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The addition of small amounts of xanthan gum to water yields viscoelastic solutions. In this letter, we show that the viscoelasticity of aqueous xanthan gum solutions can be tuned by different types of salts. In particular, we find that the decrease in viscoelasticity not only depends, as is known, on the salt concentration, but also is affected by the counterion ionic radius and the valence of the salt. *Published by AIP Publishing.* https://doi.org/10.1063/1.5026573

The effect of salt on the rheology of polyelectrolyte solutions is important for understanding how to engineer complex fluids with tailored rheological properties. For instance, aqueous solutions of xanthan gum, an anionic polyelectrolyte, have been used as a model fluid in a variety of studies, including swimming of bacteria,[1] drag reduction in turbulent flows,[2] and drop formation in non-Newtonian fluids.[3] The mechanism behind the rheological effects of salt type on polyelectrolyte solutions has been stated as a topic to be clarified in the literature.[4]

In the theory of linear elasticity, the stress in a sheared body is proportional to the magnitude of strain. On the other hand, in a Newtonian fluid, the shear stress is proportional to the rate of strain. A material is called viscoelastic when the effects of elasticity and viscosity are both present.[5] The relaxation time is one of the parameters that indicates the degree of viscoelasticity of a material; it denotes the time for the strain to relax when an applied stress is removed. Conventionally, as the relaxation time of a material increases, it is said to become more *viscoelastic*.

Salts in aqueous solutions of polyelectrolytes influence materials properties and have been studied extensively.[6,7] For example, it has been shown that the addition of salts affects the rheology of xanthan gum solutions and reduces their viscoelasticity in the semi-dilute regime.[8] In addition, when there is zero added salt, electrostatic repulsion of the charged backbone makes individual molecules more similar to rigid rods. With the addition of salt, the electrostatic interactions between the charged units of xanthan gum molecules are screened,[9–11] and the individual molecules are more collapsed[12] as depicted in Fig. 1. These conformational features influence the rheology. For instance, the addition of salt in solutions of even uncharged polymers such as poly(ethylene oxide) (PEO)[13] has been shown to cause conformational modifications and even affect the interfacial dilational rheology. Most of the experimental studies of these systems investigate the effects of a single type of salt and report the reduction of the relaxation time to be due to the charge screening mechanism,[8] which depends on the concentration of the salt; other chemical properties are not studied or

considered. For example, the relaxation time τ_R of a polyelectrolyte solution in the presence of a monovalent salt has been estimated for semi-dilute polymer solutions as[8]

$$\tau_R \propto (\eta_s/k_bT)(b/B)^{3/2}N^2c^{-1/2}(1 + 2Ac_s/c)^{-3/4},$$
$$c^* < c < c_e, \quad (1)$$

where η_s is the solvent viscosity, k_b is the Boltzmann constant, T is the temperature, b is the monomer size, B is the dimensionless contour length, N is the number of monomers along the polymer chain, c is the polymer concentration, A is the number of monomers between charges, and c_s is the salt concentration. This scaling for relaxation is predicted to be valid for the semi-dilute regime where the polymer concentration satisfies $c^* < c < c_e$, where $c^* = (B/b)^3(1/N)$, $c_e = n^4c^*$ and n is a universal number,[14] $5 \leq n \leq 10$. Relation (1) is used in the literature to explain the reduction in the relaxation
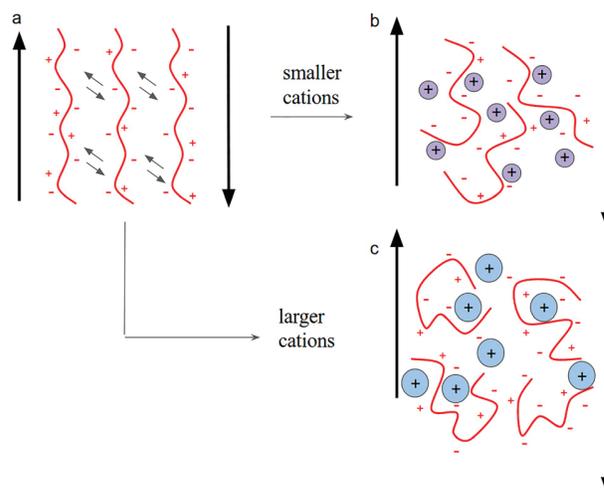

FIG. 1. Representation of the attachment of cations at the sites of an anionic polyelectrolyte under shear stress in the semi-dilute regime. (a) An aqueous solution of polyelectrolytes exhibits viscoelasticity as the material resists an applied shear stress. Positive charges in the salt-free solution are carried by counterions and they are free to move, while the negative charges are localized on the chains. The electrostatic interactions between the polymer chains are shielded, and therefore the solution exhibits weaker viscoelasticity than the salt-free solution. We suggest (as discussed later in the text) that larger cations (b) would shield the electrostatic interaction between chains more strongly compared to smaller cations (c) and result in a larger decrease in the viscoelasticity. Cations from added salts are shown with filled circles.

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time of polyelectrolyte solutions with one type of monovalent salt.[15] While there have been studies in the literature wherein the rheology of xanthan gum is reported with the addition of different salts,[16–18] no specific trends have been found. In this study, we show that the decrease in viscoelasticity also depends on the type of salt in addition to the concentration.

We choose a variety of salts, changing the valence of both cations and anions. In particular, we use NaCl, $C_7H_5NaO_3$ (sodium salicylate or NaSal), KCl, CsCl, $CaCl_2$, and $ZnCl_2$ as viscoelasticity modifiers in xanthan gum solutions. The properties of the cations of these salts are presented in Table I. The aqueous xanthan gum solutions with salt are prepared by adding the xanthan gum (Sigma-Aldrich, product no.: G1253, molecular weight $M_w = 2.7 \times 10^6$ g/mol) and the salt together in deionized water at their corresponding concentrations. The solutions are then stirred for 24 h to ensure good mixing before performing the rheology measurements.

The shear rheology is evaluated at room temperature (23 °C) using a stress-controlled Anton Paar Physica MCR-301 rheometer equipped with a double gap geometry (DG26). We measure a shear-rate dependent viscosity along with the elastic and viscous moduli, respectively, G' and G'', as a function of the oscillation frequency ω of the rheometer. The moduli can be measured by small amplitude oscillatory shear (SAOS) rheometry in the linear viscoelastic regime. We note that studies in the literature also employed other rheological techniques to characterize the rheology of their solutions such as optical tweezers[22] and microfluidic methods[23] because the solutions exhibit a very weak viscoelasticity. On the other hand, the concentrations we use with xanthan gum allow us to use standard oscillatory shear rheometry.

The experimental results presented in Fig. 2 show that the zero-shear viscosity increases with the xanthan gum concentration, as expected.[24] The viscosity versus the shear rate exhibits a power-law behavior of the form $\mu = a\dot{\gamma}^n$, which is preserved after the addition of salt. We also observe that the relative change in the viscosity due to the addition of salt decreases with increasing xanthan gum concentration. In particular, the results in Fig. 2 for NaCl show that for the two higher xanthan gum concentrations, there is no influence of the 0.5 M salt concentration on the viscosity. At lower xanthan gum concentrations, our measurements show effects up to 20% at 0.5 M NaCl.

We examine the change in the viscoelastic properties of solutions as a function of salt type and concentration. Therefore, for the rest of this letter, we work with a constant xanthan gum concentration [XG] = 0.2 wt. % and investigate the change in the viscoelasticity of the solution. This concentration is above the limit for the transition from the dilute regime to the semi-dilute regime[25] and is observed to be
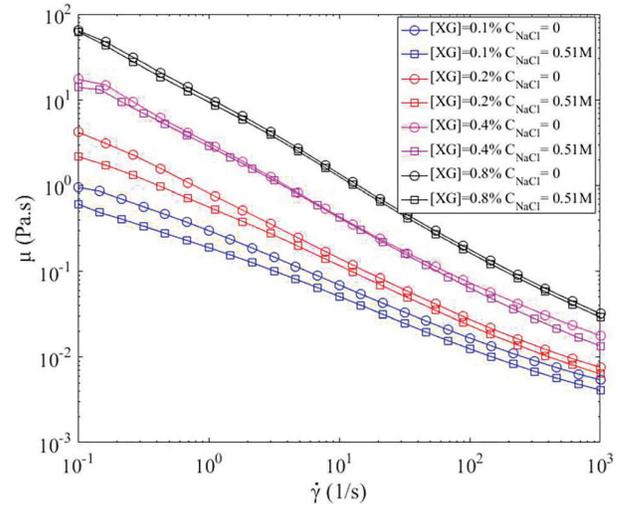

FIG. 2. Shear viscosity μ as a function of shear rate $\dot{\gamma}$. Addition of salt (NaCl) reduces the zero-shear viscosity slightly and preserves the shear-thinning behavior. The xanthan gum concentration is in wt.% and the salt concentration is given in molarity (M).

below the entanglement limit calculated using relation (1) with the material properties presented in the supplementary material. Thus, the solutions in the absence of salt can be described by the semi-dilute—unentangled regime,[8] where the "Rouse model"[26,27] should be valid, and the xanthan gum molecules can be considered as rigid rods[3,28] with electrostatic interactions in water.

We quantify the viscoelasticity using the relaxation time, for which [XG] = 0.2 wt. % with no added salt is measured as 6.7 s (see the discussion of measurements below); we note that, as indicated by others,[29] Eq. (1) predicts $\tau_R \approx 0.91$ s, which is far removed from the measurement. We believe that this highlights the need for a further understanding of this problem and the need to consider effects such as hydrogen bonding,[30] which is shown to be weakenend in solutions by the addition of salts.[31,32] Addition of salt is expected to result in the screening of the electrostatic effects in the polymer chain. Conventionally, this screening has been quantified using the Debye length,[25,33] which is defined as

$$\lambda_D = \sqrt{\frac{\epsilon k_b T}{4\pi q^2 c_s}}, \qquad (2)$$

where ϵ is the dielectric constant of the medium, q is the ion charge, and c_s is the ion concentration. For a given ion, if the calculated Debye length is shorter than the average distance ℓ_{XG} between the charged units of xanthan gum molecules, i.e., $\lambda_D < \ell_{XG} \approx 0.67$ nm,[34] it has been previously reported that the electrostatic interactions are completely shielded.[25] According to Eq. (2), for the given [XG], this condition can be satisfied if $c_s > 0.02$ M for monovalent and $c_s > 0.005$ M for divalent salts.

The relaxation time τ_R of viscoelastic solutions is defined as $\tau_R = 1/\omega_c$ according to Maxwell and Rouse models with SAOS,[35] where ω_c is the crossover frequency for the G' and G'' curves. The G' and G'' values versus the shear oscillation frequency ω applied by the rheometer are reported in Fig. 3(a). In particular, for different salt

TABLE I. Properties of cations used in this study.[19–21]

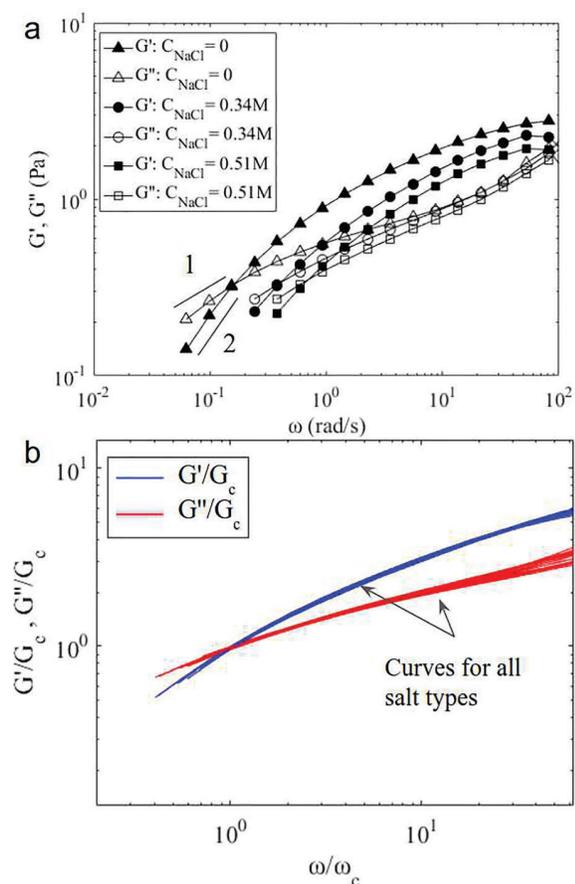| Cation	Molecular weight (g/mol)	Ionic radius (Å)	Hydrated radius (Å)
Na^+	23	1.02	3.6
K^+	39.09	1.38	3.3
Cs^+	132.9	1.67	3.3
Ca^{++}	40.1	1.00	4.1
Zn^{++}	65.38	0.74	4.3

FIG. 3. Addition of salt (NaCl) reduces the relaxation time for xanthan gum solutions. (a) Change in elastic (G') and viscous (G'') moduli as a function of shear oscillation frequency (ω) for different NaCl concentrations (C_{NaCl}) at a fixed oscillatory shear stress in the linear viscoelastic regime. (b) Normalized elastic (G'/G_c) and loss (G''/G_c) moduli as a function of normalized angular frequency (ω/ω_c) for all the salt types and concentrations in this study. G_c is the crossover modulus when two moduli intersect and $\tau_R = 1/\omega_c$ is the reciprocal of the crossover angular frequency for a given salt, which are both evident in (a). The xanthan gum concentration is [XG] = 0.2 wt. %.

concentrations, we observe that the crossover frequency shifts with the addition of salt so that the relaxation time decreases with increasing salt concentration. In Fig. 3(a), we also indicate the slopes $G' \propto \omega$ and $G'' \propto \omega^2$ below the crossover frequency in accordance with the Maxwell and Rouse models.[36] However, above the crossover frequency, the slopes do not follow the trends of either of these two models.

G' and G'' versus ω curves can be generated for all of the salts and concentrations used in this study. After calculating the corresponding crossover modulus G_c and the frequency ω_c for each salt type and concentration, we normalize the G' and G'' values along with the frequency ω. As a result, all of the data we obtain can be collapsed on master curves as presented in Fig. 3(b). This result is significant because it shows that both monovalent and divalent salts result in a decrease in viscoelasticity that can be collapsed on the same curve.

The τ_R values for all of the salts and concentrations used in this study are shown in Fig. 4 and is the most important finding we report here. The different monovalent and divalent cations result in different decreases in the relaxation time. Even for the same anion type and concentration, there is an
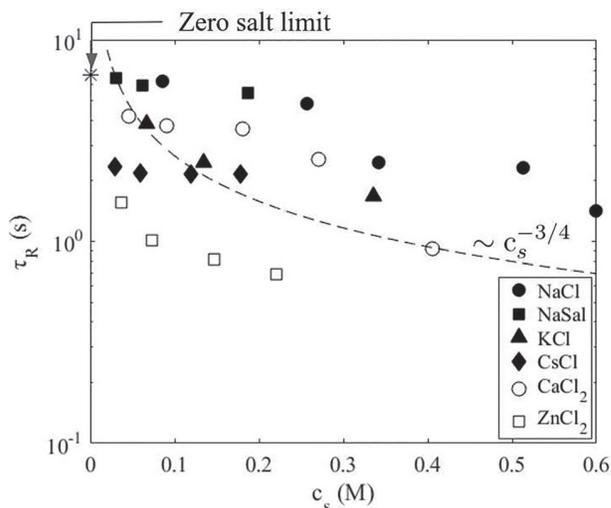

FIG. 4. Change in the relaxation time (τ_R) with the salt concentration (c_s). Increasing salt concentration decreases the relaxation time ($\tau_R = 1/\omega_c$), while the decrease depends on the salt type in addition to the concentration. The scaling proposed in Eq. (1) as $\tau_R \propto c_s^{-3.4}$ is fitted to the monovalent salt data. The data points do not follow the trend proposed by theory.

effect of changing the cation; e.g., τ_R decreases in the order Na$^+$, Ca^{2+}, K$^+$, Cs$^+$, and Zn^{2+}. Also, the salt concentrations used in this study are well above the concentration that would satisfy the $\lambda_D < \ell_{XG}$ condition for both monovalent and divalent salts, which means that charge screening cannot be the only mechanism and the Debye screening length cannot be the only criterion to explain the reduction in the relaxation time. Also, according to Eq. (1), the relaxation time should scale as $c_s^{-3/4}$, and this scaling with an adjusted prefactor is fitted to the data points as presented in Fig. 4, which shows that the theory in its current form cannot capture the effects of different salts. Furthermore, we also found that even if the relaxation time monotonically decreases with decreasing Debye length, the relaxation time follows a similar trend presented in Fig. 4 as a function of the Debye length (see supplementary material Fig. S1). We also note that the Hofmeister effect[37–39] has been shown previously to correlate with the effects of added salt on the rheology of protein solutions.[40] The Hofmeister series indicates that the cations in our study can be ranked as Cs$^+$ > K$^+$ > Na$^+$ > Ca^{2+} > Zn^{2+}, where the ions on the left tend to stabilize the native folded structure of a protein and decrease its solubility, while the ions on the right tend to increase solubility.[41] However, according to Fig. 4, we observe that this trend correlates only among the monovalent salts and does not account for the above-mentioned effects associated with the divalent salts.

We have found for monovalent salts that the salt-dependent decrease in the relaxation time is correlated with the ionic radius of the cations (see Table I) and is not affected by the anion of the salt (compare NaCl and NaSal). Also, we note that the hydrated radius should play a role in the conformation of the polyelectrolyte.[4] Accordingly, we observe that divalent ions, which have a larger hydrated radius than monovalent salts, affect the relaxation time more strongly than monovalent ions (Fig. 4). However, the picture can be more complicated. In particular, ZnCl$_2$ is not pH-neutral as opposed to all the other salts used in this study.

Indeed, the addition of $ZnCl_2$ to xanthan gum solutions results in a sharp decrease in the pH value, which we show to be correlated with the viscoelasticity of these solutions (see supplementary material, Fig. S5). Moreover, multivalent salts can easily create polyelectrolyte aggregates[42] depending on chain flexibility[43] and the counterion hydration shell.[44]

The decrease in the relaxation time of polyelectrolytes with the salt concentration has been attributed previously to the charge screening mechanism.[45] However, we show in this letter that the salt concentration is not the only reason for the decrease in the viscoelasticity of polyelectrolyte solutions and there are salt-dependent effects, not in existing theory, including the counterion ionic radius, and the pH of the solution with the added salt, which regulate the decrease in the relaxation time such as the valence. Our results also show that it is possible to engineer solutions with customized viscoelastic properties by the choice of concentration and the type of salt.

See supplementary material for the comparison of relaxation time as a function of the Debye length and pH of the xanthan gum solutions with added salt.

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