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Bo-Chy Wang; Richard J. Spontak

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Phase behaviour of aqueous hydroxypropylcellulose mesophase mixtures: Molecular weight considerations

by BO-CHY WANG and RICHARD J. SPONTAK*

Department of Materials Science and Engineering, North Carolina State
University, Raleigh, NC 27695, U.S.A.

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As a self-organizing macromolecule, hydroxypropylcellulose serves as an excellent candidate for studies of complex polymer mixtures. In this work, we examine aqueous mixtures composed of two hydroxypropylcellulose grades, Klucel-F (HPC) and Klucel-H (HHPC), with molecular weights of 10^5 and $10^6\,\mathrm{g\,mol^{-1}}$, respectively. Polarized light microscopy and deuterium nuclear magnetic resonance have been utilized to ascertain changes in the chiral nematic mesophase of HPC upon addition of <15 wt % HHPC. Results obtained here suggest that the HHPC either disrupts the molecular organization of the HPC mesophase, or induces immiscibility and partitions between HPC- and HHPC-rich phases.

1. Introduction

Hydroxypropylcellulose, prepared by the base-catalysed reaction of propylene oxide with cellulose, constitutes an important commercial derivative of cellulose. Since it retains stiff anhydroglucose linkages along the backbone, it serves as an excellent example of a semi-rigid macromolecule capable of exhibiting liquid crystallinity (LC) both at elevated temperatures and in a wide variety of organic solvents, as well as in water. Numerous studies addressing the effects of temperature [1–3], solvent [4–11] and molecular weight [12, 13] on the phase behaviour of this synthetic polymer have been conducted since the pioneering report of mesomorphic hydroxypropylcellulose by Werbowyj and Gray [4]. The phase diagram of intermediate-molecular-weight hydroxypropylcellulose (Klucel-E, with a molecular weight of *c.* 80 000 $\mathrm{g\,mol^{-1}}$) in water exhibits a chiral nematic mesophase when the polymer concentration exceeds $\approx$41 wt % at ambient temperature. While this water-soluble polymer has proven valuable in commercial applications such as rheology modification, encapsulation, stabilization and chemical delivery (especially if LC order is locked-in through, for example chemical crosslinking [14]), it also facilitates fundamental studies aimed at exploring the self-organization behaviour of one LC polymer in the presence of a second, but not necessarily LC, polymer [13, 15–22].

Early studies have shown that aqueous hydroxypropylcellulose tends to be immiscible with non-LC polymers such as poly(ethylene glycol) [13, 17] poly(acrylic acid) [16, 17], poly(*N*,*N*-dimethylacrylamide) [16] and poly(-vinylidene fuoride) [18]. Miscibility of hydroxypropylcellulose with non-LC polymers can, however, be greatly affected by promoting interpolymer association through site-specific interactions with, for instance, *p*-styrenesulfonate/3-methacryloxypropyltrimethoxysilane copolymers [22]. While these previous efforts have focused on phase miscibility between hydroxypropylcellulose and a non-LC water-soluble polymer, related studies have sought to discern the extent of molecular mixing and cooperativity in solutions containing two chemically dissimilar LC polymers. As in the solutions described above, binary LC polymer solutions, such as those composed of hydroxypropylcellulose and ethyl cellulose in either acetic [15] or acrylic [19] acid, also tend to be immiscible, even in the isotropic phase.

In aqueous solutions, the phase behaviour of anisotropic hydroxypropylcellulose solutions has been investigated in the presence of xanthan gum (XG), a helical polysaccharide exhibiting LC behaviour at very low polymer concentrations [23]. At relatively low concentrations, XG added to anisotropic hydroxypropylcellulose solutions enhances solvent binding (and consequently LC order), as discerned from an increase in the magnitude of the quadrupolar peak splitting ($\Delta\upsilon_q$) measured by deuterium nuclear magnetic resonance (^{2}H NMR) spectroscopy [21, 21, 24]. An increase in either the concentration of XG or hydroxypropylcellulose yields $\Delta\upsilon_q$ values that are comparable to those obtained for hydroxypropylcellulose solutions in the absence of XG, suggesting that XG molecules partition between hydroxypropylcellulose- and XG-rich phases. In the case of mixtures of hydroxypropylcellulose and deoxyribonucleic acid (DNA) in concentrated aqueous solutions,

*Author for correspondence.

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however, site-specific interactions again affect phase miscibility [25].

In the present work, we employ polarized light microscopy (PLM) and ^{2}H NMR to examine the phase behaviour of aqueous solutions consisting of two commercial grades of hydroxypropylcellulose differing by about an order of magnitude in molecular weight (M). Results obtained here are also compared with those reported earlier [21] regarding the scaling dependence of ^{2}H NMR quadrupolar peak splitting on polymer concentration.

2. Experimental

2.1. *Materials*

The two hydroxypropylcellulose grades used in this study were Klucel-F ($M \approx 10^5\,\mathrm{g\,mol^{-1}}$) and Klucel-H ($M \approx 10^6\,\mathrm{g\,mol^{-1}}$), supplied by Hercules Inc. as powders and used as-received. To facilitate description, these hydroxypropylcellulose grades are hereafter referred to as HPC and HHPC, respectively. Two series of solutions were examined in both distilled H_2O or 99·9 per cent pure D_2O purchased from Aldrich Chemical Co. The first series consisted of HPC solutions at weight-fraction concentrations (ϕ_{HPC}) ranging from 45 to 70 wt %, whereas the HPC/HHPC solutions comprising the second series were limited to total polymer concentrations (ϕ_{P}) of less than 60 wt % (due to viscosity and, hence, homogeneity considerations).

2.2. *Methods*

Solutions for PLM analysis were prepared by adding predetermined quantities of HPC and HHPC to H_2O and mixing at ambient temperature until dissolution of the HPC/HHPC powder was visually detected. The resulting solutions were sealed and placed in a constant-humidity desiccator for two weeks to ensure equilibration without H_2O evaporation. A small quantity of each solution was then smeared onto a glass slide, and a cover slip was placed over the solution and epoxied to the slide so that the sheared solution could relax for an additional week with virtually no change in solution composition. Micrographs were recorded under crossed polars using a Nikon Optiphot optical microscope with a 20 × objective lens. Solution for ^{2}H NMR were prepared by adding either HPC, HHPC or HPC/HHPC and D_2O piecewise, little by little, to NMR glass tubes measuring 10 mm in diameter. The tubes were sealed, and the solutions were allowed to equilibrate for a period of 3 weeks prior to analysis (to avoid transient effects [24]). Measurements were performed on an AMX-300 spectrometer operated at 46·1 MHz and 20·5°C.

3. Results and discussion

Optical micrographs of the aqueous HPC and HPC/HHPC solutions, obtained under crossed polars, are displayed in figure 1 for all of the HPC/HHPC solution concentrations examined here. Figure 1 (*a*) corresponds to the solution containing 50 wt % HPC and reveals a polygonal chiral nematic texture. The inset in figure 1 (*a*) is a higher magnification image of a more well-defined polygonal texture that arises as the HPC concentration is increased to 60 wt %. From the subsequent micrographs in figure 1, it is clear that this morphology is highly disrupted upon addition of HHPC. In figure 1 (*b*)–(*d*), the concentration of HPC is maintained constant at 45 wt % (near the isotropic→mesophase transition concentration), while the HHPC concentration is progressively increased from 5 wt % (figure 1 (*b*)) to 15 wt % (figure 1 (*d*)). Large, highly birefringent regions are seen to exist in the 45/5 and 45/10 wt % HPC/HHPC solutions (figures 1 (*b*) and 1 (*c*), respectively), whereas comparable regions appear to be significantly smaller as the HHPC concentration is increased further (figure 1 (*d*)).

When the HPC concentration is 50 wt % and HHPC is added, large birefringent regions are again evident at 5 wt % HHPC (figure 1 (*e*)), but give rise to a more intimate mixture of small birefringent regions at 10 wt % HHPC (figure 1 (*f*)). Note that the solutions displayed in figures 1 (*b*) and 1 (*e*) both contain the same fraction of HHPC (ϕ_{HHPC}), while those corresponding to figures 1 (*c*) and 1 (*e*) have the same ϕ_{P}. It is therefore not surprising that these three images appear very similar. Likewise, figure 1 (*c*) ($\phi_{\mathrm{HHPC}} = 0{\cdot}15$) most closely resembles figure 1 (*f*) ($\phi_{\mathrm{HHPC}} = 0{\cdot}10$), despite the larger population of small birefringent regions in figure 1 (*c*). This similarity is particularly interesting, since both solutions have the same ϕ_{P} and, as seen in the next section, comparable deuteron binding and, by inference, overall supramolecular order.

Examples of ^{2}H NMR data are shown in figure 2 for HPC/D_2O and HHPC/D_2O solutions, each containing 50 wt % polymer. The one-dimensional ^{2}H NMR pattern obtained from the HHPC solution (figure 2 (*a*)) appears as a single peak with a flattened, and slightly asymmetric, top. The HPC solution (figure 2 (*b*)), on the other hand, clearly exhibits quadrupolar peak splitting, the magnitude of which ($\Delta\upsilon_{\mathrm{q}}$) is given by

$$\Delta\upsilon_{\mathrm{q}} = \frac{3}{4}\frac{e^2|q|Q}{h}\langle 3\cos\theta - 1\rangle \tag{1}$$

where $e^2|q|Q/h$ is the quadrupole coupling constant [24] (≈220 kHz for D_2O [26]), θ is the angle between the O–D bond vector and the applied magnetic field, and the angled brackets denote a time average. Such

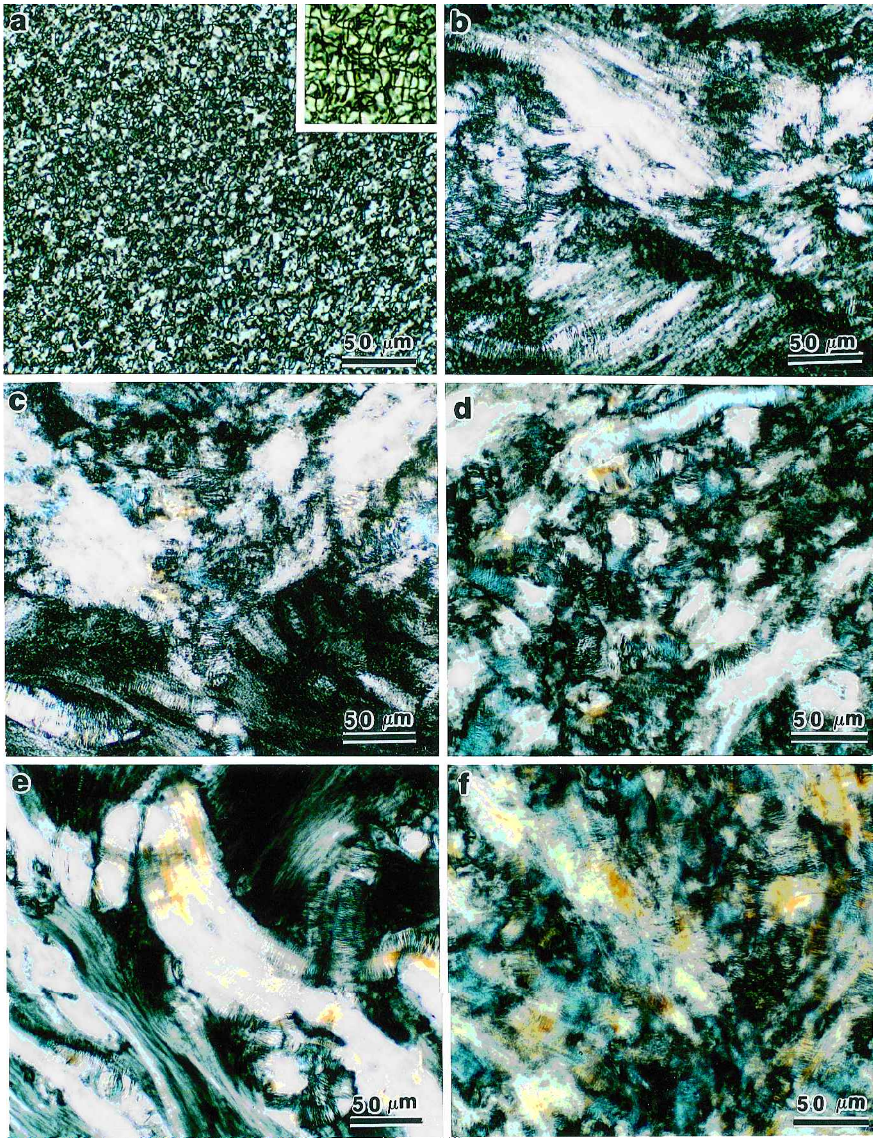

Figure 1. Optical micrographs obtained under crossed polars from several HPC/H_2O solutions: (*a*) $\phi_{HPC}=0{\cdot}50$ (inset: $\phi_{HPC}=0{\cdot}60$); (*b*) $\phi_{HPC}=0{\cdot}45$, $\phi_{HHPC}=0{\cdot}05$; (*c*) $\phi_{HPC}=0{\cdot}45$, $\phi_{HHPC}=0{\cdot}10$; (*d*) $\phi_{HPC}=0{\cdot}45$, $\phi_{HHPC}=0{\cdot}15$; (*e*) $\phi_{HPC}=0{\cdot}50$, $\phi_{HHPC}=0{\cdot}05$; (*f*) $\phi_{HPC}=0{\cdot}50$, $\phi_{HHPC}=0{\cdot}10$.

splitting occurs as a result of highly anisotropic deuteron binding, and consequently provides a measure of supramolecular organization in LC solutions [24]. Thus, figure 2 indicates that at 50 wt % polymer, the HHPC solution is far more isotropic than the HPC solution possessing chiral nematic order. This observation is consistent with data [27] revealing that aqueous HHPC solutions undergo a dramatic viscosity increase (and probable gelation) at relatively low polymer concentrations at ambient temperature. Since ^{2}H NMR profiles reflect the anisotropy of D_2O molecules in these solutions, polymer–solvent binding must be explicitly considered. The mobility of a fluorescein dye can be used to probe such binding in dilute and concentrated aqueous hydroxypropylcellulose solutions and has been found [28] to be strongly (exponentially) dependent on polymer concentration, but virtually independent of polymer molecular weight.

A series of ^{2}H NMR patterns for HPC/D_2O solutions varying in ϕ_{HPC} is presented in figure 3, revealing that the magnitude of quadrupolar peak splitting (and the extent of supramolecular order) increases with increasing ϕ_{HPC}. Similar behaviour has been reported earlier [20, 21, 24] for HPC/D_2O solutions prepared in beakers, inserted into NMR tubes and allowed to equilibrate. A comparison of these data is provided in figure 4, in which $\Delta\upsilon_q$ is shown as a function of ϕ_{HPC}. While the values of $\Delta\upsilon_q$ are generally larger for solutions prepared

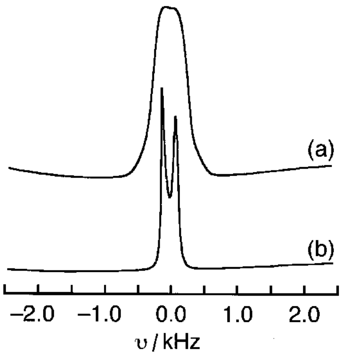

Figure 2. ^{2}H NMR patterns of (*a*) HHPC/D_2O and (*b*) HPC/D_2O solutions at $\phi_P = 0{\cdot}50$. Quadrupolar peak splitting due to the existence of a chiral nematic mesophase is evident in (*b*).

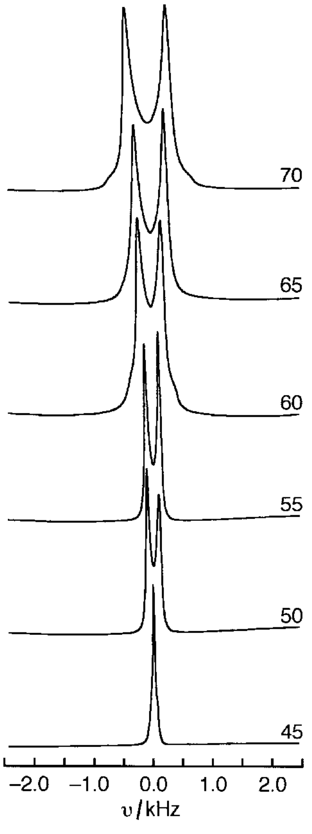

Figure 3. ^{2}H NMR patterns of HPC/D_2O solutions in which ϕ_{HPC} is varied from 0·45 to 0·70 in 0·05 increments from top to bottom (concentrations are designated as $100^*\phi_{HPC}$). The pattern for $\phi_{HPC} = 0{\cdot}45$ exhibits a broad base, but quadrupolar peak splitting is not observed until $\phi_{HPC} \geqslant 0{\cdot}50$.

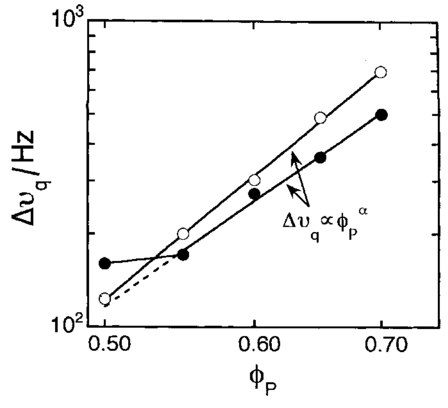

Figure 4. Variation of $\Delta\upsilon_q$ with HPC concentration in two series of mesomorphic HPC/D_2O solutions: (●) this study and (○) reference [21]. In this double-logarithmic representation, $\Delta\upsilon_q$ is seen to scale as ϕ_{HPC} over most of the concentration range examined.

outside the NMR tubes relative to those measured from solutions mixed in the tubes, this difference is not surprising and may be attributed to either or a combination of the following two factors: (i) a difference in HPC molecular weight (Klucel-E, with $M \approx 80\,000\,\mathrm{g\,mol^{-1}}$, was utilized in the previous study) and (ii) a difference in residual stresses (after the externally prepared specimens were sheared during insertion into the tubes). In general, however, the $\Delta\upsilon_q$ measured from the two different studies are in reasonably good agreement and demonstrate that, over most of the solution concentration range examined, $\Delta\upsilon_q \sim \phi_{HPC}^{\alpha}$, where α is approximately 4·4 for solutions prepared inside the NMR tubes and 5·2 for solutions mixed externally. An anomalous feature of the data collected in the present work is that this power-law relationship fails at low HPC concentrations ($\phi_{HPC} = 0{\cdot}50$), where $\Delta\upsilon_q$ appears to be only very slightly dependent on ϕ_{HPC}. This characteristic is not evident in the data reported elsewhere [21].

A series of ^{2}H NMR profiles is displayed in figure 5 for HPC/HHPC/D_2O solutions in which ϕ_{HPC} is held constant at 0·45 and ϕ_{HHPC} is varied from 0·00 to 0·15 (bottom to top). As seen in this figure (as well as in figure 3), quadrupolar peak splitting does not occur when $\phi_{HPC} = 0{\cdot}45$, even though the isotropic→mesophase transition for Klucel-F is expected to lie between 40 and 45 wt % HPC. Close examination of the pattern for the $\phi_{HPC} = 0{\cdot}45$ system reveals a broad, somewhat asymmetric base, unlike the distinct line pattern of an isotropic solution [20], suggesting that HPC is weakly liquid crystalline at this concentration. Upon addition of 5 wt % HHPC, quadrupolar peak splitting becomes evident, superimposed on a third, middle peak corresponding to a weakly ordered (or possibly isotropic) HPC fraction. Similar, but more pronounced, behaviour is seen in figure 5 when ϕ_{HHPC} is increased to 0·10. Finally, when $\phi_{HHPC} = 0{\cdot}15$ and the total polymer concentration is 60 wt %, the middle peak vanishes completely, leaving behind a pair of split peaks. Note that disappearance of the middle peak does not necessarily imply that

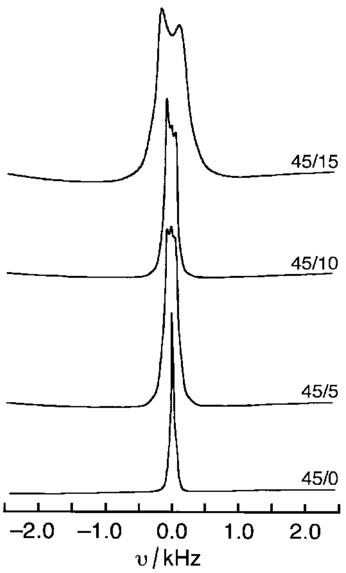

Figure 5. ^{2}H NMR patterns for HPC/HHPC/D_2O solutions in which $\phi_{\mathrm{HPC}} = 0{\cdot}45$ and ϕ_{HHPC} is varied from 0·00 to 0·15 in 0·05 increments (bottom to top). Blends are labelled as $\phi_{\mathrm{HPC}}/\phi_{\mathrm{HHPC}}$.

the nearly isotropic HPC fraction responsible for the middle peak does not exist; it simply means that this fraction is measurably less than the anisotropic fraction responsible for quadrupolar peak splitting. It is important to recognize from the patterns displayed in figure 5 that the 45/15 HPC/HHPC solution exhibits a substantially larger $\Delta\upsilon_q$ than any of the other solutions with $\phi_{\mathrm{HPC}} = 0{\cdot}45$.

If ϕ_{HPC} is increased to 0·50, then addition of HHPC to HPC/D_2O solutions results in the ^{2}H NMR patterns shown in figure 6. As ϕ_{HHPC} is increased from 0·00 to 0·10 (bottom to top), the extent of quadrupolar peak splitting appears almost invariant, indicating that $\Delta\upsilon_q$ is not strongly dependent on ϕ_{HHPC} in these solutions. Recall that, at this HPC concentration, the HPC molecules order into a well-established LC mesophase (see the inset of figure 1 (*a*)). Close examination of the profiles in figure 6 reveals that the peak intensities relative to the local minimum that separates the split-peak pairs decreases steadily as ϕ_{HHPC} increases. This trend is not surprising, since the profile must gradually evolve, as ϕ_{HHPC} is increased, into the one shown in figure 2. While solutions with higher concentrations of ϕ_{HHPC} are initially targeted for analysis in this study, they proved highly problematic due to the accompanying rise in solution viscosity (and corresponding reduction in solution homogeneity) and were subsequently abandoned.

Figure 7 illustrates the dependence of $\Delta\upsilon_q$ on total polymer concentration (ϕ_P) for HPC/D_2O solutions with and without added HHPC. In all cases, $\Delta\upsilon_q$ is seen to increase as ϕ_P increases. For solutions with $\phi_{\mathrm{HPC}} = 0{\cdot}45$, addition of $\leqslant 10$ wt % HHPC induces quadrupolar peak splitting in an otherwise isotropic solution (see figure 5) and is therefore responsible for enhancing the extent of deuteron binding and, hence, supramolecular order in the solution. The magnitudes of $\Delta\upsilon_q$ corresponding to these solutions are significantly lower than are those for single-phase HPC/D_2O solutions in the absence of HHPC. Note that, when $\phi_{\mathrm{HHPC}} = 0{\cdot}15$, however, $\Delta\upsilon_q$ increases abruptly. For solutions with 50 wt % HPC, addition at 5 wt % HHPC has very little measurable effect on $\Delta\upsilon_q$, whereas 10 wt % HHPC yields a slight increase in $\Delta\upsilon_q$.

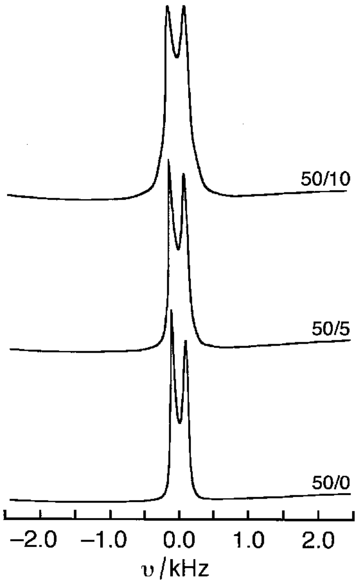

Figure 6. ^{2}H NMR patterns for HPC/HHPC/D_2O solutions in which $\phi_{\mathrm{HPC}} = 0{\cdot}50$ and ϕ_{HHPC} is varied from 0·00 to 0·10 in 0·05 increments (bottom to top). As in figure 5, the blends are labelled as $\phi_{\mathrm{HPC}}/\phi_{\mathrm{HHPC}}$. Note that $\Delta\upsilon_q$ appears to be nearly independent of ϕ_{HHPC} (and ϕ_P).

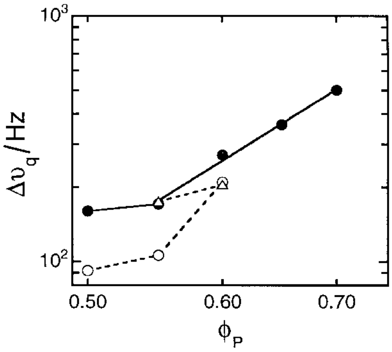

Figure 7. Dependence of $\Delta\upsilon_q$ on ϕ_P shown on double-logarithmic axes for HPC/HHPC/D_2O solutions in which $\phi_{\mathrm{HHPC}} = 0{\cdot}00$ (●), $\phi_{\mathrm{HPC}} = 0{\cdot}45$ (○) and $\phi_{\mathrm{HPC}} = 0{\cdot}50$ (△). The dashed lines serve to connect the data points.

An interesting feature in figure 7 is that both series of HPC/HHPC solutions exhibit comparable $\Delta\upsilon_q$ when $\phi_P = 0{\cdot}60$. Recall from figure 1 that polarized light micrographs of these solutions (one with 15 wt % HHPC and the other with 10 wt % HHPC) appear very similar. These two HPC/HHPC/D_2O solutions exhibit the same $\Delta\upsilon_q$ as single-phase HPC/D_2O solutions containing about 57 wt % HPC. Since the actual concentrations of HPC in these solutions are only 45 and 50 wt %, a fraction, if not all, of the added HHPC must be responsible for the observed increase in $\Delta\upsilon_q$. Due to the present absence of data regarding the ternary HPC/HHPC/D_2O phase diagram, we refrain here from trying to estimate this fraction. According to light microscopy, however, these systems appear phase-separated, in which case it follows that mesomorphic HPC, while chemically identical to HHPC, does not accommodate all of the HHPC molecules even at relatively low concentrations of added HHPC. Whereas immiscibility between dissimilar LC and non-LC polymers in chiral nematic HPC can, to some extent, be attributed to chemical differences (which yield positive deviations from Raoultian behaviour), the data presented here indicate that molecular weight disparity alone may induce entropically-driven phase separation in complex solutions containing at least one LC-forming polymer. This mechanism may not be surprising in light of calorimetry measurements [29] that imply entropic considerations are likewise responsible for the isotropic→mesophase transition in aqueous HPC solutions.

Molecular-weight-induced immiscibility in mixtures of mesomorphic macromolecules is not peculiar to the chiral nematic HPC-based systems examined here. Diblock copolymers, composed of two long contiguous sequences of chemically dissimilar repeat units, microphase-order into periodic nanoscale structures if the sequences ('blocks') are sufficiently incompatible [30]. While it must be remembered that diblock copolymers, which exhibit thermotropic mesophases in the melt, differ from the HPC solutions examined here, phase separation induced solely by molecular weight disparity has, nonetheless, been observed [31, 32] in, as well as predicted [33] for, binary mixtures of diblock copolymers of comparable composition. While the complex phase behaviour of such mixtures can be correlated with molecular characteristics and described by existing theoretical formalisms, the same cannot be said for aqueous mixtures of HPC and HHPC. No quantitative correlations elucidating the effect of hydroxypropylcellulose molecular weight on the mixing behaviour of HPC/HHPC solutions can yet be established due to insufficient comparative data.

4. Conclusions

The mixing behaviour of anisotropic aqueous solutions containing both HPC ($M \approx 10^5\,\mathrm{g\,mol^{-1}}$) and HHPC ($M \approx 10_6\,\mathrm{g\,mol^{-1}}$) have been investigated using polarized light microscopy and deuterium nuclear magnetic resonance spectroscopy. Optical micrographs reveal that the polygonal chiral nematic texture observed in LC-ordered HPC/H_2O solutions is lost upon addition of as little as 5 wt % HHPC. As the concentration of HHPC is increased, regions of strong LC birefringence are observed to gradually decrease in size. From ^{2}H NMR analysis, quadrupolar peak splitting is first observed here in HPC/D_2O solutions at a concentration of 50 wt % HPC. At higher HPC concentrations, the magnitude$_{\alpha}$ of quadrupolar peak splitting is found to scale as ϕ_{HPC}, in agreement with previous work [21]. While further studies are clearly needed to ascertain the universality of α, the slight variation in the magnitude of α observed here may reflect differences in sample characteristics and preparation.

When HHPC is added to isotropic HPC/D_2O solutions, quadrupolar peak splitting is induced, indicating that HHPC molecules cooperate with HPC molecules to enhance solvent binding and overall LC ordering. In chiral nematic HPC/D_2O solutions, addition of HHPC has very little effect on the magnitude of the observed quadrupolar peak splitting. Comparison of optical micrographs and $\Delta\upsilon_q$ values between HPC/D_2O and HPC/HHPC/D_2O solutions suggests that, at sufficiently high HPC or HHPC concentrations, the HHPC molecules partition so that a cooperative fraction remains within the ordered HPC/D_2O matrix and increases $\Delta\upsilon_q$, the extent of deuteron binding and, by inference, the degree of supramolecular order. The data presented in this work demonstrate that mesomorphic HPC/HHPC solutions undergo (athermal) phase separation induced solely by molecular weight disparity. It would be highly desirable to ascertain if such entropically-driven phase immiscibility, observed in mixtures of other self-organized macromolecules (for example, diblock copolymers), is a general feature of mixtures of chemically identical mesomorphic macromolecules.

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