Local structural correlations in anisotropic aqueous solutions of hydroxypropyl cellulose

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Wide-angle X-ray scattering procedures are utilized to study the local structure of isotropic and anisotropic aqueous solutions of hydroxypropyl cellulose (HPC). The X-ray scattering data for a systematic series of solutions with 0–100% w/v HPC are reported and these curves show distinct and significant variations as the concentration of HPC is increased. In particular, a diffuse scattering peak whose position ($s \sim 0.34$–0.54 Å^{-1}) is composition dependent, develops in parallel with the formation of the anisotropic liquid crystal phase. There is no evidence to support the concept of clusters of HPC molecules in the anisotropic phase. The variations in peak positions and the synergistic nature of the scattering suggests that the water is largely associated with each HPC chain.

(Keywords: WAXS; hydroxypropyl cellulose; local structure; solution)

Introduction

Hydroxypropyl cellulose (HPC), in common with other cellulose derivatives forms single phase anisotropic solutions with a range of solvents, when the concentration of HPC exceeds a critical value[1,2]. These anisotropic solutions usually exhibit a cholesteric liquid crystal phase, the particular characteristics being dependent upon the concentration and the temperature[3]. The formation of such anisotropic solutions has been associated with the relatively stiff cellulose chain. A number of studies have shown correlations between chain flexibility and the phase boundaries for different cellulose derivatives and solvent combinations[2,4]. At the heart of this type of approach is that the impenetrability of the 'stiff' molecules leads at increasing concentrations to a spontaneous molecular alignment[5,6]. Much of the current understanding has not included anisotropic intermolecular potentials or the role of the solvent. The interactions between the molecules which lead to the formation of the liquid crystal state and those between the solvent and the chain segments fall within the scale of structure of ~1–50 Å. Little has been reported in the literature on this scale of structure especially in the solution state[2,7], although a comprehensive study of the solid state has been reported by Samuels[8]. However, there have been proposals that the anisotropic solutions consist of localized bundles of HPC chains in an isotropic matrix[9] and that the side chains in HPC and other cellulose derivatives act as an internal solvent[1]. In this study we have set out to clarify these matters by systematically exploring the local correlations which arise in both anisotropic and isotropic solutions of HPC in water using quantitative wide-angle X-ray scattering (WAXS) procedures.

Experimental

Materials. All solutions were prepared[10] using HPC from Aqualon (Klucel E) with a molecular weight of 60000. Such polymers have a random distribution of hydroxypropyl chains with average degree of molar substitution[10] of 3.0. The polymer was dried *in vacuo* at 50°C for 12 h before use. Freshly distilled water was used as the solvent. Appropriate quantities of HPC were mixed thoroughly by stirring with distilled water to yield solutions of concentrations 0, 30, 40, 45, 50, 55, 60 and 65 wt% HPC. Thereafter the solutions were centrifuged at 4000 rev min^{-1} for 4 h to remove air bubbles. The pure material was considered in both powdered and compressed pellet forms of the dried HPC. The samples were sealed into cells ~1 mm thick using mica windows with a stainless steel spacer. Each of the cells was examined optically before and after the X-ray scattering studies to determine the phase state of that sample. Samples containing 40% w/v HPC in water or less exhibited isotropic solutions; this was in accord with previous studies[1,2].

WAXS measurements. A computer controlled three-circle diffractometer operating in a symmetrical transmission mode was used to collect X-ray scattering data. All measurements were performed at room temperature (~22°C). The X-ray source was a copper targeted sealed tube equipped with pinhole collimation and monochromator set to pass CuKα radiation. The intensity function $I(s_{exp})$* was recorded over the range $0.2 < s < 6$ Å^{-1} in steps of $\Delta s = 0.02$ Å^{-1}. The counting time was

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*$s = 4\pi\sin\Theta/\lambda$, where 2Θ is the scattering angle and λ is the incident X-ray wavelength

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adjusted to ensure a statistical accuracy of <1%. The intensity data so obtained were corrected, using standard methods[11,12], for the angular-dependent absorption, sample volume, polarization, and multiple and incoherent scattering. The corrected intensity data were normalized to the independent scattering for a composition unit involving both the HPC and the water using the procedure described by Krogh Moe[13]. An intensity function:

$$I(s) = [KI_{\mathrm{corr}}(s) - I_{\mathrm{incoh}}(s)]/\sum w_i Z_i \qquad (1)$$

was calculated where K is a scaling constant which normalizes the scattering intensities to the composition unit, $I_{\mathrm{corr}}(s)$ is the fully corrected intensity data, $I_{\mathrm{incoh}}(s)$ is the calculated Compton scattering and w_i is the number of atoms with atomic number Z_i in the composition unit. The denominator ensures that all sets of scattering data are normalized to the same absolute electron unit intensity scale, regardless of solution concentration thus facilitating comparison and analysis.

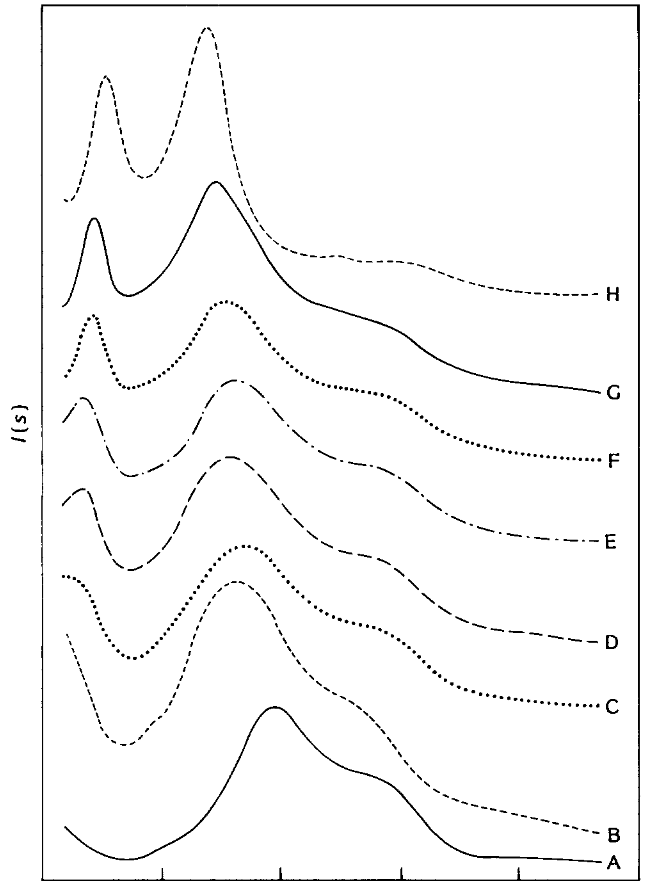

Figure 1 Plots of the corrected and normalized scattering functions $I(s)$ for solutions of HPC in water of varying concentrations: (A) 0; (B) 30; (C) 40; (D) 45; (E) 50; (F) 60; (G) 65; (H) 100% w/v HPC

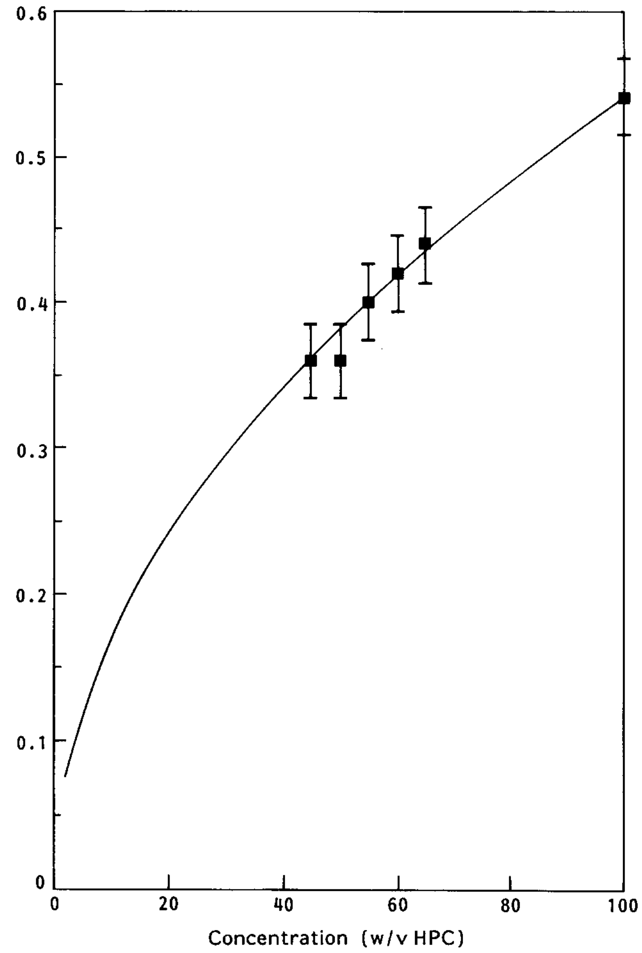

Figure 2 Position of the first diffuse maximum observed in the scattering functions of *Figure 1* plotted as a function of HPC concentration. The dotted line represents a fit to the function $s_0 = kc^{1/2}$, where k is a constant

Results and discussion

The X-ray scattering functions $I(s)$ [equation (1)] for the full range of solution concentrations from 0 to 100% w/v HPC are displayed in *Figure 1*. In the case of 100% HPC, identical data were obtained for both the powdered and compressed pellet samples. The curves shown in *Figure 1* show clear systematic changes as the concentration of HPC increases. Generally there are three features in the scattering vector range considered here. There is an intense but broad feature whose maximum shifts from ~1.8 to ~1.3 Å^{-1} with increasing HPC concentration. At higher scattering vectors there are much weaker but still distinct diffuse peaks whose positions are also composition dependent. These features in the region $s \sim 1.6$ Å^{-1} and at higher scattering vectors may be largely attributed to intrachain correlations. The third feature is a broad peak in the range 0.36–0.54 Å^{-1}. This is most pronounced in the solutions exhibiting a liquid crystal phase and it is apparently absent in the curves of isotropic solutions. The position and the strength of this peak are very dependent upon the concentration. As *Figure 2* shows the position of this peak varies continuously with concentration within the range of concentrations which exhibit the anisotropic phase. The strength of the peak develops at the isotropic/anisotropic boundary in a manner expected for a structural feature related to a phase change. Thus it can be concluded that there is an additional degree of ordering within anisotropic solutions. Although direct translation to real space distances is not straightforward in scattering curves from non-crystalline systems[12], this additional peak corresponds to separations in the range of 11.6–17.5 Å. It clearly has the same origin as the equivalent peak in 100% HPC. This was attributed by Samuels to an interchain correlation[8]. X-ray scattering studies of deformed lyotropic liquid crystal elastomers

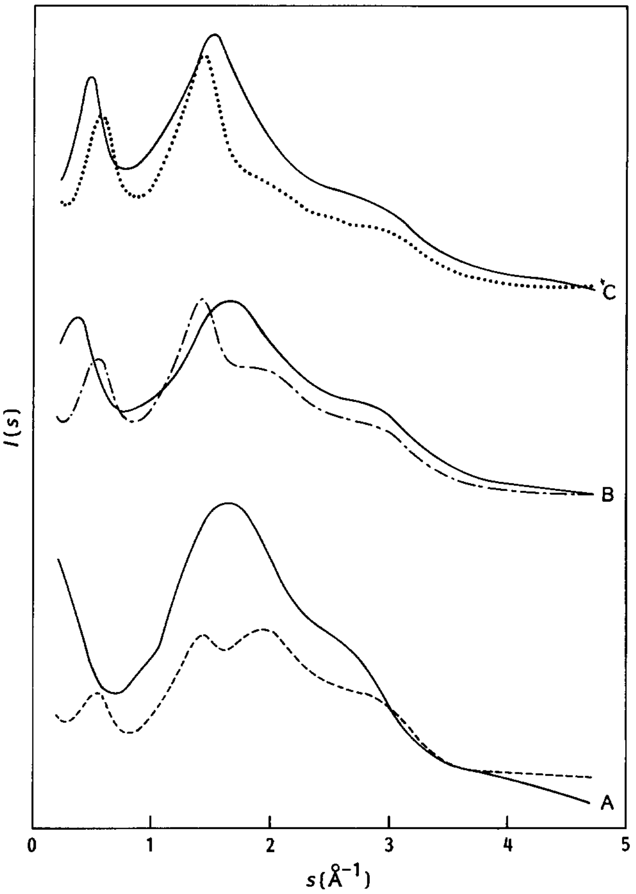

Figure 3 Plots of the corrected and normalized scattering functions $I(s)$ for (A) 30%, (B) 50% and (C) 65% w/v HPC solutions obtained directly by experiment (solid line). The broken lines represent scattering functions calculated by adding in the appropriate proportions of the scattering curves for water and HPC

based on HPC[14] show an intensification of this peak in the plane normal to the extension axis confirming the interchain origin of this scattering feature.

One proposal for the local structure of the anisotropic solutions is that the HPC chains are in clusters. In *Figure 3* a comparison is shown between the scattering functions $I(s)$ and those obtained by adding the scattering functions for the parent components, namely HPC and water, in the appropriate proportions for the 30, 50 and 65% w/v HPC solutions. If a two-phase model was appropriate, then clearly the simulated functions would match the observed functions. Inspection of *Figure 3* shows this not to be the case. There are distinct and significant differences which must arise as a consequence of a more intimate mixing of the HPC molecules and water. The fact that the interchain peak shifts its position with composition is another indication that molecular microscale fixing of the two components must take place. The functional form of the variation in peak position (s_0) with concentration approaches:

$$s_0 \propto c^{1/2} \qquad (2)$$

This relation suggests a two-dimensional packing arrangement, which is a natural consequence of the local parallelism of the HPC chain segments. However, the fact that there is this relationship which holds for both the anisotropic solutions and the solid HPC suggests that the interaction distance is defined by the number density of HPC chains and not by the cross-section of the HPC chain. It seems appropriate to relate this observation to the fact that the water is largely associated with each HPC chain.

Although anisotropic solutions form above the critical concentration, phase separation results[1] if such solutions are heated above 40°C. X-ray scattering patterns of such phase-separated solutions exhibit a pattern which is much more clearly related to the arithmetic sum of the scattering patterns of the constituent components. In particular on heating the interchain scattering peak moves towards the same scattering vector as observed for the solid sample. In other words, samples which are clearly two phase show a constant interchain interaction distance, whereas the anisotropic solutions exhibit peaks with a concentration-dependent position.

Figure 1 shows that the development of an anisotropic phase is accompanied by increasing well defined correlations between the HPC molecules. Since it is assumed that the liquid crystal phase results from intermolecular interactions, which in the simplest models are of the hard repulsive form, it is natural that such correlations are observed in the anisotropic solutions. However what is the nature of these interactions and what is the role of the solvent?

The breadth of the scattering peak for $s \sim 0.36$–0.54 Å^{-1} indicates a highly disordered structure with a correlation length of ~20–30 Å or effectively two or three chains. In both the liquid crystal and isotropic phases the centres of gravities of the constituent chain segments are distributed randomly, although of course in the liquid crystal phase the chain segments are arranged more or less in a parallel manner. The high level of mutual alignment of neighbouring chain segments means that the interchain interactions are more or less two-dimensional. The two-dimensional nature of the correlations is confirmed by the $c^{1/2}$ dependence of the position of the interchain peak. We shall represent the interchain correlations as those arising from randomly packed discs. These discs were generated by considering the HPC molecules to be parallel rigid rods, the water molecules to be spheres and considering a cross-section through the solution, perpendicular to the rods. There is no analytical solution to the structure factor for a system of randomly packed discs or mixtures of discs in contrast to the situation for three-dimensional spheres[15,16]. We have calculated the scattering based on a model of randomly packed discs described elsewhere[17,18]. When the water and the HPC molecules are disposed randomly, the first peak in the structure factor remains at a more or less constant scattering vector with increasing intensity as the concentration of 'HPC molecules' increases. This is a consequence of the fact that the defining distance in the model, i.e. the disc diameter or cross-section of the HPC molecule, remains constant.

In contrast, when the water molecules are associated with each HPC chain, such that the cross-section of the HPC chain varies with concentration, the position of the first peak in the structure factor for the randomly packed discs varies with concentration in a similar manner to that observed experimentally.

Whilst these models are by their nature somewhat first order, they do highlight the distinct and significant changes which take place in the scattering patterns of HPC/water solutions as the concentration changes. There are marked changes in the scattering at low scattering vectors when the structure of the solution changes from an isotropic to anisotropic form. To observe such peaks in a dilute system, there must be well defined potentials whose dimension is greater than the chain diameter. This is only possible if the majority of the solvent is structurally associated with each HPC chain. These observations differ from the preliminary results of a limited study of the same HPC system[7]. There is substantial evidence to confirm that the anisotropic solutions do not consist of discrete clusters of HPC chains. It is clear that the phase transition to the anisotropic solutions is accompanied by or is driven by the development of short range interchain interactions. The concentration dependence of the scattering patterns points to an association of the solvent with the HPC chains. The nature of this association and the role of the solvent is unclear and a more detailed study is in progress.

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