Carbohydrate Polymers **12** (1990) 443–459

Viscometric and Spectroscopic Studies on the Solution Behaviour of Hydrophobically Modified Cellulosic Polymers

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(Received 24 March 1989; revised version received 27 May 1989;
accepted 15 June 1989)

ABSTRACT

The solution properties of hydroxyethyl cellulose (HEC) and hydrophobically modified hydroxyethyl cellulose (HM-HEC) have been investigated by means of viscometric and spectroscopic techniques involving free radical and fluorescent probes. The greater viscosity of HM-HEC solutions above a critical polymer concentration (C_p) *of approximately 0·2% has been interpreted in terms of the formation of a three-dimensional network structure in which the polymer chains are effectively cross-linked by the intermolecular association of neighbouring hydrophobic side chains.* C_p *is considerably less than the predicted polymer coil overlap concentration* (C^*) *of approximately 1%.*

The interaction of the polymers with an anionic surfactant, sodium dodecyl sulphate (SDS) has also been investigated. A mechanism involving the interaction of free surfactant with the regions of intermolecular hydrophobic association is suggested to account for the considerable differences in the rheological behaviour of the polymers in the presence of SDS.

INTRODUCTION

Hydrophobically associating water-soluble polymers (HAPs) represent a comparatively new class of industrially important macromolecules. They

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Carbohydrate Polymers 0144-8617/90/$03.50 —

possess unusual rheological characteristics which are thought to arise from the intermolecular association of neighbouring hydrophobic substituents (Schaller, 1985; Shaw & Leipold, 1985), which are incorporated into the polymer molecule through chemical grafting (Landoll, 1982; Sau, 1987), or suitable co-polymerisation procedures (Schulz *et al.*, 1987). The level of incorporation of the hydrophobic groups is limited so as not to render the final modified polymer water insoluble (Landoll, 1982; Gelman, 1987). The hydrophobic associations give rise to a three-dimensional polymer network as illustrated in Fig. 1. Solutions of HAPs have high viscosities at low shear rates and exhibit strong shear thinning characteristics. As a result of their unique properties, HAPs have found use in various industrial fields such as enhanced oil recovery (Constein, 1986; Evani & Rose, 1987) and the formulation of latex based paints (Shaw & Leipold, 1985; Hall *et al.*, 1986).

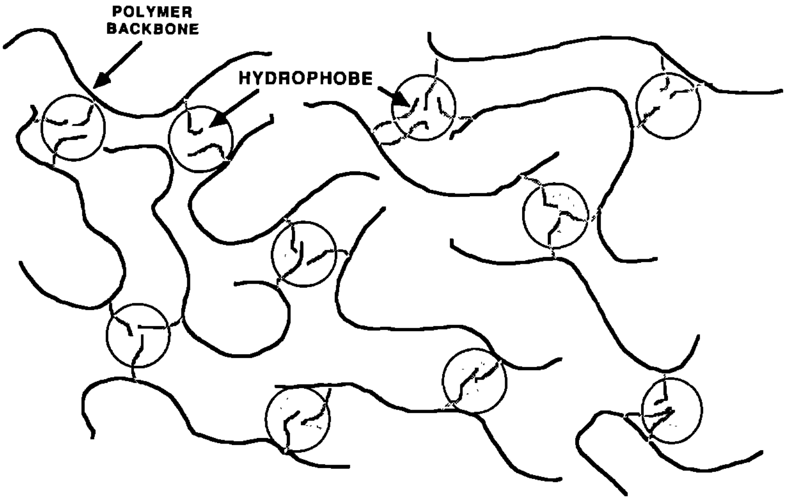

Fig. 1. Network structure of HM-HEC (from Ref. 2).

Whilst there is a growing amount of literature concerning the rheological characterisation of solutions of HAPs there has, to date, been few direct investigations into the nature of the hydrophobic associations (Siano *et al.*, 1987). To this end, we report on some viscometric measurements on solutions of HEC and HM-HEC together with spectroscopic investigations into the nature of the hydrophobic interactions using fluorescence and electron spin resonance techniques.

MATERIALS

HEC and HM-HEC were kindly supplied by Aqualon (UK) Ltd, Warrington, UK, under the trade names Natrosol 250 GR and Natrosol Plus Grade 330 respectively. The manufacturer reports the polymers to be of comparable molecular weight (*c.* 250 000) and to have a degree of substitution of 2·5 and 3·3 respectively. Both polymers were extensively dialysed against distilled water and freeze dried before use.

Previous investigators (Landoll, 1982; Gelman, 1987) have reported HM-HEC as containing 1–2% w/w of chemically grafted C_{12}–C_{24} alkyl side chains. For the sample used in these experiments, this corresponds to 4–6 bound hydrophobes per molecule.

Sodium dodecyl sulphate (specially pure grade) was obtained from BDH Chemicals Ltd, Liverpool, UK, and used without further purification.

Pyrene was obtained from Koch-Light Laboratories Ltd, Bucks, UK, and used as supplied. The 4-amino-2,2,6,6-tetramethylpiperidine-1-Oxyl(4-amino-Tempo) and 5-doxyl-stearic acid (5-DSA) were obtained from Sigma Chemicals Ltd, Poole, UK, and used as supplied. The structures of these probes are given in Fig. 2.

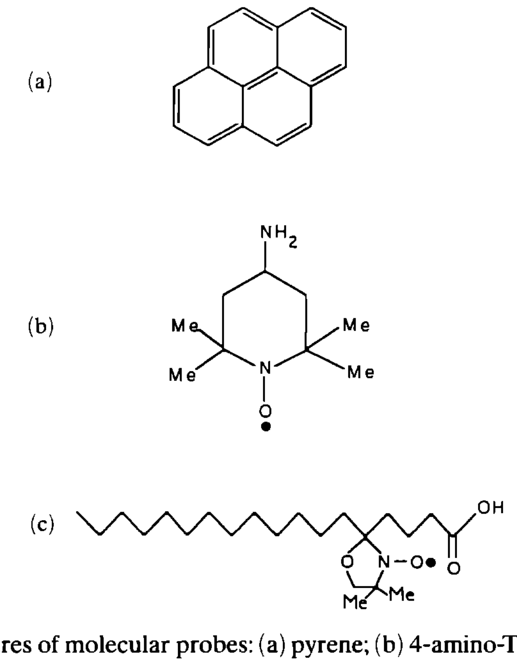

Fig. 2. Structures of molecular probes: (a) pyrene; (b) 4-amino-Tempo; (c) 5-DSA.

METHODS

To ensure complete dissolution, all polymer solutions were continuously stirred for at least 18 h prior to use. In experiments performed in the presence of free surfactant, the polymers were completely solubilised before the addition of the appropriate amount of SDS.

VISCOMETRIC STUDIES

Capillary viscometry

The reduced viscosities of aqueous solutions of HEC and HM-HEC covering the concentration range 0·02–0·5% were determined using a Canon-Ubbelohde simple dilution-type capillary viscometer positioned in a thermostatically controlled water bath at 25 ± 0·05°C. Flow times for each solution were recorded in triplicate and readings agreed to within ± 0·5%.

Shear-flow viscosity measurements

The viscosities of various polymer solutions were recorded over the shear rate range 0–50 s^{-1} using a Carri-med CS100 controlled stress rheometer (Carri-med Instruments Ltd, Dorking, UK). Depending on the observed viscosity of the solution, measurements were performed using a double concentric cylinder, a 4 cm 2° cone and plate or a 2 cm 2° cone and plate attachment. Each measurement involved an experimental run time of 2 min, and was performed in duplicate.

ESR STUDIES

Spin-label experiments

The 4-amino-Tempo was covalently linked to the cellulosic backbones of HEC and HM-HEC using the procedure outlined by Cafe *et al.* (1976), involving cyanogen bromide. The label is attached to the polymer through the hydroxyl groups of the sugar residues. After extensive dialysis against distilled water followed by freeze drying, the degree of labelling was calculated to be 1 label per 1000 sugar residues for HEC and 1 label per 7000 sugar residues for HM-HEC.

The ESR spectra of solutions of spin-labelled HEC and HM-HEC were recorded as a function of polymer concentration over the range 0–2% on a JEOL JES-ME 1X x-band ESR spectrometer using a quartz cell suitable for aqueous solutions.

Spin-probe studies

All solutions to be studied were prepared by dissolving the appropriate amount of polymer and/or SDS in a slighty alkaline (pH 9) aqueous solution of 5×10^{-6} mol dm^{-3} 5-DSA. The ESR spectra of 5-DSA in the various solutions were recorded as outlined above.

FLUORESCENCE STUDIES

Equal volumes of a freshly prepared saturated aqueous pyrene solution (*c.* 3×10^{-7} mol dm^{-3}) were added to various polymer/surfactant solutions and the resulting mixtures tumbled overnight. The fluorescence emission spectrum of each solution was recorded over the range 350–500 nm using a Perkin–Elmer MPF-43A fluorescence spectrophotometer. The excitation wavelength used was 276 nm. The relative intensities of the first (I_1; 372 nm) and third (I_3; 383 nm) vibronic bands of the pyrene monomer emission spectrum were recorded and the ratio I_1/I_3 calculated.

RESULTS

Viscosity measurements

Plots of reduced viscosity against polymer concentration for solutions of HEC and HM-HEC obtained from capillary viscometry are given in Figs 3 and 4. For HEC, a linear relationship is observed over the entire concentration range studied. However, the curve for HM-HEC shows a distinct deviation from linearity above a polymer concentration of approximately 0·2%. Such deviation is indicative of some form of aggregation occurring between the polymer molecules. The values for the intrinsic velocities obtained by extrapolation of the curves in Fig. 4 to infinite dilution were found to be 4·41 and 3·83 dl g^{-1} for HEC and HM-HEC respectively.

The viscosities of solutions of HEC and HM-HEC at the arbitrary shear rate of 1 s^{-1}, obtained using a constant stress rheometer are given

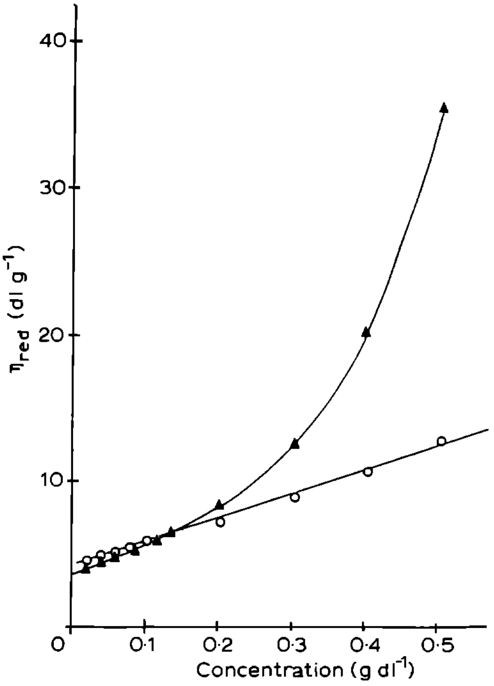

Fig. 3. Reduced viscosities as a function of polymer concentration for solutions of (○) HEC and (▲) HM-HEC.

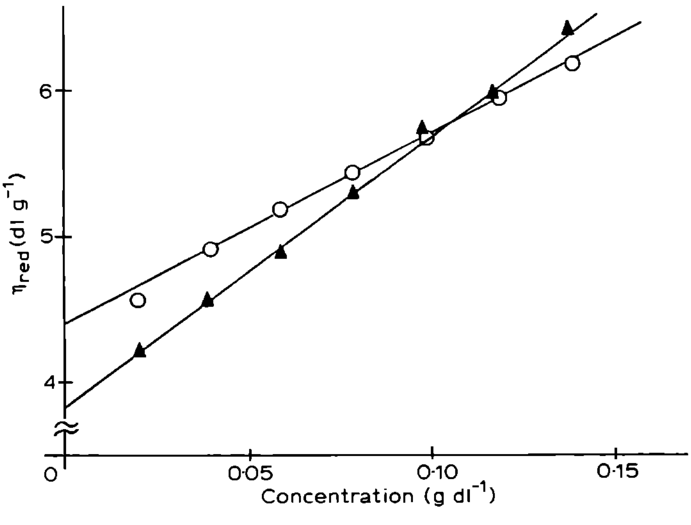

Fig. 4. Reduced viscosities as a function of polymer concentration for solutions of (○) HEC and (▲) HM-HEC.

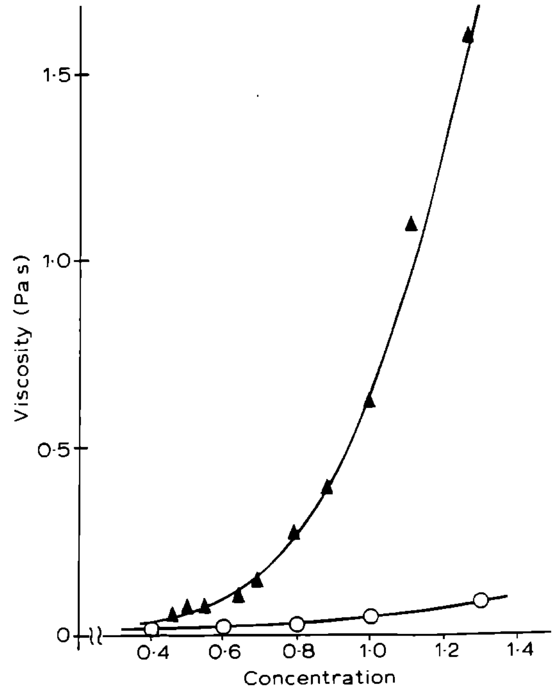

Fig. 5. Viscosity as a function of polymer concentration (%) for solutions of (○) HEC and (▲) HM-HEC at shear rate 1 s^{-1}.

in Fig. 5. Despite the fact that at infinite dilution the coil dimensions of the HM-HEC are less than those of HEC (as inferred by the intrinsic viscosity values), HM-HEC yields much more viscous solutions at concentrations greater than 0·2%.

ESR studies

The ESR spectrum of a nitroxide free radical consists of three lines and, due to anisotropic effects, their relative shapes and intensities are a function of the mobility of the nitroxide moiety. The ESR spectra of 5-DSA in aqueous solution, in a viscous solution of 80% aqueous glycerol, and in an aqueous solution containing SDS above its CMC are given in Fig. 6. When motion is relatively unrestricted and the nitroxide moiety has a high degree of mobility, the anisotropy is averaged out and the three spectral lines are narrow and are of similar intensities (Fig. 6(a)). When movement is restricted, however, the anisotropic effects become apparent, resulting in line broadening (Figs 6(b) and 6(c)).

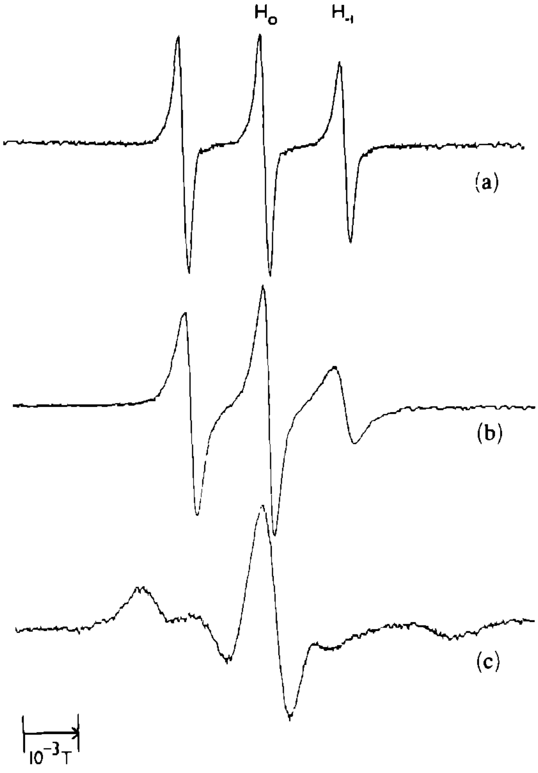

Fig. 6. ESR spectra of 5-DSA (5×10^{-6} mol dm^{-3} in (a) water at 20°C; (b) 5% aqueous SDS solution at 20°C; (c) 80% aqueous glycerol at 5°C.

For fast isotropic motion, the rotational correlation time, τ_c, of the spin label may be calculated from the spectra using the equation of Kivelson (1960). For slow anisotropic motion, an alternative procedure is required (Goldman *et al.*, 1974). In this study we have used the ratio of the intensities of the central and high field lines (H_0/H_{-1}) as a convenient arbitrary measure of molecular motion. The ratio H_0/H_{-1} increases as mobility of the nitroxide moiety is decreased.

Spin-label studies

Plots of H_0/H_{-1} for spin-labelled HEC and HM-HEC as a function of polymer concentration are given in Fig. 7. For both polymers, the value of the ratio was found to be constant over the entire concentration range studied indicating that the polymer molecules had a high degree of segmental motion even at concentrations of 2%, where HM-HEC in

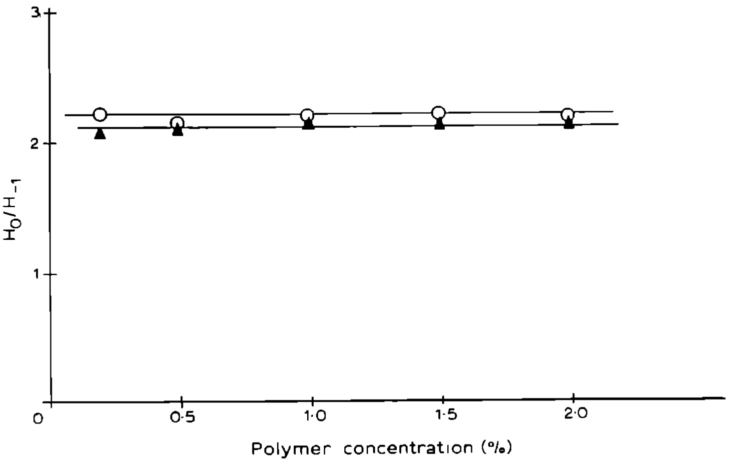

Fig. 7. Relative mobility ratio (H_0/H_{-1}) as a function of solution concentration for (○) spin-labelled HEC and (▲) spin-labelled HM-HEC.

particular was shown to form extremely viscous solutions (Fig. 5). This can be explained by the fact that the mobility of the spin label reflects the viscosity of its microenvironment rather than the viscosity of the solution as a whole.

Spin-probe studies

The ESR spectra of the 5-DSA spin probe in the presence of varying concentrations of HEC and HM-HEC are given in Figs 8 and 9 respectively, with the corresponding H_0/H_{-1} ratios plotted in Fig. 10. Whereas the ratio and hence mobility of the probe appears constant in solutions of HEC up to concentrations of 1·5% polymer, H_0/H_{-1} increases in solutions of HM-HEC above concentrations of 0·2% polymer indicating a reduction in probe mobility. It is interesting to note that the mobility of the spin probe appears very much more restricted in solutions of HM-HEC than when incorporated in a surfactant micelle (compare Figs 9(c) and 6(b)). The change in mobility of the spin probe occurs as a result of its association with the hydrophobic junction zones responsible for the network structure of the polymer molecules. Such partitioning between hydrophobic and hydrophilic environments has enabled the ESR spin probe technique to be used in the study of several different polymer/surfactant interactions (Witte *et al.*, 1987; Witte & Engberts, 1988).

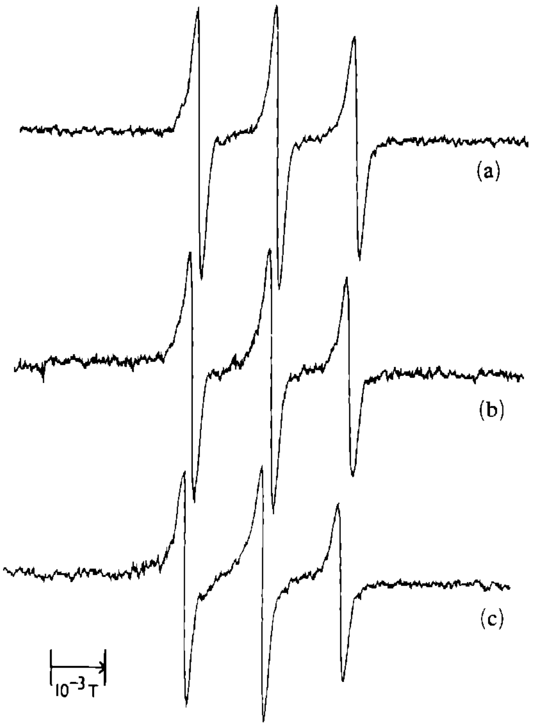

Fig. 8. ESR spectra of 5-DSA (5×10^{-6} mol dm^{-3}) in aqueous solutions of HEC. (a) 0·025% HEC; (b) 0·4% HEC; (c) 1·0% HEC.

Addition of surfactant

The effects of added SDS on the viscosity of 2% solutions of HEC and HM-HEC are shown in Fig. 11. For 2% HM-HEC, the solution viscosity increases dramatically with increasing concentration of SDS up to a point approximately equivalent to the expected critical micelle concentration of SDS (8×10^{-3} mol dm^{-3}). Above this point, further increases in SDS concentration produce a marked decrease in the observed solution viscosity. Very similar trends have been observed by Shaw and Leipold (1985) for the addition of non-ionic surfactant to solutions of HM-HEC. The viscosity of solutions of HEC showed negligible dependence on the concentration of added SDS.

The value of H_0/H_{-1} for 5-DSA in solutions containing varying amounts of SDS, both in the presence and absence of 0·2% HEC or HM-HEC are given in Fig. 12. The concentration of polymer used in this set of experiments was limited to 0·2% as the presence of any higher con-

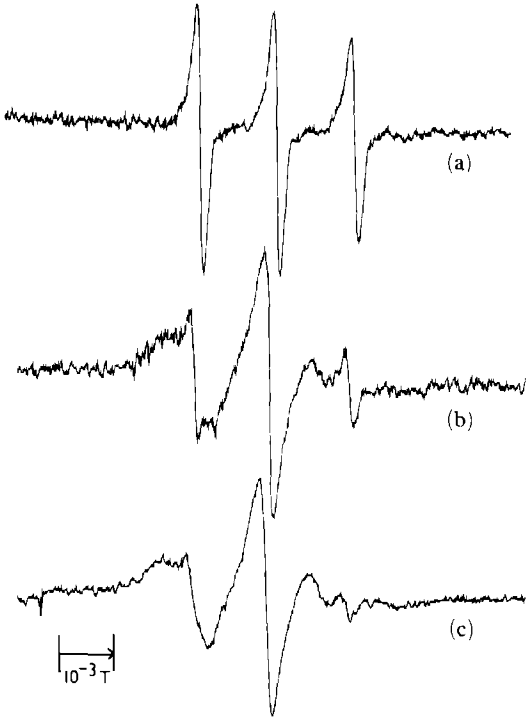

Fig. 9. ESR spectra of 5-DSA (5×10^{-6} mol dm^{-3}) in aqueous solutions of HM-HEC. (a) 0·2% HM-HEC; (b) 1·0% HM-HEC; (c) 2·0% HM-HEC.

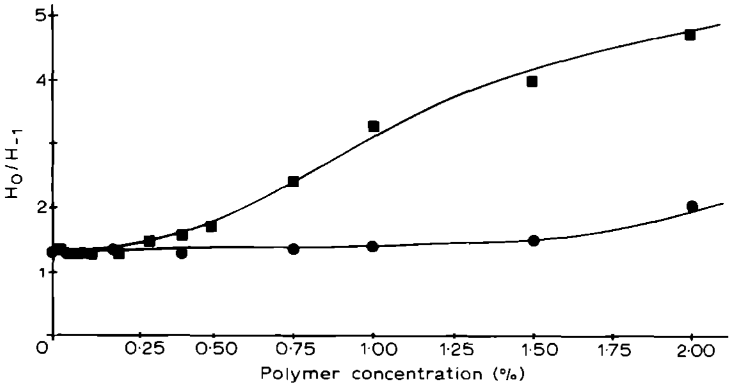

Fig. 10. Relative mobility ratio (H_0/H_{-1}) of 5-DSA (5×10^{-6} mol dm^{-3} in the presence of varying concentrations of (●) HEC and (■) HM-HEC.

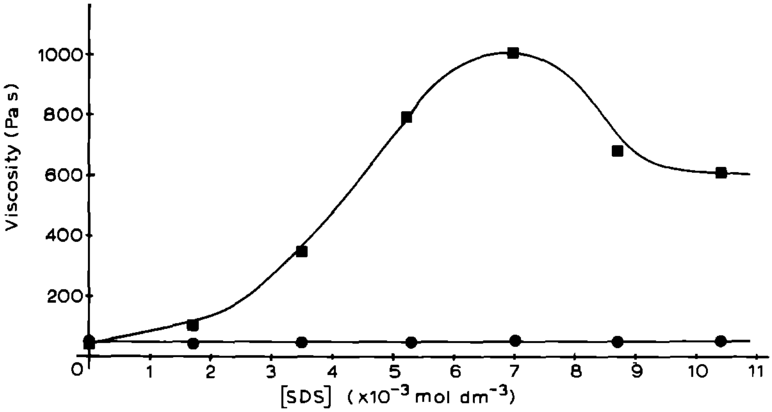

Fig. 11. The effect of SDS on the viscosity of 2% solutions of (●) HEC and (■) HM-HEC at shear rate 0·1 s^{-1}.

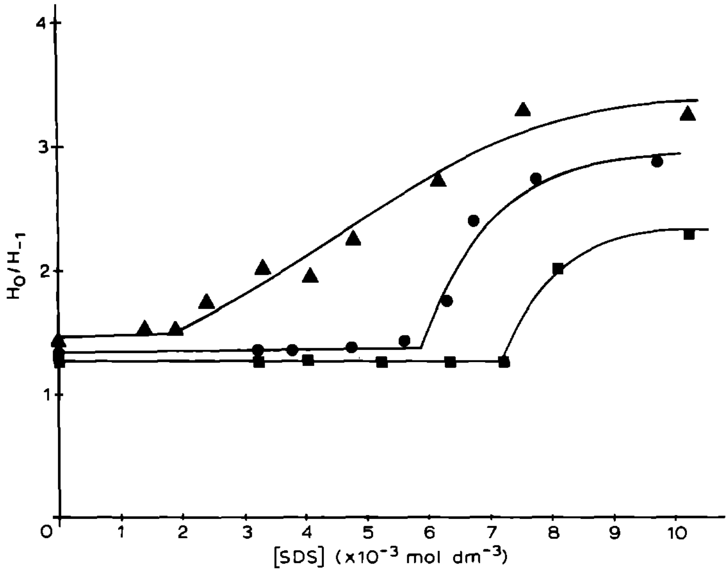

Fig. 12. Relative mobility ratio of 5-DSA (5 × 10^{-6} mol dm^{-3} in various polymer/surfactant solutions. (■) SDS alone, (●) SDS + 0·2% HEC and (▲) SDS + 0·2% HM-HEC.

centrations of HM-HEC would itself affect the mobility of the spin probe (Fig. 10).

In the absence of polymer a sharp transition occurs in the H_0/H_{-1} curve at an SDS concentration of 7–8 × 10^{-3} mol dm^{-3}, which corresponds closely to the CMC of the surfactant. In the presence of HEC, a similar sharp transition occurs but at a slightly lower SDS concentration (~ 6×10^{-3} mol dm^{-3}). In solutions containing HM-HEC a much larger, albeit more gradual, change in the H_0/H_{-1} ratio commences at an SDS concentration of approximately 2×10^{-3} mol dm^{-3}. It is reasonable to assume that any change in mobility of the spin probe is due to its hydrophobic association with polymer/surfactant complexes and therefore that the point of transition in H_0/H_{-1} represents the point of formation of such micellar-like complexes. It can therefore be concluded that there is a more pronounced interaction between HM-HEC and SDS than between HEC and SDS.

Similar conclusions were drawn from studies using the fluorescent pyrene probe. In this work, as in other reported studies (Kalyanasundaram & Thomas, 1977; Winnick *et al.*, 1987) the ratio of the intensities of the first (I_1; 372 nm) and the third (I_3; 383 nm) peaks of the pyrene monomer emission spectrum was taken as a measure of the hydrophobicity of its surrounding environment. The ratio I_1/I_3 decreases as hydrophobicity increases.

The variation in I_1/I_3 of the monomer emission spectrum of pyrene in aqueous solutions of SDS, and SDS in the presence of 0·01% HEC or 0·01% HM-HEC are given in Fig. 13. It was not possible to carry out reliable measurements on solutions containing higher concentrations of polymer due to the interference arising from the UV absorbance of the turbid solutions.

In solutions of SDS alone and SDS in the presence of 0·01% HEC, well-defined transition points in I_1/I_3 are observed at SDS concentra-

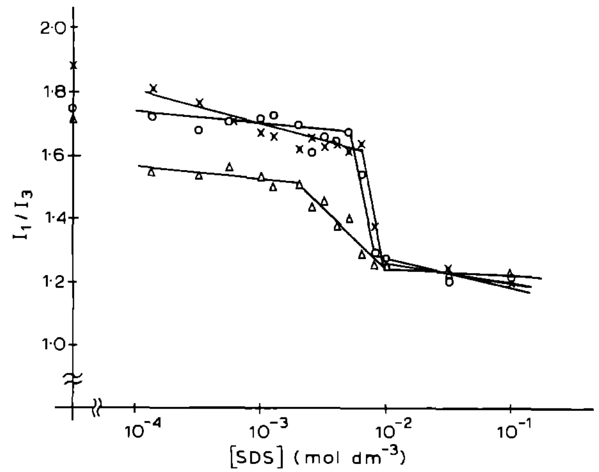

Fig. 13. I_1/I_3 ratio for pyrene probe in various polymer/surfactant solutions. (×) SDS alone, (○) SDS + 0·01% HEC and (△) SDS + 0·01% HM-HEC.

tions of approximately $7{\cdot}0 \times 10^{-3}$ and $5{\cdot}5 \times 10^{-3}$ mol dm^{-3} respectively. In solutions of SDS in the presence of 0·01% HM-HEC, there is a more gradual transition in I_1/I_3 which occurs over the entire concentration range 10^{-3}–10^{-2} mol dm^{-3} SDS. Again, it is assumed that the change in the I_1/I_3 ratio of the pyrene probe is a consequence of its hydrophobic association with polymer/surfactant complexes and therefore, that the point of transition in the I_1/I_3 ratio can be taken as the point of formation of these micellar-type complexes.

DISCUSSION

Whereas HEC produces viscosification of solutions through simple chain entanglements, the greatly increased solution viscosity of HM-HEC (Fig. 5) is thought to arise from the intermolecular association of pendant hydrocarbon side chains resulting in the formation of a reversibly cross-linked three-dimensional network structure (Fig. 1, Shaw & Leipold, 1985). The driving forces for such associations are thought to be entropic in nature, stemming from the desire to minimise the disruption of the water structure surrounding the hydrophobes. Rather like micellisation, formation of the regions of intermolecular hydrophobic association is thought only to occur above a critical polymer concentration, but whether or not this corresponds to a critical concentration of bound hydrophobe is still a matter for speculation.

For the HM-HEC used in this study, viscometric data (Fig. 3) indicate the critical polymer concentration to be approximately 0·2%. This value is considerably less than the expected coil overlap concentration (C^*) of ~1%, as calculated from the relationship proposed by Morris *et al.* (1981), i.e. $C^* = 4/[\eta]$.

Whatever the mechanism behind the enhanced viscosity of solutions of HM-HEC, the segmental motion of the polymer backbones, as monitored by the spin-label experiments, remains unaffected even at much higher polymer concentrations (Fig. 7). This suggests that only a very small proportion of polymer segments are closely associated with the junction zones linking the polymer molecules together.

ESR spin probe experiments suggest that distinct regions of hydrophobicity are present within HM-HEC solutions of concentration above 0·2%, and that no such regions appear to exist within solutions of HEC (Figs 8–10). At the probe concentrations used in these experiments (5×10^{-6} mol dm^{-3}), the number of bound hydrophobes in solution, even at the lowest polymer concentrations studied, is at least one order of magnitude greater than the number of molecules of the probe. Thus, one can reasonably assume that all of the 5-DSA molecules will be preferentially associated with the hydrophobic regions. The continual decrease in mobility of the probe with increasing polymer concentration (Figs 9 and 10) can therefore be attributed to the progressive strengthening of these associative interactions through the incorporation of an increasing number of hydrophobes into any one region of association.

The viscometric and spectroscopic evidence presented above is in complete agreement with the structure depicted in Fig. 1 in that, above a certain concentration, HM-HEC forms a network in solution in which relatively flexible polymer backbones are reversibly cross-linked through the formation of regions of association between neighbouring hydrophobic side chains.

Whilst producing viscosity-enhancing effects at higher polymer concentrations, the presence of hydrophobic substituents in water-soluble polymers can result in a contraction of the coil dimensions at very low polymer concentrations, as inferred by intrinsic viscosity measurements (Gelman & Barth, 1986; Gelman, 1987).

There is now growing evidence (Gelman & Barth, 1986; Gelman, 1987; Siano *et al.*, 1987) that this phenomenon may be attributed to intramolecular hydrophobic associations. For example it has been shown that, relative to that of HEC, the intrinsic viscosity of HM-HEC decreased with increasing amount, and chain length, of grafted hydrocarbon side chains (Gelman, 1987). However, if solvent conditions were manipulated (for example by the addition of sufficient methanol) so that the entropic driving forces were diminished and the hydrophobic associations disrupted, then the intrinsic viscosities of HM-HEC and HEC became equivalent (Gelman & Barth, 1986). The lower value of the intrinsic viscosity obtained for HM-HEC compared to HEC in our studies is supportive of intramolecular associations but does not constitute conclusive evidence since there may be slight differences in the molecular weights of the supplied polymers.

The presence of bound hydrophobes results in there being considerable differences in the rheological behaviour of HEC and HM-HEC in the presence of surfactants (Shaw & Leipold, 1985; Gelman, 1987). Unlike sodium oleate which Gelman (1987) found only to produce viscosity increases in solutions of HM-HEC at concentrations just below its expected CMC, SDS produces viscosity enhancement at all levels of addition up to its expected CMC (Fig. 11).

Over the years, several workers have reported similar dramatic increases in the viscosity of various polymer solutions following the addition of SDS. Among the various mechanisms proposed to explain these observations have been the adsorption of the charged surfactant onto the polymer molecule causing a polyelectrolyte-type expansion of the coil dimensions (Saito, 1957; Takagi *et al.*, 1975) and the effective cross-linking of the polymer molecules through electrostatic interactions with the charged micelles (Greener *et al.*, 1987). Whilst the former mechanism may play a role within our system, similar effects to those shown in Fig. 11 have also been observed for the addition of non-ionic surfactants to HM-HEC (Shaw & Leipold, 1985). We therefore suggest that the increased viscosity of solutions of HM-HEC in the presence of free SDS is due to the incorporation of SDS molecules into existing regions of intermolecular associations, thus strengthening the association and thereby increasing the apparent viscosity of the solution. It is also possible that the presence of free SDS may induce additional interchain association between previously non-interacting hydrophobic groups. At levels of addition above its CMC, the pure SDS micelles offer an alternative environment for the solubilisation of the bound hydrophobe, thereby disrupting intermolecular associations (Gelman, 1987). As a result, further increases in SDS concentration above its CMC produces a decrease in the average number of bound hydrophobes in any one region of intermolecular association — hence the reduction in viscosity shown in the latter stages of the curve given in Fig. 11.

The increased interaction between HM-HEC and SDS compared to HEC and SDS is illustrated in Figs 11–13. The observation of interaction between HEC and SDS at concentrations of the latter just below its CMC is in good agreement with the viscometric data of Goddard and Hannan (1977).

CONCLUSIONS

The marked differences in the solution properties of HEC and HM-HEC can be attributed to the hydrophobic associations present within the latter system. Spectroscopic probe techniques provide a convenient method of investigating the nature of such hydrophobic interactions and, hence, elucidating the mechanism responsible for the unusual rheological properties of hydrophobically associating polymers.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the Oji Paper Company Ltd, Japan, for permitting Ryohei Tanaka's extended period of study at the North East Wales Institute.

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