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Viscosity study of interactions between sodium alginate and CTAB in dilute solutions at different pH values

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ABSTRACT

Interactions between anionic polyelectrolyte sodium alginate and the cationic surfactant cetytrimethylammonium bromide (CTAB) have been investigated by viscosity measurement techniques. The polymer–surfactant interactions are observed between alginate and CTAB at different pH in dilute solution. The results show that the rheological response of alginate dilute solutions is sensitive to a change of pH in the low pH range. The steady shear and intrinsic viscosity measurements reveal that the strong association between alginate and CTAB by electrostatic attraction above pH 5.0. However, as the pH value of solution decrease from 5.0 to 3.0, the strong association between alginate and CTAB is affected by not only electrostatic attraction but also hydrophobic interaction.

1. Introduction

Polyelectrolyte–surfactant systems often have physicochemical characteristics that differ from non-ionic polymer–surfactant systems (Chu & Thomas, 1986; Fijan, Šostar-Turk, & Lapasin, 2006; Winnik et al., 2000; Yeh, Sokolov, Khokhlov, & Chu, 1996; Yeh, Sokolov, Walter, & Chu, 1998). Considerable studies have dealt with interactions between polyelectrolytes and oppositely charged surfactants (Khokhlov, Kramarenko, Makhaeva, & Starodubtzev, 1992; Ren, Gao, Lu, Liu, & Tong, 2006). The strong association between polyelectrolytes and oppositely charged surfactants is driven by electrostatic attraction and hydrophobic interactions. Polyelectrolytes interact with oppositely charged surfactant micelles so strongly that in many cases irreversible macroscopic phase separation occurs (Guillemet & Piculell, 1995).

Alginate is both biopolymer and polyelectrolyte that are considered to be biocompatible, non-toxic, non-immunogenic and biodegradable. It can be characterized as an anionic copolymer, comprising of mannuronic acid (M block) and guluronic acid (G block) units arranged in an irregular blockwise pattern of varying proportion of GG, MG and MM blocks (Matsumoto, Kawai, & Masuda, 1992). Alginate is known to form a hydrogel in the zpresence of divalent cations, such as calcium (Ca^{2+}), which act as crosslinkers between the functional groups of alginate chains. Besides hydrogels induced by divalent cations, alginate can form acid gels at pH below the pK_a value of the uronic acid residues (Bu, Kjøniksen, Knudsen, & Nyström, 2004). These gels have been proposed to be stabilized by intermolecular hydrogen bonds. Just as we know, alginates have $-COO^-$ and $-COOH$ groups along the chain conferring different charge densities depending on the pH. The hydrophilic and hydrophobic groups along a molecule chain can be altered by the protonation and deprotonation of carboxyl groups in the backbone chain. Our previous research demonstrates that the aggregation between alginate and SDS can be shown in dilute aqueous solution owing to hydrophobic interaction at lower pH (Yang, Zhao, & Fang, 2008).

Rheological measurements are used to probe the interactions between hydrophobically modified polymers and surfactants (Bu, Kjøniksen, Knudsen, & Nyström, 2007). In this paper, the interaction between the cationic surfactant cetytrimethylammonium bromide (CTAB) and alginate, in dilute solutions, has been studied by steady shear and intrinsic viscosity. Effects of surfactant concentration and aqueous pH values on rheological and structural properties will be reported. The aim of this paper is to elucidate factors that play an important role in the interactions between a surfactant and alginate. This work provides new insights into the interactions between a surfactant and alginate.

2. Experiments

2.1. Materials

Sodium alginate, purchased from Sinopharm Chemical Reagent Co., Ltd., was refined twice by dissolving it in distilled water,

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filtered, precipitated with ethanol, and finally dried in a vacuum at 60 °C. The viscous-average molecular weight of sodium alginate used was 430 kDa, determined by viscometric methods (Martinsen, Skjåk-Bræk, Smidsrød, Zanetti, & Paoletti, 1991). The alginate was analyzed by ^{1}H NMR spectroscopy at 70 °C using a Bruker AVANCE 600 (600 MHz) spectrometer (Grasdalen, 1983; Grasdalen, Larsen, & Smidsrød, 1979). The molar fraction of guluronic acid residues (F_G) was determined by NMR to be $F_G = 0.85$, $F_M = 0.15$. Hydrochloric acid and sodium hydroxide were of analytical grade. CTAB was obtained from Aldrich. They were used as received without further purification.

2.2. Solution preparation

Doubly distilled water was used for the preparation of all solutions. A biopolymer solution was prepared by dissolving 1.0 wt% NaAlg in the water, stirring for at least 4 h to ensure complete dispersion, and then storing overnight at room temperature. By mixing biopolymer solutions with the water, adjusting to the desired pH (3–7) using HCl or NaOH, dilute NaAlg solutions were obtained. A stock of 0.005 M CTAB was prepared by dissolving CTAB in the water. The pH of each of the solutions was adjusted to the appropriate value prior to mixing.

2.3. Methods

Rheological measurements: Steady shear measurements were conducted in a rheometer (Haake RS600, Thermo Electron Co., USA) using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 60 mm. The samples were introduced onto the plate for 5 min to eliminate residual shear history, and then carry out experiments immediately. The measuring device was equipped with a temperature unit that gave good temperature control (25 ± 0.05 °C) over an extended time in this work. The zero-shear viscosity readings were taken from the Newtonian values at shear rates ranging from 0.01 to 1 s^{-1}. Intrinsic viscosity measurements were conducted in an Ubbelohde Viscosimeter.

3. Results and discussion

3.1. Effect of pH on alginate dilute solutions viscosity

Effect of pH on the shear viscosity for alginate (0.1 wt%) dissolved in water is shown in Fig. 1. The general trend is that the viscosity increases with lowering pH, and pronounced rises of the viscosity at low shear rates are observed at pH 3.0 and 4.0, where also strong shear-thinning features are detected in the low to the intermediate shear rate region due to the breakup of the intermolecular associations. At pH values below 3.0, macroscopic phase separation occurs. These results clearly demonstrate that the rheological response is sensitive to a change of pH in the low pH range, which probably reflects enhanced intermolecular interactions.

Influences of pH on the zero-shear viscosity for 0.1 wt% alginate solutions is depicted in Fig. 2. As the pH value of solution decrease from 6.6 to 5.0, the system show generally small viscosity changes, which probably indicates no intermolecular interactions owing to electrostatic repellence. With the progressive decrease of pH value from 5.0 to 3.0, the system exhibit a marked viscosity enhancement, suggesting that the electrostatic repellence are suppressed, enhanced intermolecular hydrogen bonds and possible entanglements emerge and association structures are formed.

The initial pH value of the neutral alginate solution of 0.1 wt% concentration is 6.6, which means that the carboxylic acid groups are slightly dissociated. Two types of interactions play an important role in aqueous alginate solution, namely the charge repulsion between dissociated carboxylic groups and the hydrogen bonding formed between carboxylic acid and ionized carboxylate groups (Bu, Kjøniksen, & Nyström, 2005). With the decrease of pH, the number of dissociated carboxylic groups in alginate chains decreases, which makes alginate lose its hydrophilicity to some extent. When some dissociated carboxylic groups in alginate chains are gradually protonated, the hydrophobic segments appear in alginate chains. Cao et al. (2005) showed that the alginate molecules can form hydrophilic–hydrophobic aggregates in aqueous solution depending on the pH of the medium. They postulated this pH dependence of 'aggregation' as a signature for self-assembly caused by the partial protonation of dissociated carboxyl groups in the alginate main chain. Here, in Fig. 2, as the pH value decreases from 5.0 to 3.0, the hydrophobic segments in the alginate chains increase, and the hydrophilic segments decrease. Meanwhile, the weakening of the mutual repulsion of ionized carboxyl groups promotes the development of intermolecular hydrogen bonds and possible entanglements.

3.2. Effect of CTAB addition on alginate dilute solutions viscosity

Fig. 3 depicts the effect of shear rate on the viscosity for 0.1 wt% alginate solutions in the indicated concentrations of CTAB at differ-

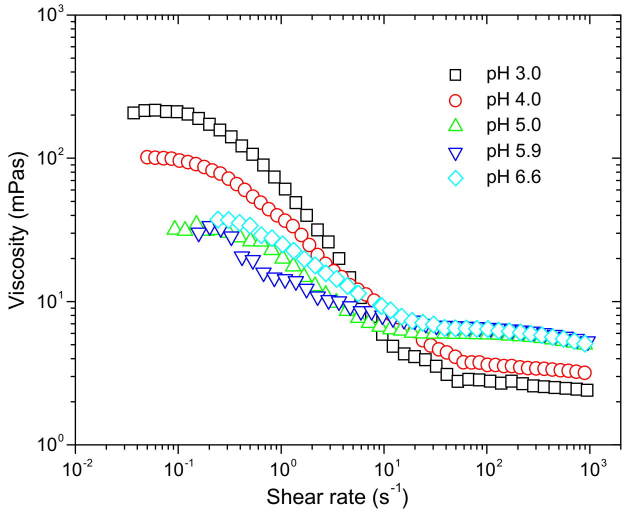

Fig. 1. Effect of pH on the shear rate dependence of the viscosity for a 0.1 wt% alginate solution.

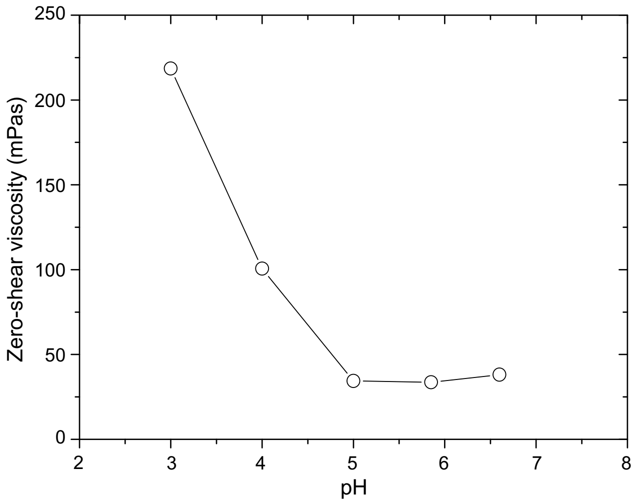

Fig. 2. Zero-shear viscosity plotted as a function of pH for 0.1 wt% alginate solution.

ent pH values. In all cases, shear-thinning features are detected in the low to the intermediate shear rate region, followed by a Newtonian plateau at high shear rates. As shear rates increasing, the intermolecular junctions are disrupted at a rate faster than their rate of reformation, resulting in a decrease in the junction density and hence a drop in the viscosity.

The zero-shear viscosity of dilute alginate solutions versus CTAB concentration at different pH values is shown in Fig. 4. It shows that CTAB interacts strongly with alginate at concentrations below the critical micelle concentration (cmc) of pure CTAB (ca. 0.92 mM) (Zhao & Zhu, 2003). The sharp rise in the viscosity begins at a concentration over an order of magnitude lower than the cmc. The

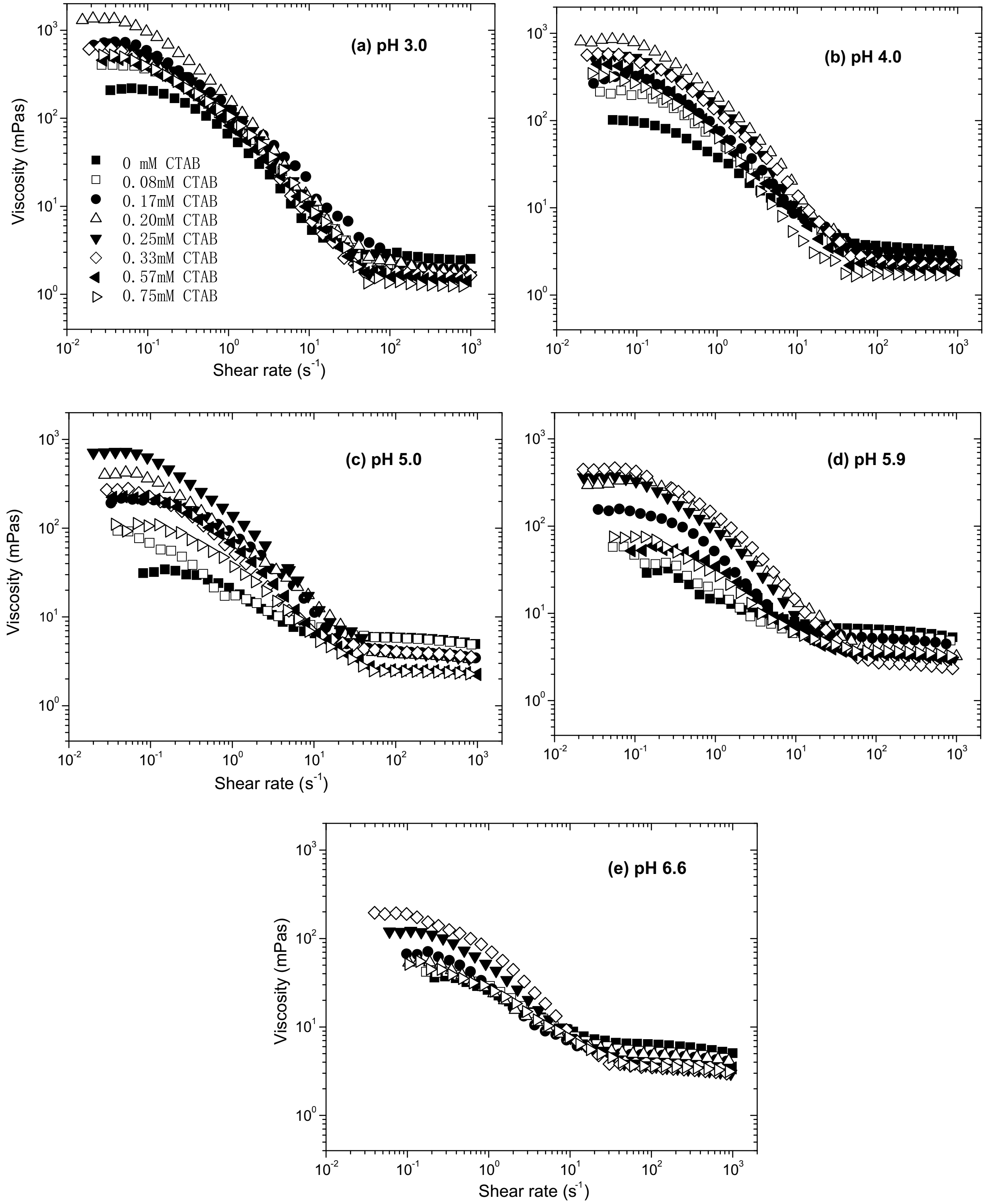

Fig. 3. Effects of CTAB addition on the shear rate dependence of the viscosity for 0.1 wt% alginate solutions at different pH values. The symbols have the same meaning in all panels.

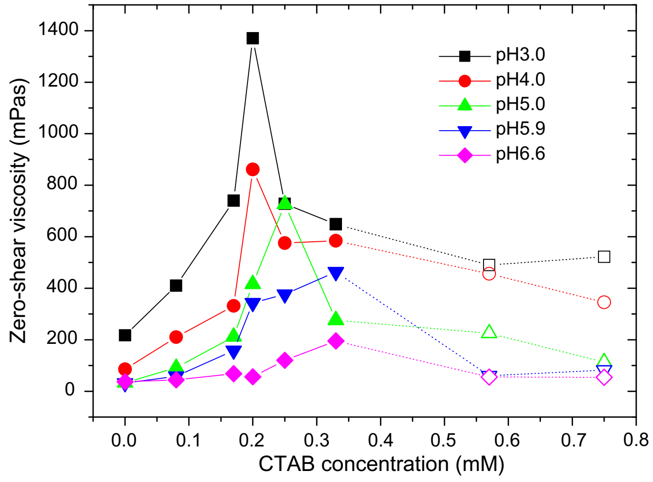

Fig. 4. Effects of CTAB concentration on the zero-shear viscosity of 0.1 wt% alginate solutions at different pH values. Blank symbols and dotted line denote phase separation region.

coulombic interactions between the anionic polymer and the cationic surfactant lead to a strongly cooperative binding – the signature being that the critical aggregation concentration (cac) occurs at concentration much lower than the cmc. At higher CTAB concentrations, the interactions become strong enough to result in phase separation. At pH 3.0, 4.0 and 5.0, the zero-shear viscosity first increases and then decreases with increasing CTAB concentration. This is an indication of micellar crosslinking followed by solubilizing of the hydrophobe as reported previously (Dualeh & Steiner, 1991). The maximum value in the viscosity of each dilute alginate–CTAB solution increases obviously with the decrease of pH value from 5.0 to 3.0. This effect probably occurs because enhancement of hydrophobicity and the creation of a fragmented network consisting of large aggregates or clusters with little connectivity. We presume that mixed polymer–surfactant micelles are formed and these participate in the evolution of crosslink zones that increase the viscosity. The decrease of viscosity with further increasing CTAB concentrations is a result of ‘masking’ of the hydrophobes by micelles. That is, each hydrophobe is sequestered in a micelle, and since the micelle–micelle interactions are repulsive the polymers are prevented from associating.

3.3. Effect of CTAB addition on alginate solutions intrinsic viscosity

The intrinsic viscosity is a measure of the hydrodynamic volume of the polymer at infinite dilution. The effect of CTAB on the electrostatic and hydrophobic interaction in dilute solutions of alginate is further examined by the determination of the intrinsic viscosity [η] at different levels of CTAB. The values of [η] are obtained by extrapolation of the reduced viscosity curve to zero polymer concentration using the Huggins’ equation (Huggins, 1942).

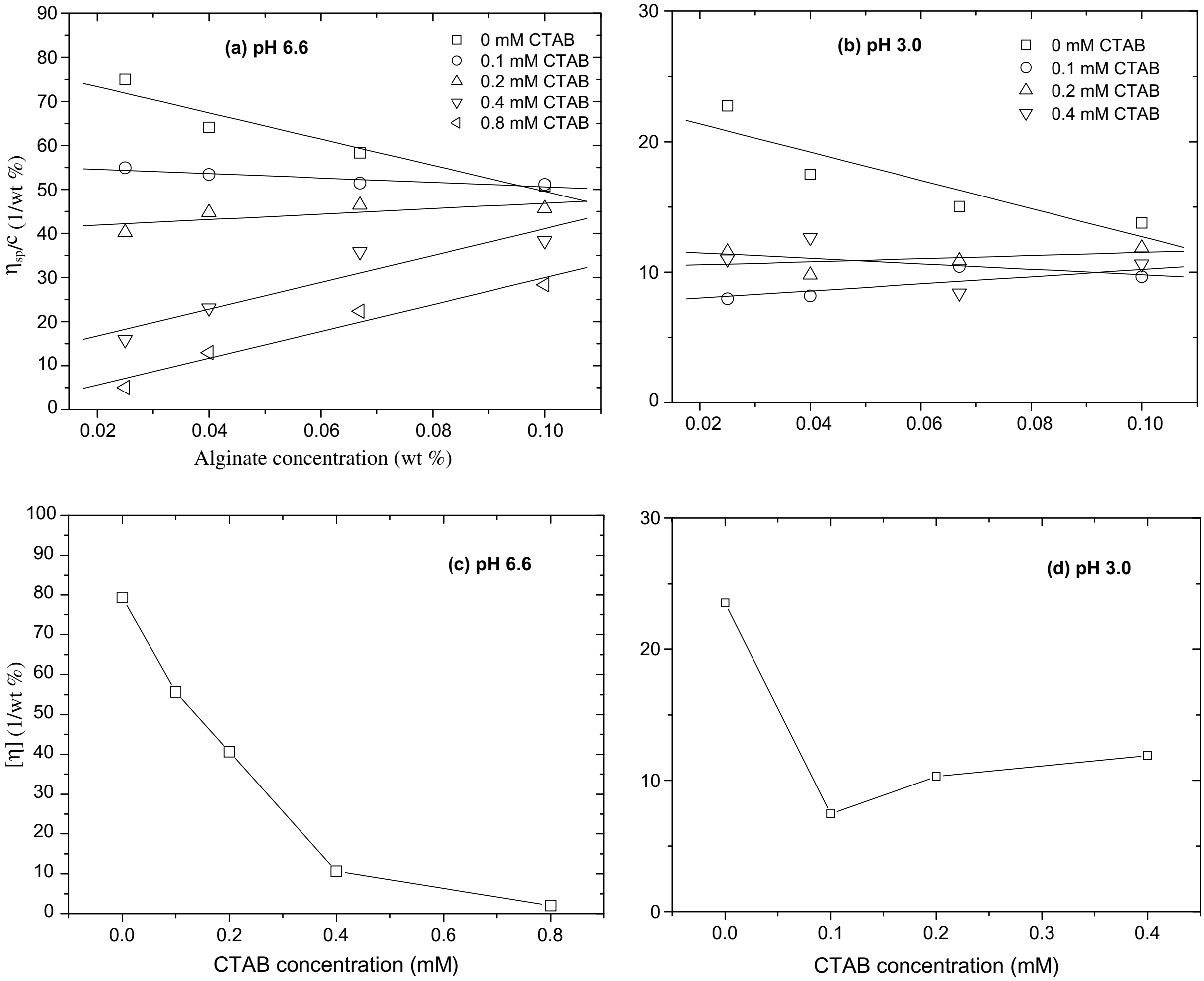

Fig. 5. Concentration dependence of the reduced viscosity (η_{sp}/c) of dilute solutions of alginate at the surfactant concentrations indicated. (a) pH 6.6, (b) pH 3.0; the effects of CTAB addition on the intrinsic viscosity [η] of alginate solutions (c) pH 6.6, (d) pH 3.0.

$$\frac{\eta_{sp}}{c} = [\eta] + k'c[\eta]^2 \quad (1)$$

where $\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c$, η is the viscosity of the solution; η_0 is the solvent viscosity; c is the polymer concentration; and k' is the Huggins coefficient, which depends on the molecular architecture and interactions. All the investigated samples exhibit a linear dependence of the reduced viscosity (η_{sp}/c) as a function of the polymer concentration (see Fig. 5a and b). It is evident that the aqueous solution of alginate without CTAB displays a typical polyelectrolyte behavior, that is, the reduced viscosity rises at low polymer concentrations. The effect of CTAB concentration on $[\eta]$ for alginate solutions is depicted in Fig. 5c and d. The value of $[\eta]$ falls off with increasing CTAB concentration at pH 6.6 (see Fig. 5c), suggesting that the size of the anionic polymer molecules shrink with increasing cationic surfactant addition. It is a result of 'charge neutralization' of the polymer by CTAB. This effect is reminiscent of that observed by the steady shear measurement as shown in Fig. 3e, that is, the viscosity under the highest shear rate decreases with rising CTAB concentration, indicating a reduction of the size of the polymer molecules with CTAB addition. The values of $[\eta]$ decrease with the decrease of pH, due to the number of dissociated carboxylic groups in alginate chains decreases, which makes alginate lose repulsion of intramolecule to some extent and shrink easily. At pH 3.0 (see Fig. 5d), the values of $[\eta]$ decrease sharply with increasing CTAB concentration to 0.1 mM, due to the effect of 'charge neutralization', which consume magnitude of CTAB lower than that at pH 6.6. Then, the values of $[\eta]$ are nearly constant and increases slowly with increasing CTAB concentration, starting from 0.1 mM. We postulate that hydrophobic segments of the alginate chain are sequestered in bonded micelles, and since the micelle–micelle interactions are repulsive the contractive polymers are swelled.

4. Conclusions

The results show that the rheological response of alginate dilute solutions is sensitive to a change of pH in the low pH range, which reflects enhanced intermolecular interactions. As the pH value decreases from 6.6 to 3.0, the hydrophobic segments in the alginate chains increase, and the hydrophilic ionized carboxyl groups decrease, suggesting that the electrostatic repellence are suppressed, and intermolecular possible entanglements and hydrogen bonds are enhanced, and association structures are formed. The coulombic interactions between the anionic polymer and the cationic surfactant lead to a strongly cooperative binding. The shear rheology and intrinsic viscosity measurements reveal that the strong association between alginate and CTAB by electrostatic attraction above pH 5.0. However, as the pH value of solution decrease from 5.0 to 3.0, the strong association between alginate and CTAB is affected by not only electrostatic attraction but also hydrophobic interaction.

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