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Review

Concentration selective hydration and phase states of hydroxyethyl cellulose (HEC) in aqueous solutions

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ABSTRACT

Solution behaviour of hydroxyethyl cellulose (HEC) is reported in the polymer concentration range spanning over two decades (c = 0.002–5% (w/v)). The results conclude the following: (i) dilute solution regime prevailed for c < 0.2% (w/v), flexible HEC fibres of typical length ≈1 μm and persistence length ≈10 nm were found here, (ii) for 0.2 < c < 1% (w/v), a semidilute phase comprising soluble aggregates of hydrated HEC fibrils were observed with the material exhibiting viscoelastic behaviour and (iii) when 1 < c < 5% (w/v) the solution behaved with melt-like attributes with substantial embedded heterogeneity; viscous to elastic transition was observed in this region. Raman spectral, and DSC data indicated distinctive hydration of HEC fibres in the aforesaid concentration regimes. Cole–Cole plots revealed phase homogeneity and miscibility was limited to concentrations less than ∼2% (w/v). For higher polymer concentrations, strong fibre–fibre interactions prevailed and samples became heterogeneous.

Contents

1. Introduction

Cellulose is world's one of the most abundant biopolymers. It forms skeletal material of plant cell walls. The polymorphic forms and derivatives of cellulose are the subject of a large body of work [1–10]. Hydroxyethyl cellulose (HEC) is a low charge density hydrophilic biopolymer. Cationic polymers, particularly biopolymers, have found applications as stabilizers and thickeners in paint formulations and as hair and eye-care solutions. The remarkable physical properties associated with cellulose polymers accrue from their water and organic solvent solubility, their thermal plasticity, their thickening and colloid stabilizing abilities, which is described in excellent details by Eastman and Rose [1], and Archer [2]. Native cellulose is known to comprise long microfibrils with different cross-sectional dimensions, depending on the source of the specimen [3–6]. However, most of the cellulose samples show presence of regular fibrils having 3.5 nm diameter. These elementary fibrils have a tendency to coagulate and produce larger

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crystallite widths in the range 5–10 nm, identified as microfibrils [7]. Viscoelasic evaluation of average length of cellulose nanofibres was reported by Ishii et al. recently [7]. This study concluded that each cellulose nanofibre in solution behaved as a semi-flexible rod-like structure. The same study clearly established a distinct boundary between the terminal relaxation and rubbery plateau region.

Quaternary ammonium salt of HEC, available in the commercial name Polymer-JR, has been extensively characterized by Liu et al. [8]. Degradation of HEC using sodium persulfate (NaPS) as free radical generator was reported by Erkselius and Karlsson [9]. Choi et al. [10] carried out a detailed molecular dynamics simulation to examine the solubility properties of hydroxyethyl and hydroxylpropyl cellulose polymers. Their results predict that the 3D solubility parameters of this class of polymers are governed by polar and hydrogen bonding interactions. A systematic extensional and shear viscosity characterization of aqueous HEC solutions was carried out by Meadows et al. [11] where dilute solution to semidilute regime crossover was observed from intrinsic viscosity data. Roy et al. [12] reported observation of a dilute solution regime for cellulose concentration less than 1% (w/v) whereas irreversible aggregate based gelation was observed at higher polymer concentrations. A cursory examination of literature reveals the absence of any systematic study pertaining to the solution state phase stability of this biopolymer in water over a wide range of concentration which constitutes the main objective of this work. In fact, solution properties of a few cellulose polymers have been fully characterized until now.

2. Materials and methods

Three molecular weight preparations ($M_v = 9 \times 10^4$, 7.2×10^5 and 1.3×10^6 Da) of hydroxyethyl cellulose was procured from Sigma–Aldrich Chemicals, USA and used as received. All samples were prepared by addition of the required amount of HEC to a known amount of double distilled deionized water. In order to achieve homogeneous mixing, these stock solutions were stirred using magnetic stirrers overnight. Low concentration solutions ($c < 1\%$ (w/v)) were centrifuged at 20,000 rpm for 15 min to sediment dust and big aggregates, if any. The experimental samples were drawn using micropipettes from the upper portion of the stock solution. For higher concentrations ($c > 1\%$ (w/v)), the preparations were used without centrifugation. These samples were stored in air tight borosilicate glass tubes for further analysis which, in all instances, did not exceed more than 48 h after preparation. These samples appeared optically clear and transparent to the naked eye. Samples having concentration, $c > 1\%$, appeared viscous with slowly moving meniscus. All procedures were performed at room temperature, 25 °C and relative humidity in the room was close to 50%.

Rheology experiments were performed using an AR-500 model stress controlled rheometer (T.A. Instruments, UK) with the objective to inter-relate the stiffness and thermal stability of the networks in frequency and temperature sweep modes. The dynamic rheology of the samples was measured using cone-plate geometry (4-cm diameter, 2° cone angle, and 50-mm truncation gap) with oscillatory stress value set at 0.1 Pa for 0.7% and 1% w/v samples specially to observe the low frequency behaviour of storage and loss modulus. The oscillatory stress value was changed to 0.5 Pa with cone-plate geometry (2-cm diameter, 2° cone angle, 50 mm truncation gap) for samples having concentration greater than 1% (w/v) for all other rheological experiments. These studies exclusively determined the frequency dependence of in-phase storage modulus (G') and out-of-phase loss modulus (G''). The solution viscosity, η and intrinsic viscosity, $[\eta]$ of samples were measured using a vibro viscometer (model-SV10, A and D Co., Japan). This instrument uses a matched pair of gold plated flat electrodes. The mechanical vibrations (frequency ≈30 Hz) set in one of these propagate through the sample and is picked up by the other electrode. The viscous properties of the sample are deduced from the response function through the software provided by the manufacturer.

DSC experiments were performed by using a DSC 4000 (Perkin-Elmer, USA) instrument. Here, the objective was to determine the thermal properties of the solutions and to correlate the same with the results obtained from rheology. In a DSC experiment, typically 10 mg samples were taken in aluminum pans, and the temperature sweep was performed with the heating rate maintained at 10 °C/min. The measurement protocol was as specified by the manufacturer of the instrument. SEM images were taken by using Carl Zeiss EVO instrument. Samples were prepared by dropping cellulose solution on the sample holder followed by leaving it for natural drying, subsequently it was gold coated for improved contrast. The information obtained from SEM data was treated as indicative as these pertained to dry samples.

Raman spectra of all HEC solutions were recorded on a FT-IR/Raman Spectrometer with Microscope – Varian 7000 FTIR, Varian FT-Raman and Varian 600 UMA. We have adopted Raman spectroscopy to investigate the hydration of this biopolymer because vibrational spectra are very sensitive to the local molecular environment. DLS experiments were performed at scattering angle of $\theta = 90°$ and laser wavelength of $\lambda = 632.8$ nm on a 256-channel Photocor-FC (Photocor Inc., USA) that was operated in the multi-τ mode (logarithmically spaced channels). The goniometer was placed on a Newport (USA) vibration isolation table. Dilute solutions, in the concentration range 0.05–0.5% (w/v) were studied to know the apparent hydrodynamic radius of the biopolymer molecule (R_H). The time scale spanned 8 decades, i.e., from 0.5 μs to 10 s. The samples were housed inside a thermostated bath, and the temperature was regulated by a PID temperature controller to an accuracy of ±0.1 °C. In all the experiments, the difference between the measured and calculated baseline was not allowed to go beyond ±0.1%. The data that showed excessive baseline difference were rejected. In this method, the system is physically seen over a length scale q^{-1} where $q = (4\pi n/\lambda)\sin\theta/2$. The laser wavelength in the scattering medium is λ/n, where n is index of refraction. The diffusion coefficient is related to corresponding hydrodynamic radius through Stoke–Einstein relation as

$$D = \frac{k_B T}{(6\pi\eta_0 R_H)} \quad (1)$$

where solvent viscosity is η_0, k_B is Boltzmann constant, and T is absolute temperature. Radius of gyration (R_g) was determined from Guinier plot following standard procedure. Details of DLS is described elsewhere [13].

3. Results and discussion

Fig. 1 depicts the variation of relative viscosity as function of polymer concentration in the range 0.002–2% (w/v) which is very revealing. This plot unambiguously defines three concentration regimes: $0.002 < c < 0.2\%$, $0.2 < c < 1\%$ and $1 < c < 3\%$ (w/v). These will be referred to as dilute, semidilute and melt regimes, and the justification for the same will be established as we discuss these regions in finer details. The viscosity data is often displayed as a master plot of η_{sp} versus $c[\eta]$ to demarcate the dilute and semidilute regions [11]. The change in the slope in the data occurs due to progressive overlap of coils as semidilute region is approached.