring'. This is effective at 10°C, and may be indicated by the upward shift of the linear dependence of $\log \eta_{sp_0}$ on $\log C[\eta]_0$ in the semi-dilute concentration region (Fig. 2).

Furthermore, in the high concentration range ($C > 0{\cdot}5$ gdl^{-1}) a significant increase is found in the calculated B values from less than 3·5 at 40·5°C to more than 3·7 and 3·8 for 25 and 10°C, respectively.

This observation could be explained by the varying secondary contributions of the temperature-dependent long-range hydrophobic interactions of the hydrated HEMC oligo(ethyleneoxide) side groups (Claesson *et al.*, 1986), to the main 'entanglement effects' (Graessley,

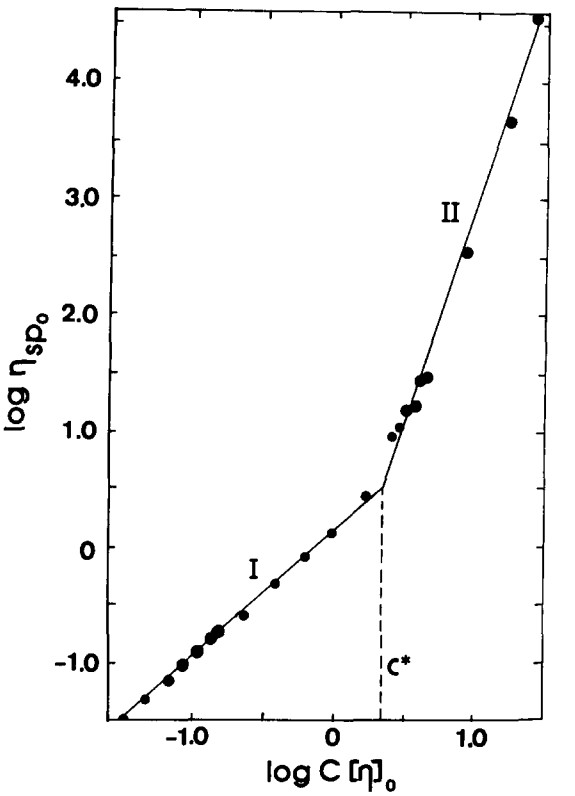

Fig. 4. Plot of $\log \eta_{sp_0}$ versus $\log C[\eta]_0$ at 40·5°C, showing the determination of the critical concentration C*.

TABLE 1
Summary of the Linear Regression Constants Calculated for the Double-Logarithmic Dependences of η_{sp_0} versus $C[\eta]_0$ for Tylose MH-4000 in Water at 10, 25 and 40·5°C

Temperature (°C)	$[\eta]_0$ *(dlg^{-1})*	*C-region*	*A*	*B*	*r*	*C* (gdl^{-1})*
10	10·0	I (<0·02)	0·1440	1·1043	1·0	0·330[a] (I–III)
		II (<0·33)	0·6893	1·0815	0·993	0·517 (II–III)
		III (>0·33)	−1·2655	3·8224	0·991	
25	8·3	I (<0·27)	0·14853	1·08434	0·999	0·267
		II (>0·27)	−0·75786	3·70352	0·994	
40·5	7·1	I (<0·34)	0·3726	1·312	0·996	0·344
		II (>0·34)	−0·4482	3·482	0·993	

[a]Result of an extrapolation.

1974) among its chains under the high-concentration regime. These contributions seem to decrease significantly with increasing temperature from 10°C through 25°C to about 40°C.

CONCLUSION

The preliminary results for the concentration dependence of the 'zero-shear' specific viscosities of Tylose MH-4000 water solutions over a very wide range of concentration at the temperatures 10, 25 and 40·5°C can be summarised as follows: Firstly, for 10°C, a phenomenon is revealed in the semi-dilute concentration region that may be related to the hydrophobic hydration of the oligo(ethyleneoxide) groups, which is known to occur at temperatures lower than 18°C; and secondly, there is a significant effect of temperature on the entanglement ability of the hydrated HEMC at high concentrations as shown by the log η_{sp_0} versus concentration relationship which changes from a $C^{3.82}$ dependence at 10°C, to $C^{3.7}$ at 25°C, and to $C^{3.48}$ at 40·5°C.

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