# Altering the viscosity of cationically modified cellulose polymers by the addition of salt

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**ABSTRACT:** The concentration dependence of viscosity is examined for four cationically modified cellulose polymers (UCARE[TM] JR400, UCARE[TM] JR30M, UCARE[TM] LR400, and UCARE[TM] LR30M) in both salt-free and 50 m$M$ NaCl solution. Similarities in the four polymer systems include: Newtonian viscosity in the dilute regime, shear thinning at higher concentrations, four concentration regimes in salt-free solution, and three concentration regimes in salt solution. The zero shear rate viscosity and the degree of shear thinning increase with increasing polymer concentration in both salt and salt-free solutions. While the addition of salt to the lower molecular weight polymers JR400 and LR400 resulted in small changes in viscosity across all concentrations, JR30M and LR30M exhibited significant decreases (up to 81%) and increases (up to 57%) in viscosity upon the addition of salt in the semidilute and entangled regimes, respectively. This viscosity increase in the entangled regime (when comparing salt-free and 50 mM NaCl solutions) is reported for the first time in cationically modified cellulose polymers. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41616.

## INTRODUCTION

Polyelectrolytes are polymers with ionizable groups attached to the main backbone.[1,2] Polyelectrolytes dissociate into charged polymer chains and counterions upon solvation in a polar solvent. Charged polymer systems are commonly encountered in nature as proteins, polypeptides, and DNA as well as in industrial applications such as drag reducers, viscosity enhancers, and thickeners.[2–5] The electrostatic interactions between polyelectrolytes and the solvent result in interesting rheological behaviors, which merit further study.[6–8]

Polyelectrolyte rheology varies strongly with concentration of polymer as well as the salt concentration. The effect of salt on polyelectrolytes is well studied in dilute and semidilute regimes. In these lower concentration regimes, the extended polyelectrolyte chains in salt-free solution (i.e., deionized water) shrink upon the introduction of added salt causing significant decreases in the viscosity (as much as 99% in some cases).[9–11] However, at higher concentrations in the entangled concentration regime, the addition of salt has been shown to significantly increase the viscosity (above critical concentration $c_D$).[9–11]

With the understanding of polyelectrolyte rheology guiding this study, a set of modified biopolymers under the trade name UCARE[T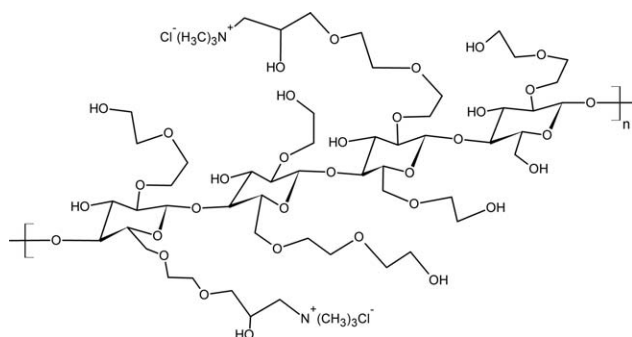M] are investigated.[12,13] UCARE[TM] polymers are used extensively in cosmetic products, e.g., body wash, hair conditioner, and shampoo. The unique properties of these cationic polymers are particularly prevalent in shampoos and conditioners because they decrease mechanical damage to hair by reducing combing force.[14] A broader interest in phase behavior and controlled release have also implemented UCARE[TM] polymers leading to interesting tunable properties.[14–31]

UCARE[TM] polymers are cationic polymers with a cellulosic backbone linked by $\beta$-1,4 bonds with hydroxyethyl groups attached (Figure 1). The polymers are created by the addition of hydroxyethyl groups to the cellulosic backbone and reacting hydroxyethylcellulose with trimethyl ammonium-substituted epoxide to produce polymeric, quaternary ammonium salts of hydroxyethyl cellulose.[12–14] A varying amount of quaternization of the hydroxyethylcellulose by quaternary ammonium salts is present based on the specific UCARE[TM] polymer. The variations in cationic substitution have been shown to affect the rheological properties of the polymers, which will be expanded upon here.

Biopolymers such as xanthan exhibit rheological behavior indicative of multiple macromolecular conformations.[33–37] The conformation exhibited by the polymer depends on the concentration of the polymer. Electrostatic repulsions among the cationic side-chains cause the polymers to be extended and

**Figure 1.** Generalized molecular structure of UCARE[TM] polymers.[32]



**Figure 2.** Viscosity as a function of shear rate for several JR30M concentrations in both salt-free (top) and 50 m$M$ NaCl solution (bottom). Solid lines represent the Cross model fits.

disordered in salt-free solution. However, the presence of salt ions in solution stabilizes the charges on the side chains. The subsequent charge stabilized conformation is more rigid than the unordered conformation, resulting in viscosity discrepancies between salt and salt-free solutions in the dilute and semidilute regime. Extending the viscosity–salt-concentration relationships in biopolymers to the UCARE[TM] polymers will be the primary focus of this manuscript.

A study is needed to measure the viscosity of UCARE[TM] polymer solutions over a range of concentrations, identify critical concentrations, and quantify the effects of salt on solution viscosity and critical concentrations. DOW Chemical Company reports only a single viscosity for 2% aqueous solutions of UCARE[TM] polymers, which disregards the non-Newtonian nature of polyelectrolyte solutions. This study aims to address this void by experimentally measuring the dilute to entangled regimes in both salt-free and salt solution.

## EXPERIMENTAL

### Materials

The four polymers, UCARE[TM] JR400, UCARE[TM] JR30M, UCARE[TM] LR400, and UCARE[TM] LR30M, were obtained from Amerchol Corporation (a subsidiary of The Dow Chemical Company). In the UCARE[TM] series, the prefix refers to the degree of cationic substitution of the hydroxyethylcellulose backbone, where J > L. The degree of substitution was measured by titrating the chloride ions in solution. Standardized silver nitrate solution was titrated into the solutions with a potassium chromate indicator, and the end point was defined when permanent rust-colored precipitates were observed. The titrations found the degree of substitution as $0.47 \pm 0.01$ for the JR polymers and $0.29 \pm 0.01$ for both LR polymers. The suffix is a reference to the aqueous solution viscosity and acts as an indicator of molecular weight where 30M > 400.[5] Specifically, JR400 has a nominal molecular weight of 400,000–500,000 and JR30M has a molecular weight of 700,000–1,000,000.[38] The numbers in the trade names are related to the polymer's viscosity in water at 2 wt % (e.g., 400 represents a 400 cP viscosity). Deionized water (18.2 MΩ) for sample preparation was obtained by passing house deionized water through a Barnstead NANOpure Diamond UV ultrapure water system followed by a 0.2-$\mu$m filter. Reagent grade NaCl was obtained from Mallinckrodt Chemicals. Salt solutions are all 50 m$M$ NaCl, which is in the high salt limit.[9] The glassware and mixing instruments used
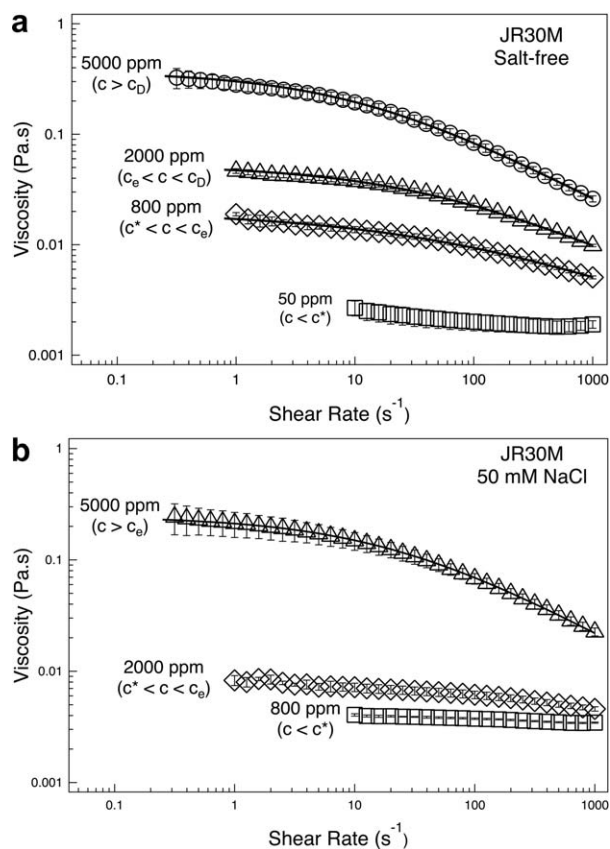
for sample preparation and storage were thoroughly cleaned with reagent grade acetone, rinsed with purified deionized water, and dried.

### Sample Preparation

Salt-free polymer samples were prepared by dissolving the dry polymer powder in deionized water. Salt solutions were prepared by dissolving the dry polymer powder in deionized water and subsequently adding the necessary amount of NaCl to create a 50 m$M$ NaCl solution. The samples were then stirred for ~1 h directly after preparation using a magnetic stir bar. The solutions were then allowed to rest for at least 24 h at room temperature before rheological measurements were taken. All measurements were taken within 1–5 days following preparation. No change in rheological properties of the polymers was observed within the 5-day period. Polymer degradation, including the formation of polymer aggregates and loss of clarity, was observed about 6 weeks after solution preparation.

### Rheology

All rheological data were collected on either a TA Instruments[®] AR-G2 Rheometer or Discovery Hybrid Series Rheometer (DHR3). Measurements were taken on the AR-G2 using a stainless steel cone (40-mm diameter, 2 degree) and on the DHR using an anodized aluminum cone (40-mm diameter, 2 degree). Data collected on different rheometers were statistically equivalent. A Peltier plate was used to control the temperature at 25.0

**Table I.** Fit Parameters for Cross Model or Newtonian Viscosity for Several JR30M Concentrations

| Concentration (ppm) | Solvent | $\eta_o$ or $\mu$ (Pa s) | $\eta_\infty$ (Pa s) | $K$ (s) | $m$ |
|---|---|---|---|---|---|
| 5000 | Water | 0.37 | $1.0 \times 10^{-3}$ | 0.08 | 0.59 |
| 2000 | Water | 0.05 | $1.0 \times 10^{-3}$ | 0.02 | 0.54 |
| 800 | Water | 0.02 | $1.0 \times 10^{-3}$ | 0.01 | 0.41 |
| 50 | Water | $2.1 \times 10^{-3}$ | – | – | – |
| 5000 | 50 mM NaCl | 0.25 | $1.0 \times 10^{-3}$ | 0.05 | 0.60 |
| 2000 | 50 mM NaCl | 0.01 | – | – | – |
| 800 | 50 mM NaCl | $3.8 \times 10^{-3}$ | – | – | – |

$\pm$ 0.1°C. A solvent trap was used in order to minimize sample evaporation.

All data reported are the averages of at least three replicate data sets. Error bars represent one standard deviation.

## RESULTS AND DISCUSSION

All four polymers exhibit the same qualitative behaviors as a function of shear rate and concentration. The rheology of JR30M will be presented in detail while analogous figures for the other three polymers are included in Supporting Information. First, in salt-free solution JR30M exhibits Newtonian behavior at very low (dilute) concentrations [Figure 2(a)]. At higher concentrations, a zero shear rate viscosity plateau is followed by shear thinning at higher shear rates. The general shape of the viscosity-shear rate curves is observed for many polymer solutions.[9,11,39] Key features of the non-Newtonian behavior of the solutions were captured using the Cross model,[40]

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (K\dot{\gamma})^m} + \eta_\infty \qquad (1)$$

where $\eta_0$ is the zero shear rate viscosity, $\eta_\infty$ is the infinite shear rate viscosity, $\dot{\gamma}$ is the shear rate, $K$ is a constant with the dimension of time, and $m$ is the rate index.

As expected, $\eta_0$ increases as polymer concentration increases, and $\eta_\infty$ is near the solvent viscosity for all concentrations (Table I). Both $\eta_0$ and $K$ for JR30M are significantly smaller than other biopolymers such as xanthan gum, which is likely due to the smaller molecular weight and number of charge groups.[9] The shear thinning index ($m$) reaches values as high as 0.6, which represents moderate shear thinning. As with $\eta_0$ and $K$, this amount of shear thinning is smaller than other biopolymers.[9] In addition, shear thinning was not strong enough to consider shear banding or flow inhomogeneities in the analysis.[41]

In 50 mM NaCl solution, the shear rate dependence of viscosity was qualitatively similar to the salt-free solution, i.e., Newtonian at lower concentrations and shear thinning fit by the Cross model at higher concentrations [Figure 2(b)]. Overall, the zero shear rate viscosity and shear thinning index are similar between salt-free and salt solutions at the highest concentrations while lower viscosities and weaker shear thinning is quantified in the salt solution at low and moderate concentrations. These trends will be examined more closely when comparing the con-

centration dependence and concentration regimes in the next section.

A series of power law relationships between viscosity and polymer concentration delineate concentration regimes and the effects of salt on the viscosity of the UCARE™ polymers. After measuring at least 20 different concentrations per polymer in both salt-free and NaCl solutions, distinct regions of viscosity scaling for each polymer were observed. UCARE™ polymer
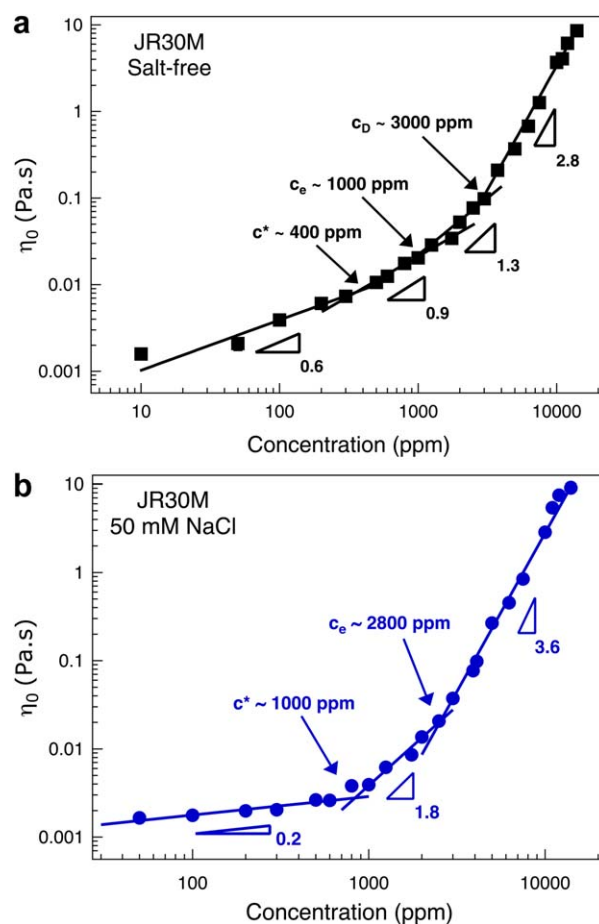


**Figure 3.** Zero shear rate viscosity scaling of JR30M as a function of polymer concentration in both salt-free (top) and 50 mM NaCl solution (bottom). Solid lines represent viscosity scaling in each region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
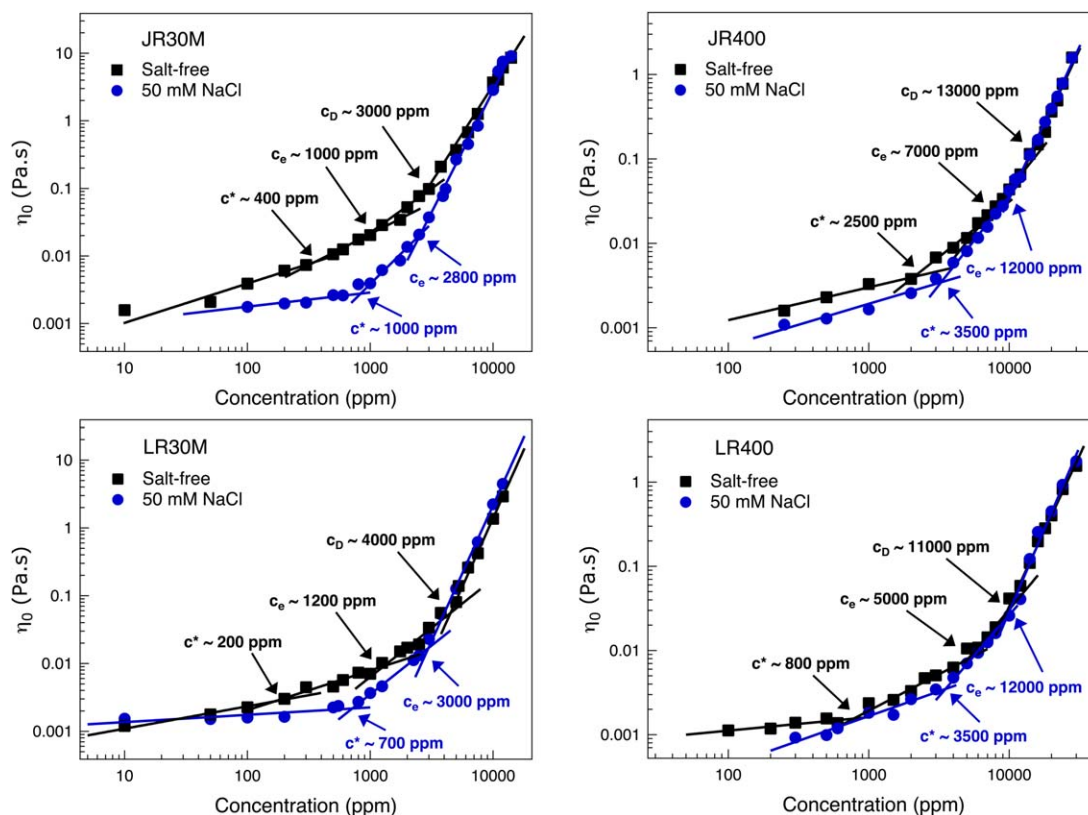
**Figure 4.** Zero shear rate viscosity scaling of JR30M (upper left), JR400 (upper right), LR30M (lower left), and LR400 (lower right) as a function of polymer concentration in salt-free solution. Solid lines represent viscosity scaling in each region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

JR30M is presented here with the other polymers of interest following similar trends, and the data is reported in Supporting Information. The critical concentrations separate the concentration regimes (Figure 3), which cover more than three decades of polymer concentration similar to other studies of polyelectrolyte rheology (e.g., Refs. 9,11. In salt-free solution [Figure 3(a)], the four concentration regimes are bound by three critical concentrations ($c^*$, $c_e$, and $c_D$). Two critical concentrations ($c^*$ and $c_e$) and three concentration regimes are observed in 50 m$M$ NaCl solution [Figure 3(b)]. The concentration transition from dilute to semidilute unentangled ($c^*$) increases upon the addition of salt. The collapsing of polyelectrolyte chains in a salt environment is well studied[9,42,43] and appears to apply for the UCARE[TM] polymers also. The entanglement concentration ($c_e$) shifts to a higher value in salt solution compared to salt-free solvent, likely demonstrating the residual effects of the collapsed chain configurations in the dilute regime. The third critical concentration is only observed in the salt-free case and marks the transition to a fully entangled solution.[6,9] With the critical concentrations identified, the viscosity scaling can be examined to learn more about the polymer–solvent behavior.

Examining the viscosity at different concentrations can help elucidate the polymers' structure in solution. The power law concentration dependence of viscosity as a function of concentration follows some general trends (Figure 3). In the dilute regime, viscosity varies with a power less than one, similar to previous reports with other biopolymers.[9,15] In dilute

solution, viscosity–concentration scaling covers a range from 0.1 to 0.6 for the four polymers examined. In the dilute limit, neutral polymers in good solvent exhibit viscosity varying with concentration to the first power,[44] which does not apply to polyelectrolytes due to intra- and interchain electrostatic interactions.[7] However, the viscosity–concentration scaling above the dilute regime will elucidate the solvent quality for these polyelectrolytes. This behavior will be presented separately for salt-free solutions and 50 m$M$ NaCl solutions.

In salt-free solution, the next concentration regime is semidilute unentangled, and the viscosity varies with concentration in the range of 0.5–1.3 across the four polymers. These values are generally higher than predicted by polyelectrolyte theory ($c^{0.5}$) for salt-free solution.[7] The viscosity scaling exponents continue to increase at higher concentrations, i.e., in the semidilute entangled and entangled concentration regimes. Theory and other experimental polyelectrolytes in salt-free solution place the viscosity–concentration power law exponent as 1.5 in the semidilute entangled regime.[8] While LR400, JR30M, and LR30M agree with this scaling (1.3–1.6), JR400 exhibits slightly higher scaling exponent (2.1). Finally, viscosity in the entangled, or sometimes called concentrated, regime is expected to scale with concentration to the 3.75 power.[45] The higher molecular weight polymers (LR30M and JR30M) exhibit a slightly smaller scaling than expected (2.8 and 3.1); LR400 and JR400 generally agree with the expected scaling. Overall, the viscosity–concentration scaling of the UCARE[TM] polyelectrolyte generally follows

the behavior of other polyelectrolytes and related theories in salt-free solution.

In addition to the dilute regime, two other concentration regimes in 50 m$M$ NaCl were observed for all four polymers. In the semidilute regime, polyelectrolytes in high salt solutions commonly revert to neutral polymer scaling behavior. Neutral polymer scaling in good solvent[7] finds $\eta \sim c^2$, and the UCARE™ polymers generally agree with this value (1.4, 1.8, 1.9, 2.1). The agreement between viscosity–concentration scaling for neutral polymer in a good solvent also holds in the entangled concentration regime. The predicted exponent is 3.9,[7] and the UCARE™ polymers scaled to the 3.2, 3.6, 3.6, and 3.9 powers. Thus, cationically modified cellulose polymers behave as neutral polymers in good solvent when in high salt solvent.

Comparing salt-free and 50 m$M$ NaCl solutions (Figure 4), the viscosity of JR400 and LR400 show relatively little deviation with the addition of salt. This behavior can likely be attributed to the lower molecular weight (and entanglements per chain). However, the viscosity of JR30M and LR30M are altered by the presence of added salt, most dramatically in the semidilute concentration regimes. The viscosity in 50 m$M$ NaCl is up to 5.2-fold lower than in water at the same polymer concentration (e.g., JR30M at 1000 ppm). The polymer chains are interacting in semidilute regimes, thus, the addition of salt is postulated to decrease the number of interactions due to the more collapsed polymer chains (discussed earlier) leading to a lower viscosity.

Once the UCARE™ polymers are at a concentration to be sufficiently entangled (i.e., above $c_D$ in salt-free solution), the viscosity is nearly independent of solvent (salt or salt-free solution). Interestingly, the introduction of 50 m$M$ NaCl resulted in an increase in viscosity in the entangled regime. For example, the zero shear rate viscosity of LR30M is 1.4 Pa s in salt-free and 2.2 Pa s in 50 m$M$ NaCl at 10,000 ppm (1 wt %), i.e., a 57% increase in viscosity. The collapse of the polymer chains due to electrostatic screening does not seem to apply in the entangled concentration regime. The restricted movement of entangled chains likely eliminates this conformational freedom. One alternate hypothesis would be that the close proximity of the entangled chains increases the likeliness of hydrogen-bonding interactions. Increased hydrogen bonding lessens the ability of the polymer chains to move past one-another, which could increase the solution viscosity.[4]

The viscosity increase in the entangle regime for JR30M and LR30M is smaller than previous work on polysaccharides and other synthetic polymers.[10,11] Two significant differences between xanthan gum, which was the polymer studied in greatest detail,[10,11] are the lower molecular weight of the UCARE polymers (< 1M Daltons compared to >2M Daltons) and the charge density (i.e., xanthan has 1–3 anionic charges per monomer unit). Overall, leveraging the viscosity increase in the entangle regime may lead to new viscosity modifiers, personal care products, or controlled release complexes mentioned and referenced in the introduction.

## CONCLUSIONS

The viscosity as a function of concentration for four cationically modified cellulose polymers sold under the UCARE™ trade name (JR400, JR30M, LR400, and LR30M) in both salt-free and 50 m$M$ NaCl solution was measured. A number of similarities in the rheology exist across all four polymers. All of the polymers exhibit a Newtonian viscosity at dilute polymer concentrations and shear thinning in the semidilute and entangled concentration regimes. As common for polyelectrolytes in solution, the zero shear rate viscosity and the degree of shear thinning increase with increasing polymer concentration in both salt and salt-free solutions. Evaluation of viscosity as a function of concentration identified four distinct concentration regimes and three associated critical concentrations in salt-free solution. Three concentration regimes and two associated critical concentrations were observed in salt solution for all of the polymers. While the addition of salt to the higher molecular weight polymers (JR30M and LR30M) resulted in significant decreases in viscosity (up to 5-fold), the addition of salt to JR400 and LR400 had a relatively small effect. The viscosity scaling in salt solution is stronger in the entangled regime, especially for JR30M and LR30M, leading to larger zero shear rate viscosities in salt solution compared to salt-free solvent. This interesting viscosity inversion when comparing salt-free and salt solutions compares well to other biopolymer systems in the literature. Overall, the ability to tune the viscosity of these cationically modified cellulose polymers will be beneficial in designing new products from hair care to controlled release in the future.

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