



Interaction behaviors in aqueous solutions of negatively and positively charged hydrophobically modified hydroxyethylcellulose in the presence of an anionic surfactant

Neda Beheshti*, Kaizheng Zhu, Anna-Lena Kjøniksen, Bo Nyström

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

ARTICLE INFO

Article history:

Received 16 April 2008

Received in revised form 12 June 2008

Accepted 13 June 2008

Available online 21 June 2008

Keywords:

Hydrophobically modified polyelectrolytes

Surfactant interactions

Associations

Phase separation

ABSTRACT

In this study, turbidity, rheology, dynamic light scattering (DLS), and rheo-small angle light scattering (rheo-SALS) measurements have been carried out on aqueous semidilute solutions of anionic and cationic hydrophobically modified hydroxyethylcellulose (HM-HEC(−) and HM-HEC(+)) (with the same degrees of charge and hydrophobic modification) and their uncharged (HM-HEC) and unmodified (HEC) analogues in the presence of the anionic surfactant sodium dodecyl sulfate (SDS). The effect of various surfactant concentrations on the association behavior has been examined. Addition of low or moderate levels of the oppositely charged surfactant to the solutions of HM-HEC(+) leads to the formation of polyelectrolyte complexes and associative phase-separation behavior, whereas at surfactant concentrations above the charge neutrality point, a single phase emerges. At high SDS concentrations the hydrophobic interactions are reduced and this leads to lower viscosity values as well as a faster relaxation process from DLS. For the polymer (HM-HEC(−)) with charges of the same sign as the surfactant, complete miscibility was found at all solution conditions. In this case, a maximum strength of the network was observed at a surfactant concentration of approximately 5 mM, where mixed polymer–surfactant micelles are formed. The scattered intensity monitored from rheo-SALS experiments for the HM-HEC(−)/SDS and HM-HEC(+)/SDS solutions revealed significant structural changes under the influence of high shear rates. The hydrophobically modified HM-HEC polymer precipitates in water but it becomes soluble at higher levels of SDS addition. As the surfactant concentration is increased, more hydrophobic moieties are gradually deactivated and lower viscosity values are registered. At high levels of surfactant addition, the hydrophobic associations are disrupted and the electrostatic interactions are screened, leading to virtually the same behavior of all the investigated polymers.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The interaction between polyelectrolytes and ionic surfactants has attracted significant interest in recent years in different areas of research [1–4]. This type of interaction has found widespread applications both in biological and technological fields [5–8], and a variety of methods have been utilized to characterize the complex association behavior in polyelectrolyte–surfactant mixtures [9].

The main driving forces responsible for the association in polyelectrolyte–ionic surfactant mixtures are the electrostatic and hydrophobic interactions that exist between surfactant molecules, polymer molecules, and/or cooperative interactions of polymer chains and surfactant arising from either the hydrophobic associations of polymer hydrophobic moieties and the hydrophobic tail

of the surfactant, or from attractive Coulombic forces between the opposite charges of the polymer and the ionic surfactant.

The polyelectrolytes considered in this study are derivatives of hydroxyethylcellulose (HEC). HEC is a nonionic hydrophilic and biodegradable biopolymer with a typical polysaccharide structure. In this investigation, we have synthesized a hydrophobically modified HEC sample (HM-HEC) from the commercially available nonionic precursor HEC. The HM-HEC polymer was further modified by incorporating positively or negatively charged groups to produce hydrophobic polyelectrolytes. The hydrophobically modified anionic and cationic polymers will be referred to as HM-HEC(−) and HM-HEC(+), respectively.

In the present work, turbidity, dynamic light scattering (DLS), rheology, and rheo-small angle light scattering (rheo-SALS) measurements have been carried out on semidilute aqueous solutions of HEC (the reference polymer) and of HM-HEC(−) and HM-HEC(+) and the corresponding uncharged analogue HM-HEC in the presence of various amounts of the anionic surfactant sodium dodecyl

* Corresponding author. Tel.: +47 22854513; fax: +47 22855441.

E-mail address: neda.beheshti@kjemi.uio.no (N. Beheshti).

sulfate (SDS). We have especially focused on the features of the HM-HEC(–)/SDS and HM-HEC(+)/SDS systems.

It has been well documented that mixtures of polyelectrolytes and oppositely charged surfactants exhibits associative phase separation originating from the attractive electrostatic forces between the two species [10–12]. In the light of this, the measurements for the HM-HEC(+)/SDS mixture were limited to fairly high amounts of SDS concentration since at low or moderate levels of surfactant addition, close to the charge neutralization point, macroscopic phase separation was encountered. This phenomenon is the most prominent feature of a hydrophobically modified charged polymer and an oppositely charged surfactant. The surfactant molecules start to bind to the polymer when their concentration exceeds a critical value, denoted by CAC (critical aggregation concentration), which is the onset of cooperative surfactant binding to the polymer [13]. The CAC value is normally several orders of magnitude lower than the critical micelle concentration (CMC) in surfactant solutions without polymer [6].

In general, in solutions of a polyelectrolyte with an oppositely charged surfactant a single phase appears at low and high surfactant concentrations, whereas at intermediate levels of surfactant addition phase separation takes place [14]. In this investigation, it was observed that even at very low SDS addition, the system turns into two phases. It can be due to the high degree of hydrophobic modification of HM-HEC that exposes more hydrophobic groups available for binding to the surfactant. This indicates that for the HM-HEC(+)/SDS system the CAC value is very low or non-existent.

HM-HEC is not soluble in pure water due to the high hydrophobicity. The addition of salt (0.01 M NaCl) to aqueous solutions of HM-HEC(+) and HM-HEC(–) resulted in phase separation due to screening of the charges, and the effect of ionic strength has therefore not been examined further.

The aim of this study is to gain insight into how the polymer–surfactant interactions affect the structural, dynamical, and rheological features of aqueous mixtures of the above-mentioned polymers with SDS at various surfactant concentrations. Some novel structural and dynamical results are reported, and the changes at different conditions in the systems have been elucidated.

2. Experimental

2.1. Materials

The anionic surfactant SDS was supplied by Fluka and was used without further purification. A hydroxyethylcellulose sample with the commercial name Natrosol 250 GR (lot. no. A-0382), obtained from Hercules, Aqualon Division, was used as a reference and as a precursor for the synthesis of the hydrophobically modified analogue (HM-HEC) and the hydrophobic polyelectrolytes (HM-HEC(–) and HM-HEC(+)). The degree of molar substitution of hydroxyethyl groups per repeating anhydroglucose unit is 2.5 (given by the manufacturer). The weight-average molecular weight of this sample was found [15] to be 400 000 by using intensity light scattering. The HEC sample was also characterized by means of asymmetric flow field-flow fractionation (AFFFF). The results on dilute aqueous HEC solutions gave the same molecular weight as the intensity light scattering, and showed that the sample has a broad molecular weight distribution with a polydispersity index $M_w/M_n \approx 7$ (see Fig. 1). The main chemicals for the synthesis of the modified polymers were glycidyl hexadecyl ether (Aldrich), 3-chloro-2-hydroxy-1-propanesulfonic acid sodium salt hydrate (Aldrich, 95%) and glycidyltrimethylammonium chloride (2,3-epoxypropyltrimethylammonium) (Fluka, 90%).

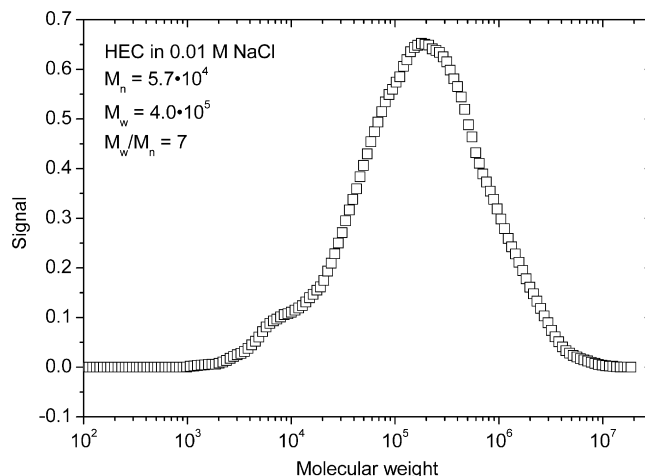


Fig. 1. Illustration of the molecular weight distribution of 0.34 wt% HEC in aqueous solution (0.01 M NaCl) with the aid of AFFFF.

The HM-HEC and HM-HEC(–) samples were synthesized according to a modified method described previously [16], and the details and characterization of that HM-HEC fraction have been described elsewhere [17]. These polymers were further purified by dialyzing against Millipore water for 7 days and isolated by freeze-drying. Regenerated cellulose with a molecular weight cutoff of about 8000 (Spectrum Medical Industries) was utilized as dialyzing membrane. ^1H NMR ascertained the chemical structure and purity of HM-HEC, and the degree of substitution of the glycidyl hexadecyl ether groups (hydrophobic modification) was calculated from the peak ratios between the anomeric protons (4.9 ppm) and the methyl protons (0.8 ppm) of the alkyl group. The degree of hydrophobic substitution was 2.5 mol% (HM-HEC). The degree of substitution of the sulfonic group (sulfo-2-hydroxypropyl) in the negatively charged hydrophobically modified hydroxyethylcellulose (HM-HEC(–)), determined from ^1H NMR, was 7.0 mol%.

2.2. Synthesis of HM-HEC(+)

The cationic HM-HEC analogue (HM-HEC(+)) was prepared by reacting the above-synthesized HM-HEC with 2,3-epoxypropyltrimethylammonium (Fluka) following a slightly modified procedure described elsewhere [18,19]. First, 10.0 g of HM-HEC was added to an alkaline solution containing 1.5 g of sodium hydroxyl in 400 mL water and mixed for 24 h at room temperature. An aqueous solution of the reactant (4.7 g of 2,3-epoxypropyltrimethylammonium dissolved in 40 mL of water) was then added, and the reaction bath was heated and kept at 50 °C for 24 h under nitrogen. The solution was then neutralized by addition of 6 N HCl until a pH of 6 was reached. The polymer was further purified through dialysis (a regenerated cellulose membrane with a molecular weight cutoff of 8000) against water, and after freeze-drying 8.6 g of HM-HEC(+) was recovered. The degree of substitution (DS), corresponding to the incorporation of the ammonium group per repeating anhydroglucose unit, was calculated from the ratio of integration of the peak value at $d=3.2$ ppm, assigned to the proton $-\text{CH}_3$ which is linked to the ammonium group (N+), to that of the anomeric protons signal of the HEC, was calculated to be 7.2 mol%, which is very close to the charge density observed for the HM-HEC(–) sample. The chemical structures of the synthesized polymers are depicted in Fig. 2.

Download English Version:

<https://daneshyari.com/en/article/596647>

Download Persian Version:

<https://daneshyari.com/article/596647>

[Daneshyari.com](https://daneshyari.com)