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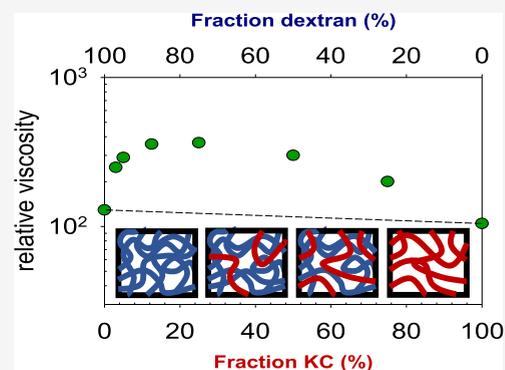
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Viscosity of Aqueous Polysaccharide Solutions and Selected Homogeneous Binary Mixtures

Mathieu Potier, Lingsam Tea, Lazhar Benyahia, Taco Nicolai,* and Frederic Renou

ABSTRACT: The viscosity (η) of dextran (Dex), methyl cellulose (MC), hydroxypropylmethyl cellulose (HPMC), κ -carrageenan (KC), alginate (Alg), and carboxymethyl cellulose (CMC) was measured as a function of the shear rate ($\dot{\gamma}$) over a broad range of concentrations both in salt-free water and in 0.1 M NaCl. The concentration (C) dependence of the Newtonian viscosity (η_0) was found to be universal for neutral polysaccharides and anionic polysaccharides in 0.1 M NaCl when C was multiplied with the intrinsic viscosity. The dependence was compared with theoretical predictions assuming dominant hydrodynamic or dominant topological interactions. The effect of electrostatic interactions was observed for anionic polysaccharides in salt-free water but not at higher concentrations. Master curves of the shear thinning behavior at different concentrations were obtained when η/η_0 was plotted versus $\tau \cdot \dot{\gamma}$, with τ being a concentration-dependent time that characterizes the onset of shear thinning. Binary mixtures of two neutral polysaccharides (MC and HPMC), two anionic polysaccharides (Alg and CMC), and a neutral (Dex) and anionic polysaccharide (KC) were investigated as a function of the composition and the total polysaccharide concentration. The behavior of the first two mixtures was similar to that of a single polysaccharide with an intermediate intrinsic viscosity. Significant synergy was observed for the third type of mixtures in salt-free water demonstrating the important effect of electrostatic interactions between charged polysaccharides at low concentrations even in concentrated solutions of neutral polysaccharides.



1. INTRODUCTION

Polysaccharides have been widely used to texturize aqueous systems with applications in the food, pharmaceutical, and cosmetics industries.¹ The Newtonian viscosity (η_0) can be controlled by varying the concentration or the molar mass of the polysaccharides.^{2,3} Shear thinning is generally observed for more viscous solutions to an extent that depends for a given η_0 on the type of polysaccharide, for example, hydroxypropylmethyl cellulose (HPMC),³ hydroxypropyl cellulose (HPC),⁴ alginate (Alg),⁵ carboxymethyl cellulose (CMC),^{3,6} xanthan,^{7,8} hyaluronan,⁹ and galactomannan.¹⁰ Therefore, one can use different polysaccharides to vary the shear rate dependence of the viscosity (η) for a given η_0 .

Rheological properties of mixtures of polysaccharides have in the past mainly been studied for polysaccharides that interact specifically, with the aim to exploit the synergy resulting from these interactions for potential applications, see for example refs. 11–13 Also, segregative phase separation of incompatible polysaccharides has been studied in some depth, see for example refs 14–16 However, we are not aware of investigations of the viscosity of homogeneous mixtures of polysaccharides without specific interactions over a broad range of concentrations. Potentially one could use such mixtures to fine tune both η_0 at a given polysaccharide concentration and the shear rate dependence for a given η_0 .

Here, we present an investigation of the viscosity of aqueous solutions of different neutral polysaccharides dextran (Dex), methyl cellulose (MC), HPMC and anionic polysaccharides κ -carrageenan (KC), Alg, CMC, and binary mixtures thereof. We investigated the concentration dependence of individual polysaccharide solutions and 50/50 mixtures over a wide range of concentrations and also studied the effect of varying the composition of the mixtures at a given total polysaccharide concentration. The results were compared to theoretical predictions of the viscosity of flexible polymers and polyelectrolyte solutions that we discuss briefly in the next section.

2. THEORY

The viscosity of solutions of flexible polymers has been studied extensively in the past. The initial concentration dependence of the relative viscosity η_r , defined as the sample viscosity

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normalized by the solvent viscosity, was extrapolated to zero shear rate and can be described as a virial expansion in terms of the intrinsic viscosity $[\eta]$ and the Huggins constant (K_h)¹⁷

$$\eta_r = 1 + [\eta] \cdot C + K_h \cdot ([\eta]C)^2 + \dots \quad (1)$$

Different theoretical approaches have been proposed to describe the dependence of the relative viscosity at higher concentrations. One approach considers primarily the hydrodynamic interaction between the polymer chains and neglects topological constraints, whereas the second does the inverse. A detailed discussion of and comparison between the two approaches can be found in the study by Phillies.¹⁸ According to the hydrodynamics approach, the relative viscosity (η_r) with respect to the solvent viscosity increases with increasing polymer concentration (C) following a stretched exponential¹⁹

$$\eta_r = \exp((a \cdot C)^\alpha) \quad (2)$$

Phillies^{19,20} reviewed the concentration dependence of η_r for a large number of systems and showed that in many cases, it can be well described by eq 2 even at low concentrations with α between 0.5 and 1.

Others using the same approach found that the viscosity of semidilute aqueous solutions of PEG with different molar mass could be well described in terms of the hydrodynamic radius (R_h) of the polymers and the correlation length (ξ) of the solution^{21,22}

$$\eta_r = \exp(b(R_h/\xi)^\beta) \quad (3)$$

with $\beta = 0.78$ independent of the molar mass. Scaling arguments for semidilute polymer solutions predict a power law dependence of ξ on the polymer concentration above the overlap concentration (C^*)

$$R_h/\xi \approx (C/C^*)^\nu \quad C > C^* \quad (4)$$

with $\nu = 0.75$ and 1 in good and theta solvents, respectively. Therefore, eq 3 is equivalent to eq 2 with $\alpha = \beta \cdot \nu$. More recently, these authors found that the viscosity of more dilute PEG solutions could also be fitted to eq 3, but with a larger exponent ($\beta = 1.3$) resulting in $\alpha = 0.96$.²² The temperature dependence of the viscosity could be described in terms of an activation energy (ΔE_a)²³

$$\eta_r = \exp(\Delta E_a/RT) \quad (5)$$

where R is the gas constant and T is the absolute temperature. Comparison with eq 3 shows that $\Delta E_a \propto (R_h/\xi)^\beta$ with a proportionality constant that depends on the chemistry of the polymers.

The topological constraints approach considers that when the concentration is above the so-called entanglement concentration (C^{ent}), the movement of the chains is constrained due to entanglement with each other.^{17,24–26} Scaling arguments lead to a power law dependence of the viscosity on the concentration above C^{ent} as long as the polymers are still relatively dilute, that is, in the so-called semidilute regime

$$\eta_r = d \cdot C^\gamma \quad C > C^{ent} \quad (6)$$

where γ depends on the solvent quality: $\gamma = 3.9$ and 4.7 in good and theta solvents, respectively. Entanglements occur when the polymers overlap significantly, and C^{ent} is therefore larger than the overlap concentration. In a relatively narrow range of concentrations between C^* and C^{ent} , a weaker power law concentration dependence is expected with $\gamma = 1.3$ and 2 in

good and theta solvents, respectively. For several systems, the concentration dependence of η_r above C^{ent} was found to be consistent with eq 6, but the concentration range between C^* and C^{ent} is too small to reliably test the predicted power law dependence for semidilute non-entangled polymers. It was found that the concentration dependence of η_r for aqueous Alg⁵ and HPMC solutions⁴ could be well described by the sum of eqs 1 and 6

$$\eta_r = 1 + [\eta] \cdot C + K_h \cdot ([\eta] \cdot C)^2 + d \cdot C^\gamma \quad (7)$$

The overlap concentration is inversely proportional to $[\eta]$ so that one expects a universal dependence of η_r on $[\eta] \cdot C$ if the solvent quality and the ratio C^{ent}/C^* are the same. The latter is expected to be the case for the same polymers with different molar masses, for which universal behavior has indeed been observed experimentally.

The difference between eqs 2 and 7 is small when $\eta_r < 10^4$, which is the case for many studies reported in the literature. It is therefore often not possible to distinguish experimentally the two approaches within the scatter of the data. However, Phillies noted in his review²⁰ that in a number of cases, a clear deviation from a stretched exponential increase has been observed at higher concentration with a transition to a power law increase. This transition could be an indication that topological constraints become the dominant effect on the viscosity at high concentrations. However, Phillies argued that the transition can also be understood in the framework of dominant hydrodynamic interactions, pointing out that a similar transition was observed in suspensions of microgels that cannot entangle.²⁰

Finally, Sato et al.^{27–29} extended the theory for the viscosity of rigid rod suspensions to cover the case of neutral semiflexible polymers for which the persistence length is not very small compared to the contour length so that they can be described as fuzzy cylinders with an effective length and thickness. They derived the following equation

$$\eta_r = 1 + [\eta] \cdot C - [\eta] \cdot C \cdot a_1 \{1 + [1 + a_2 \cdot C \cdot \exp(a_3 \cdot C)]^2\} \quad (8)$$

where parameters depend on the size and structure of the polymers. Good agreement was found with the concentration dependence of the rather stiff polysaccharides schizophyllan and xanthan and also for the more flexible cellulose tris(phenyl carbamate).²⁹

When the polymers carry charges, electrostatic interactions have a strong influence on the viscosity. Charge repulsion leads to stretching of flexible polyelectrolytes in salt-free water so that the chains start to overlap at much lower concentrations than for neutral polymers.²⁵ As a consequence, the viscosity is higher for polyelectrolytes than for neutral polymers for a given concentration. Addition of salt screens the electrostatic interactions, and at high ionic strength, the behavior of polyelectrolytes is the same as that of neutral polymers. Counterions can also screen the interactions so that even in pure water, the viscosity of polyelectrolytes and neutral polymers is expected to be close at high concentrations. In the intermediate concentration range between C^* and C^{ent} , the specific viscosity ($\eta_{sp} = \eta_r - 1$) is predicted theoretically to have a power law dependence on C with an exponent of 0.5,^{25,30,31} which has been observed experimentally. For aqueous solutions of CMC with different salt concentrations, a power law concentration dependence was observed at low concentrations with an exponent that increased with increasing

ionic strength from 0.68 to 1.33.³² At higher concentrations, the viscosity increased more steeply and became independent of the ionic strength, suggesting that the contribution of counterions became sufficient to screen the charge interactions. However, others have noted a relatively small increase of the viscosity after adding salt at high concentrations,^{33,34} that is, the opposite of the effect of adding salt at low concentrations.

Generally, shear thinning is observed for flexible polymer and polyelectrolyte solutions. The shear rate ($\dot{\gamma}$) dependence can usually be well fitted by a phenomenological equation that describes the transition between the Newtonian plateau at low shear rates and a power law decrease at high shear rates with exponent n .^{2,35}

$$\eta = \eta_0(1 + (\dot{\gamma} \cdot l)^k)^{-n/k} \quad (9)$$

Equation 9 generalizes the equations proposed by Carreau³⁶ for which k is fixed at 2 and by Cross³⁷ for which k is fixed at unity. Phillips¹⁹ proposed a theoretical approach that predicts a stretched exponential decrease of η_r at low shear rates followed by a power law decrease at high shear rates. He found good agreement with this functional form for many systems reported in the literature.

Studies of mixtures of different types of flexible polymers without specific interactions are rare. An obvious reason for this is that often larger polymers with different chemistries are incompatible and phase separate at higher concentrations. A number of so-called mixing laws have been proposed to predict the viscosity of mixtures from that of the individual liquids.³⁸ The most successful of these for binary mixtures of non-interacting macromolecules is the logarithmic mixing law

$$\log(\eta_r) = x_1 \log(\eta_{r1}) + x_2 \log(\eta_{r2}) \quad (10)$$

where x_1 and x_2 are the mass or volume fractions of the two macromolecules. Equation 10 follows from the assumption that the total activation energy controlling the viscosity is equal to the sum of that of each component at the same total concentration weighed by their mass or volume fraction. Most mixtures of polymers with different chemistries phase-separate, and there are very few studies of homogeneous binary mixtures up to high concentrations. Wisniewska et al.³⁹ avoided phase separation by studying binary mixtures of polymers with the same chemistry but different molar masses. They proposed to extend eq 2 for homogeneous binary mixtures of neutral flexible polymers with no specific interactions

$$\eta_r = \exp[b_1 x_1 (R_{h1}/\xi_1)^{\beta_1} + b_2 x_2 (R_{h2}/\xi_2)^{\beta_2}] \quad (11)$$

which is equivalent to the logarithmic mixing law. They studied mixtures of PEO with different molar mass in aqueous solutions for which b , β , and ξ are the same and found good agreement.

Sato et al.²⁷ extended their theory for semiflexible polymers to multicomponent systems. They considered that the hindrance between semiflexible polymers with different size depends on their relative size difference. They found good agreement with their theory for mixtures of xanthan with different molar masses and for a mixture of xanthan and schizophyllan.

3. MATERIALS AND METHODS

3.1. Sample Preparation. Dex, HPMC, MC, Alg, CMC, and KC were purchased from Sigma-Aldrich and used without further

purification except for KC. The KC sample contained potassium ions, which were removed by dialysis against 0.1 M NaCl followed by dialysis against Milli-Q water to remove excess salt and freeze drying. The substitution degree of HPMC was 1.1–1.6 for methoxy and 0.1–0.3 for propylene oxide. It was 2.1 and 0.9, respectively, for MC and CMC. All polysaccharides were solubilized by stirring overnight at room temperature. Heating at 70 °C was used to facilitate solubilization of concentrated very viscous Alg, CMC, and KC solutions. Mixtures were prepared by mixing stock solutions of the polysaccharides at the required ratios. All binary mixtures studied here were transparent.

3.2. Molar Mass Distribution. Molar mass (M) distributions of all polymers were determined by size exclusion chromatography combined with on-line light scattering (Dawn EOT, Wyatt technology, Santa Barbara, CA, USA) and refractive index (Shodex RI 71, Showa Denko K.K., Tokyo, Japan) detection. A TSK gel G6000PW column was used with 0.1 mol/L NaNO₃ at pH 7 as the eluent. Refractive index increments (dn/dc) used were 0.15 L/g for Dex and Alg and 0.145 L/g for HPMC, MC, CMC, and KC. Log (M) was found to have a linear dependence on the elution time, which was used to determine the molar mass distributions of the polysaccharides (see Figure S1 of the Supporting Information). The weight (M_w) and number (M_n) average molar mass were calculated from the distributions and are summarized in Table 1.

Table 1. Weight Average Molar Mass and Dispersity Index of the Polysaccharides Used in This Study

| | M_w (g/mol) | M_w/M_n |
|------|-------------------|-----------|
| Dex | 4.3×10^5 | 3.4 |
| Alg | 1.0×10^5 | 3 |
| CMC | 1.9×10^5 | 2.2 |
| KC | 5.3×10^5 | 3 |
| MC | 2.3×10^5 | 2.5 |
| HPMC | 4.3×10^5 | 3 |

3.3. Rheology. The viscosity was measured as a function of the shear rate with a stress-controlled rheometer (AR200, TA instrument) with cone-plate geometries (40 mm, 2° or 60 mm, 1°). The experiments were done at 20 °C using a Peltier plate that control the temperature within 0.1 °C. The viscosity was measured by decreasing the shear rate from 10³ to 0.01 s⁻¹ during 2 min followed by an increase back to 10³ s⁻¹. In most cases, the two ramps superimposed. However, in a few cases, time-consuming steady-state measurements were necessary in order to obtain reliable results.

4. RESULTS AND DISCUSSION

4.1. Single Polysaccharide Solutions. We studied the viscosity of the neutral polysaccharides Dex, HPMC, and MC as well as the anionic polysaccharides Alg, CMC, and KC. The viscosity was measured at different concentrations (C) as a function of the shear rate ($\dot{\gamma}$). The measurements were done at pH 7 both in salt-free water and in 0.1 M NaCl. As an example, Figure 1a shows the results for KC in pure water. In each case, shear thinning was observed at higher concentrations. The data could be superimposed by normalizing the viscosity with the zero shear viscosity and applying horizontal shift factors (τ) so that $\eta/\eta_0 = 0.8$ at $\tau \cdot \dot{\gamma} = 1$ (Figure 1b). We will discuss first the concentration dependence of η_r and then the shear thinning behavior.

4.2. Newtonian Viscosity. In Figure 2a, the specific viscosity ($\eta_{sp} = \eta_r - 1$) is plotted as a function of the concentration for the different polysaccharide solutions in 0.1 M NaCl. Figure 2b shows that the data for all polysaccharides superposed well when using horizontal shift factors. The master curve could be well-described by eq 7, which together

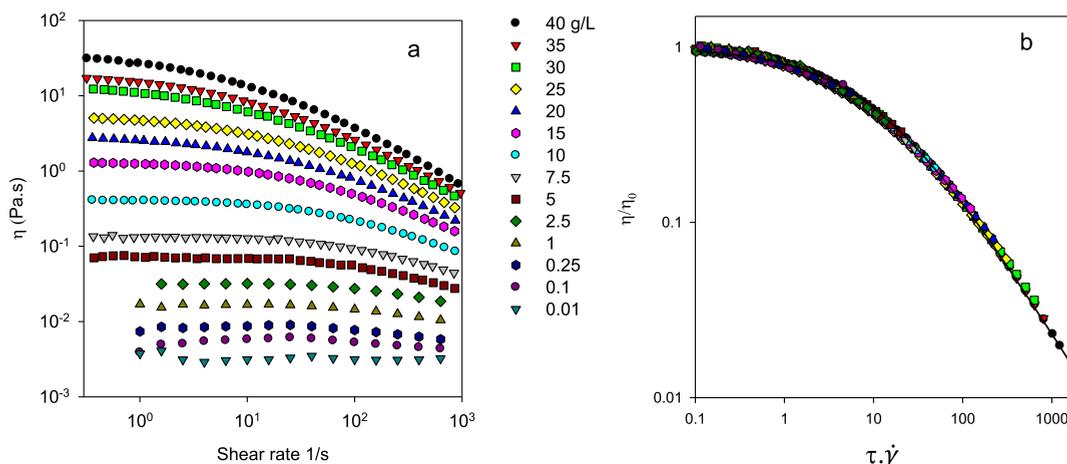


Figure 1. (a) Shear rate dependence of the viscosity of KC solutions in salt-free water at different concentrations indicated in the figure. (b) The same data that are shown in (a) after normalization of η by η_0 and $\dot{\gamma}$ by the value where $\eta/\eta_0 = 0.8$. The solid line represents a fit to eq 9.

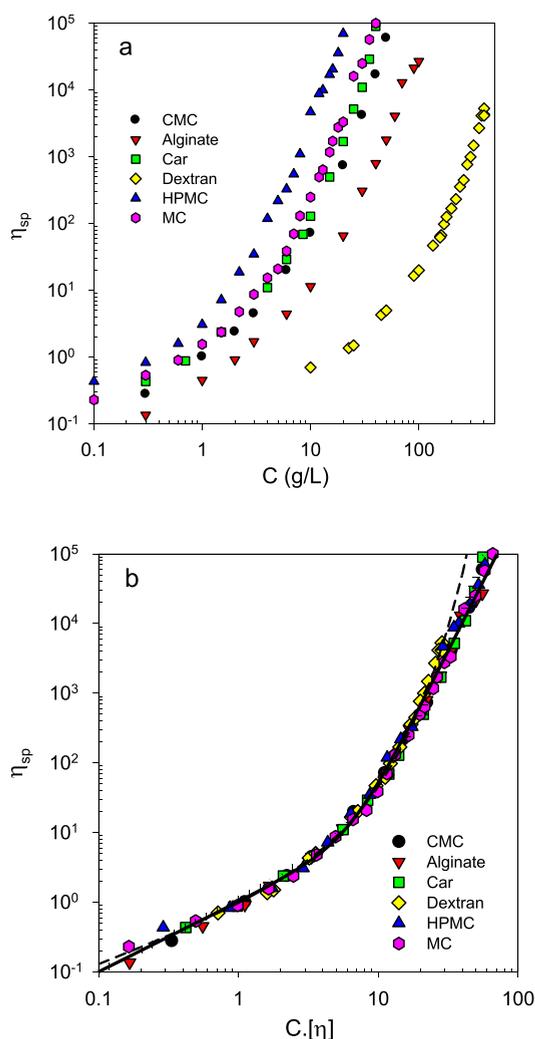


Figure 2. Specific viscosity of different polysaccharide solutions in 0.1 M NaCl as a function of the polymer concentration (a) and as a function of $C[\eta]$ (b). The dashed, solid, and dotted lines in (b) represent fits to eqs 2, 7, and 8, respectively.

with the shift factors allowed us to obtain the intrinsic viscosity of all polysaccharides. We note that we did not measure a sufficient amount of low concentrations to accurately

determine $[\eta]$ for each system, but by fitting the master curve and using the shift factors, more reliable values could be obtained. Figure 2b shows the master curve of η_{sp} as a function of $C[\eta]$ and the fit to eq 2 with $K_h = 0.02$ and $\gamma = 4$. The values of $[\eta]$ obtained in this manner are summarized in Table 2. The

Table 2. Intrinsic Viscosities and Parameters Obtained from Fits to Eq 7 for Solutions of Different Polysaccharides and Binary Mixtures

| | $[\eta]$ (L/g) | K | N | τ/l |
|------------------|----------------|------|------|----------|
| Dex ^a | 0.071 | | | |
| Alg | 0.56 | 0.41 | 1 | 300 |
| CMC | 1.1 | 0.41 | 0.7 | 130 |
| KC | 1.4 | 0.67 | 0.83 | 11.5 |
| MC | 1.65 | 0.5 | 1 | 72 |
| HPMC | 3.0 | 0.5 | 0.9 | 57 |
| HPMC/MC | 2.3 | 0.5 | 0.9 | 72 |
| Alg/CMC | 0.75 | 0.41 | 0.85 | 180 |
| Dex/KC | 0.17 | 0.9 | 0.46 | 2 |

^aShear thinning of the Dex solutions was too weak to determine K , n , and τ/l .

particularly small intrinsic viscosity for Dex reflects its branched structure, which also explains why the molar mass of Dex at a given elution time shown in Figure S1a was much larger than that for the other polysaccharides.

The observed power law exponent γ is compatible with the value predicted by scaling theory for entangled polymers in good solvents (3.9). Exponents close to 4 were earlier reported for the neutral polysaccharides HPMC,⁴⁰ HPC,^{3,4} galactomannan,¹⁰ and Dex⁴¹ as well as for the anionic polysaccharides Alg in 0.15 M NaCl,⁵ hyaluronan in 0.1 M NaCl,^{9,42} CMC in 0.01 M NaCl,³ and KC in 0.1 M NaCl.⁴³ Morris et al.⁴⁴ compared the concentration dependence of η_{sp} for different polysaccharides including Dex and found a slightly smaller exponent (3.3), which is perhaps due to the fact that they fitted a range of η_{sp} (10 to 10⁴) for which the final slope had not yet been reached. The universal behavior observed here and by Morris et al.⁴⁴ suggests that different values of the power law exponents found in the studies of individual polysaccharides reflect experimental uncertainty and differences in the concentration range used in the fit. A power law dependence with a smaller exponent (1.25) has been predicted at lower

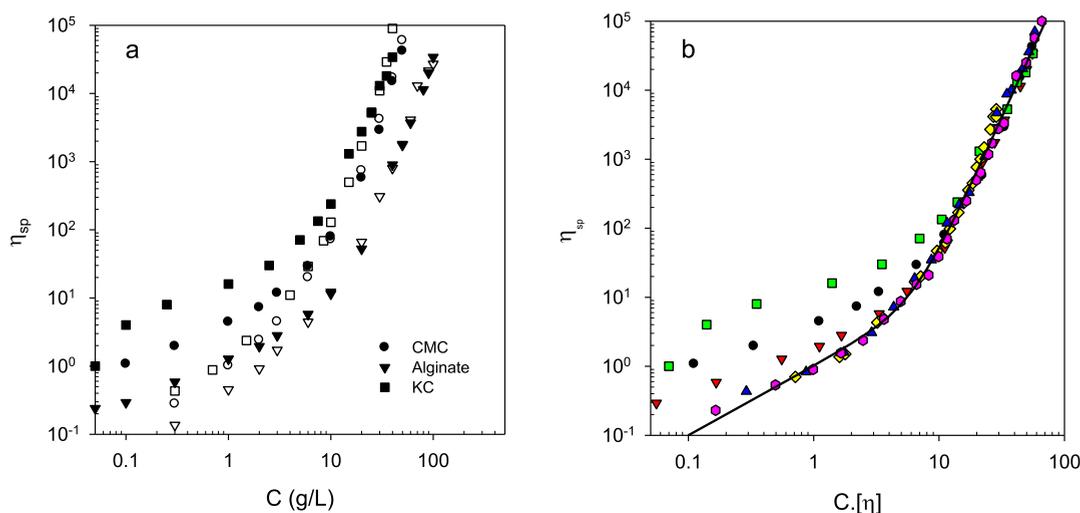


Figure 3. (a) Comparison of the concentration dependence of the specific viscosity of KC, CMC, and Alg in salt-free water (filled symbols) and in 0.1 M NaCl (open symbols). (b) Specific viscosity as a function of $C \cdot [\eta]$ of different polysaccharide solutions in pure water. The solid line represents eq 7 with the same parameters as used to fit the data obtained in 0.1 M NaCl. Symbols are as in Figure 2.

concentrations where the polymers are semidilute but not yet entangled.²⁵ One can find a region of concentrations where such a power law exponent fits the data, but we consider that the relevant concentration range is too narrow for an unambiguous test of the theory.

Up to $C \cdot [\eta] \approx 30$, the master curve could be well described both by eq 2 with $a = 0.6[\eta]$ and $\alpha = 0.75$, and by eq 8 with $a_1 = 0.5$, $a_2 = 0.06$ and $a_3 = 0.03$. The value of α is within the range found for many systems.¹⁹ Both equations predict an exponential increase at high concentrations, whereas a power law dependence appears to describe the data better for $C \cdot [\eta] > 30$. It is noteworthy that this comparison shows that one cannot judge the validity of the different theoretical approaches simply on the basis of how well they describe the experimental data.

We verified that for the neutral polysaccharides, the viscosity in salt-free water was the same as in 0.1 M NaCl. Figure 3a shows a comparison between the concentration dependence of η_{sp} for the charged polysaccharides in water and in 0.1 M NaCl. As expected, η_{sp} was significantly larger in salt-free water than in 0.1 M NaCl at low concentrations. At high concentrations, however, the effect of added salt on the viscosity was small. Figure 3b shows η_{sp} as a function of $C \cdot [\eta]$ using the intrinsic viscosities found in 0.1 M NaCl. The solid line in Figure 3b is the same as that in Figure 2b and demonstrates that for $C \cdot [\eta] > 10$, the viscosity was little influenced by the addition of salt. At lower concentrations, we observed a clear effect of electrostatic repulsions on the viscosity that depended on the type of polysaccharide. The effect was strongest for KC for which the concentration dependence can be approximated by a power law with the predicted exponent of 0.5. However, for CMC and Alg, the values of η_{sp} were smaller, the power law exponents were larger, and the transition to the steeper dependence occurred at smaller $C \cdot [\eta]$. These differences cannot be attributed to excess salt in the powders as the same results were obtained for Alg after extensive dialysis against salt-free water.

Lopez et al.⁶ measured the concentration dependence of the viscosity for CMC at different NaCl concentrations. They found that at low concentrations, η_{sp} decreased with increasing ionic strength, whereas at high concentrations, there was little

influence of the ionic strength. The results in salt-free water and in excess salt were compatible with those reported here. The data at high concentrations were fitted to a power law with slightly smaller exponent (3.5), which can be attributed to experimental uncertainty and the fact that the concentration range was somewhat smaller. Donnelly et al.³³ also found little effect of the addition of salt on the viscosity of charged cellulose polymers. However, Wyatt et al.³⁴ reported an increase of η_0 by more than a factor of two when NaCl was added to a KC solution at $C = 65$ g/L, that is, higher than the highest concentration studied here. They also observed an increase for other entangled polyelectrolyte solutions, which they attributed to hydrogen bonding interactions that were facilitated by screening of electrostatic repulsion. Here, we did not observe a significant effect, but we do not exclude that a small effect is hidden in the experimental scatter. We believe that the weak effect of charge at high polyelectrolyte concentrations can be understood by screening of the electrostatic interactions by counterions, since for $C > 10$ g/L, the counterion concentration becomes larger than 0.1 M. The different concentration dependences of η_{sp} at low concentrations for the different anionic polysaccharides reflect differences in the effect of electrostatic interactions on the chain conformation.

We may conclude from Figure 2b that neutral polysaccharides and charged polysaccharides in the presence of salt studied here show a universal dependence of the viscosity as a function of $C \cdot [\eta]$ that up to $C \cdot [\eta] \approx 30$ can be equally well described by eq 3 assuming dominant hydrodynamic interactions and by eq 7 assuming dominant topological constraints. For $C \cdot [\eta] > 30$, a power law increase with an exponent of about 4 fitted most data better. The effect of electrostatic interactions is important only in salt-free water when the polymer concentration is relatively low and depends on the type of polysaccharide. At higher concentrations, electrostatic interactions are screened by the counterions.

4.3. Shear Rate Dependence. Shear thinning was observed to different extents for all polysaccharide solutions at higher concentrations except for Dex that showed very weak shear thinning even at 400 g/L. Master curves could be obtained in the same manner as was shown above for KC

(Figure 4). The choice of the characteristic relaxation time is rather arbitrary, and different choices, such as l in eq 9, can give

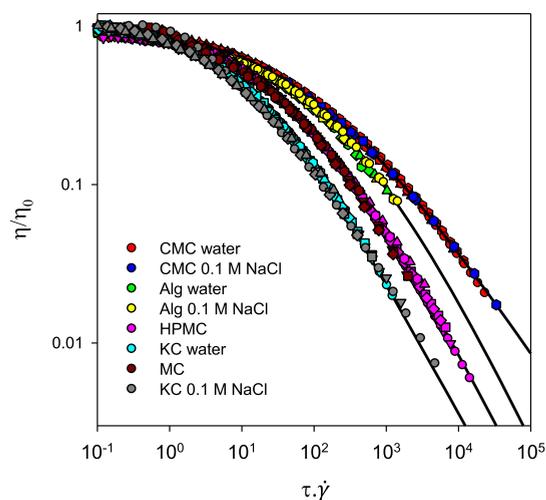


Figure 4. Master curves of the shear rate-dependent viscosity for different polysaccharides solutions. For the anionic polysaccharides, the results in water and in 0.1 M NaCl are shown. The solid lines represent fits to eq 9 with the parameters summarized in Table 1.

very different values because the transition to the power law dependence spans several decades. With our choice, the master curves overlap at low shear rates, which renders it easier to compare the different shapes. Relaxation times defined in different ways can be easily derived using eq 9 with the fit parameters given in Table 2. The fact that the results at different concentrations could be superimposed implies that the parameters n and k were independent of the concentration and that the relative concentration dependence of τ was independent of how it was chosen. For the anionic polysaccharides, the dependence of η/η_0 on $\tau \cdot \dot{\gamma}$ was found to be almost the same in water and in 0.1 M NaCl, but it was more progressive for CMC and Alg than for KC. The dependence for MC and HPMC was similar and intermediate between that of KC and Alg.

In all cases, the data could be well described by eq 9, see the solid lines in Figure 4, but the dependence of η on $\dot{\gamma}$ could also be described by a stretched exponential at lower shear rates combined with a power law dependence at higher shear rates, as was suggested by Phillies.¹⁹ Notice, however, that the fit parameters depended strongly on the range of $\tau \cdot \dot{\gamma}$ that was covered in the experiments. In particular, n increased when the maximum value of $\tau \cdot \dot{\gamma}$ increased and was strongly coupled to k . One can avoid this uncertainty by using the Carreau equation with k fixed at 2 as was done by Lopez et al. (2015)⁶ for CMC and Sittikijyothin (2005)¹⁰ for galactomannan, but this leads to a worse description of the data in the transition zone. Stortz⁵ used eq 9 to describe the shear rate dependent viscosity of Alg solutions and found $k = 0.78$ and $n = 0.77$. Clasen and Kulicke³ reported for HPMC and CMC, respectively, $k = 0.52$ and 0.73 and n increasing with increasing $C \cdot [\eta]$ reaching a constant values $n \approx 0.8$ at large $C \cdot [\eta]$. Morris et al.⁴⁴ found that the shear thinning behavior was the same for different types of polysaccharides within the experimental uncertainty. Fitting their universal curve to eq 9, we find $k = 0.78$ and $n = 0.78$. Morris proposed a further approximation of the universal curve fixing $k = 1$ and found in this manner $n = 0.76$.³⁵ Though this Cross equation may be a useful approximation, fits using both k and n as free parameters give a more precise description of the shear thinning behavior. We mention that Colby et al.⁴⁵ found that for semidilute, but non-entangled polyelectrolytes shear thinning could be well described by eq 9 with $k = 2$ and $n = 0.5$. This behavior was not observed for the systems studied here that showed significant shear thinning only above the entanglement concentration.

The values of l also depended on the range of shear rates used and coupled to k and n . Therefore, we believe that τ allows for a more reliable comparison of the onset of shear thinning between different samples because it is directly derived from the data and independent of the fit parameters. Of course, for a given polysaccharide at different concentrations, τ is proportional to l and the ratio τ/l obtained for the different polysaccharides is summarized in Table 2. Figure 5 shows that the dependence of τ on $C \cdot [\eta]$ can be approximated by a power law with an exponent close to 3 for all polysaccharides excepting CMC for which it was close to 4.

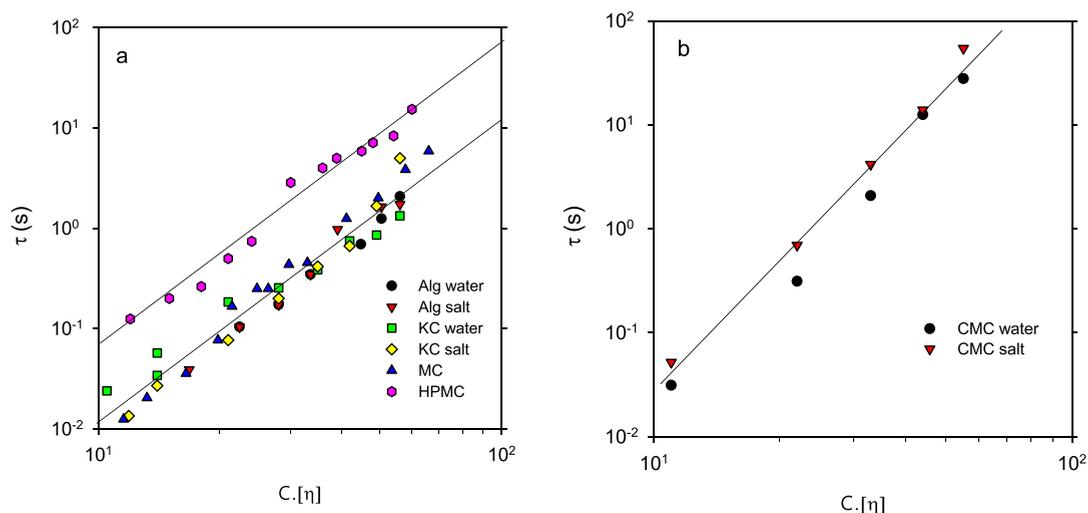


Figure 5. Dependence of τ on $C \cdot [\eta]$ for different polysaccharide solutions. For clarity, the results for CMC are shown separately. The solid lines have slope 3 in (a) and 4 in (b).

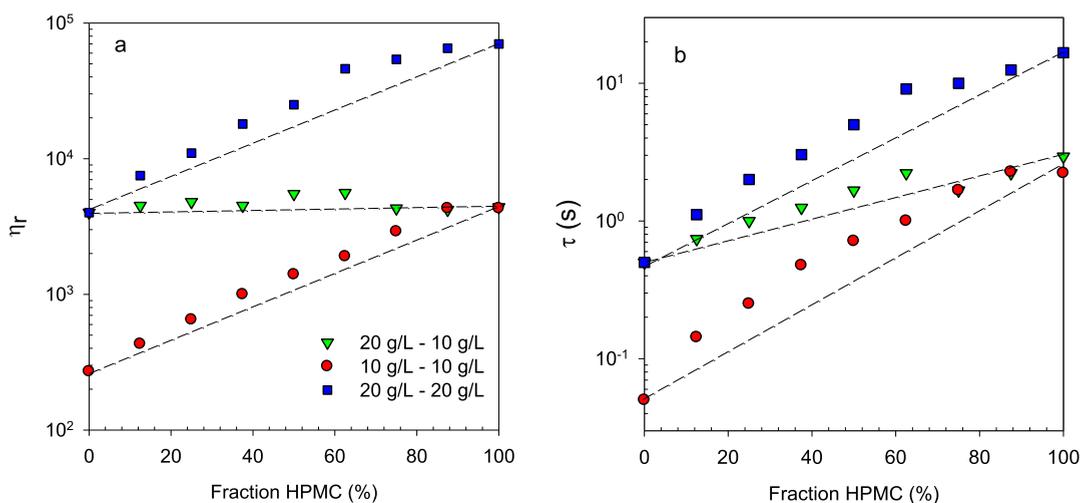


Figure 6. Dependence of η_r (a) and τ (b) on the weight fraction of the HPMC solution for mixtures of solutions containing different concentrations of MC/HPMC indicated in the figure. The dashed lines represent the logarithmic mixing law.

For Alg and KC, τ was within the experimental spread, the same as that in pure water and 0.1 M NaCl, but for CMC, τ was slightly larger in water than in salt. The small effect of added salt can be explained by the fact that shear thinning was significant only at higher concentration, that is, when counterions screened the electrostatic interactions. In the literature, exponents close to 3 were reported for Alg,⁵ CMC,⁶ and galactomannan.¹⁰ We have no explanation for the discrepancy between the exponent found for CMC by Lopez et al.⁶ and in this study.

4.4. Binary Mixtures. We have studied mixtures of two neutral polysaccharides (MC and HPMC), two anionic polysaccharides (Alg and CMC), and a neutral and an anionic polysaccharide (Dex and KC).

4.4.1. Mixtures of Neutral Polysaccharides. Solutions of 10 g/L HPMC and 20 g/L MC, which had approximately the same viscosity, were mixed with different weight fractions. A master curve was obtained when η/η_0 was plotted as a function of $\tau \cdot \dot{\gamma}$. In Figure 6a, the relative viscosity of the mixtures is plotted as a function of the weight fraction of the HPMC solutions. Within the experimental uncertainty, the viscosity of the mixtures is the same, indicating that there are no specific interactions between the two polysaccharides. τ was larger for the pure HPMC than for the pure MC solution and for the mixtures, it increased with increasing HPMC fraction (Figure 6b). This means that by mixing HPMC and MC solutions, the onset of shear thinning can be varied continuously between the two extremes while maintaining the Newtonian viscosity constant.

We have also mixed HPMC and MC solutions with the same concentration (10 or 20 g/L). In this case, the viscosity depended on the composition, whereas the polysaccharide concentration remained constant. The dependence of the viscosity on the composition deviated slightly upward from the logarithmic mixing law (eq. 10). The dependence of τ on the composition of the mixtures is shown in Figure 6b. In mixtures for which the viscosity remained almost the same, τ increased with increasing HPMC fraction, and in all mixtures, we found a weak upward deviation from a logarithmic mixing law.

Fujiyama²⁵ determined the viscosity as a function of the weight fraction for mixtures of xanthan with different molar masses and a mixtures of xanthan and schizophyllan in 0.1 M

salt in order to screen electrostatic interactions. They also observed a positive deviation of the viscosity from the logarithmic mixing law, which they could fit to the theory of fuzzy cylinders using the results obtained on the individual solutions. However, xanthan and schizophyllan are much stiffer polymers than the polysaccharides used in this study for which the persistence length is at least 100 time smaller than the contour length. For instance, the persistence length of KC,⁴⁶ Alg,⁴⁷ Dex,⁴⁸ and CMC⁴⁹ is reported in the literature as 6–7, 3–5, 2, and 5 nm, respectively. The corresponding contour lengths for the samples used here are 1.4×10^3 , 3.2×10^2 , 6.4×10^2 , and 1.4×10^3 nm, where we did not consider that Dex is branched. Therefore, it is not obvious that the polysaccharides used in this study can be considered as fuzzy cylinders. Unfortunately, we do not have the required molecular parameters needed to make a quantitative comparison of our data with this theory. There is the additional difficulty that the polysaccharides are not monodisperse.

A 50/50 mixture of 20 g/L MC and 10 g/L HPMC was progressively diluted, and the viscosity was measured as a function of the total polysaccharide concentration. The viscosity of the mixtures was close to that of the pure MC and HPMC solutions at the same dilution. A master curve was obtained when η/η_0 was plotted as a function of $\tau \cdot \dot{\gamma}$ that superimposed well with the master curves of pure HPMC and MC solutions (see Figure S2 of Supporting Information). The concentration dependence of η_{sp} is compared with that of pure HPMC and MC solutions in Figure 7. As might be expected, intermediate values were found. Interestingly, the data superimposed when plotted as a function of $C \cdot [\eta]$ using an intermediate $[\eta]$. This means that the binary mixture behaves as a single polysaccharide with intermediate $[\eta]$. The values of τ for the mixtures at different concentrations were also intermediate between that of the pure HPMC and MC solutions (Figure S3 of the Supporting Information). Shear thinning behavior of the mixtures could be described by eq 9 with the same values of k and n as for pure HPMC and MC. Shear thinning started at lower shear rates for the corresponding pure HPMC solutions than for the MC solutions and one might expect that shear thinning behavior of the mixture was more progressive than that of the pure

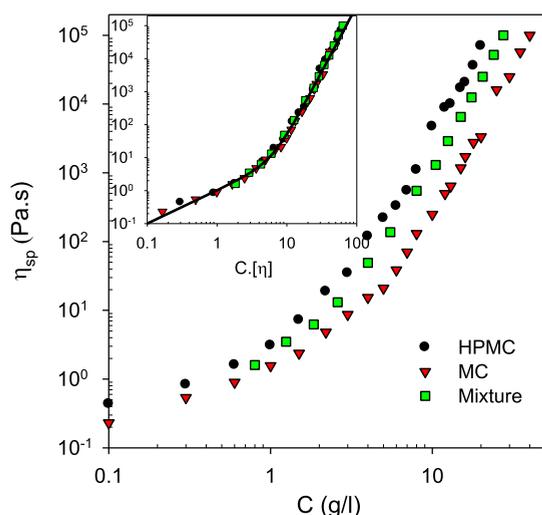


Figure 7. Specific viscosity of HPMC, MC, and mixtures as a function of the polymer concentration. The inset shows the same data as a function of $C \cdot [\eta]$ with the solid line representing eq 7 as in Figure 2.

polysaccharide solutions. However, there was no indication that HPMC chains deformed at lower shear rates than MC chains in the mixtures.

We may conclude that the viscosity of binary mixtures of neutral polysaccharides is close to that of a single polysaccharide with an intermediate intrinsic viscosity and intermediate shear thinning behavior.

4.4.2. Mixtures of Charged Polysaccharides. A similar study was done for mixtures of two anionic polysaccharides CMC and Alg in pure water and in 0.1 M NaCl. We measured the viscosity of mixtures of 10 g/L CMC and 20 g/L Alg, which had approximately the same viscosity, as a function of the composition. η_r did not depend on the composition within the experimental uncertainty and was the same in pure water and in 0.1 M NaCl, whereas τ varied continuously between the values for pure Alg and pure CMC (see Figure S4 of the Supporting Information). A mixture of 50 g/L CMC and 100 g/L Alg with approximately the same viscosity was progressively diluted, and the viscosity was measured as a

function of the total polysaccharide concentration. The viscosity of these mixtures was close to that of the pure Alg and CMC solutions at the same dilution. A master curve could be obtained when η/η_0 was plotted as a function of $\tau \cdot \dot{\gamma}$ that was intermediate between that of pure Alg and CMC solutions (see Figure S5 of the Supporting Information). The concentration dependence of η_{sp} is compared with that of pure Alg and CMC solutions in Figure 8. The data obtained in 0.1 M NaCl superimposed when plotted as a function of $C \cdot [\eta]$ with an intermediate $[\eta]$ as was found for the mixture of two neutral polysaccharides. Using the same intrinsic viscosity, the data in pure water also superimposed for $C \cdot [\eta] > 10$. At smaller $C \cdot [\eta]$, the viscosity was intermediate between that of pure CMC and Alg solutions. The values of τ were also intermediate between that of pure Alg and pure CMC solutions (see Figure S6 of the Supporting Information).

We may conclude that the behavior of binary mixtures of charged polysaccharides in the presence of salt is close to that of neutral polysaccharides and equivalent to that of using a polysaccharide with an intermediate intrinsic viscosity. The effect of electrostatic interactions was observed only in salt-free water at low concentrations, where it was intermediate between that of the individual polysaccharides similar to what was observed for individual anionic polysaccharides.

4.4.3. Mixtures of Neutral and Charged Polysaccharides.

The viscosity of mixtures of 10 g/L KC and a Dex solution with approximately the same viscosity was measured at different compositions. The viscosity of KC at 10 g/L was somewhat smaller in 0.1 M NaCl than in pure water, and therefore, we mixed solutions of 10 g/L KC with 180 g/L Dex in salt-free water and with 140 g/L Dex in 0.1 M NaCl. The dependence of η_r on the fraction of the KC solution is shown in Figure 9. Contrary to mixtures of two neutral or two charged polysaccharides, the viscosity for these mixtures varied significantly with the composition, especially in salt-free water. The viscosity of the mixtures increased sharply at small fractions of the KC solution becoming 3 times larger at a fraction of approximately 20% in water and 1.5 times larger at a fraction of about 30% in 0.1 M NaCl. Remarkably, KC

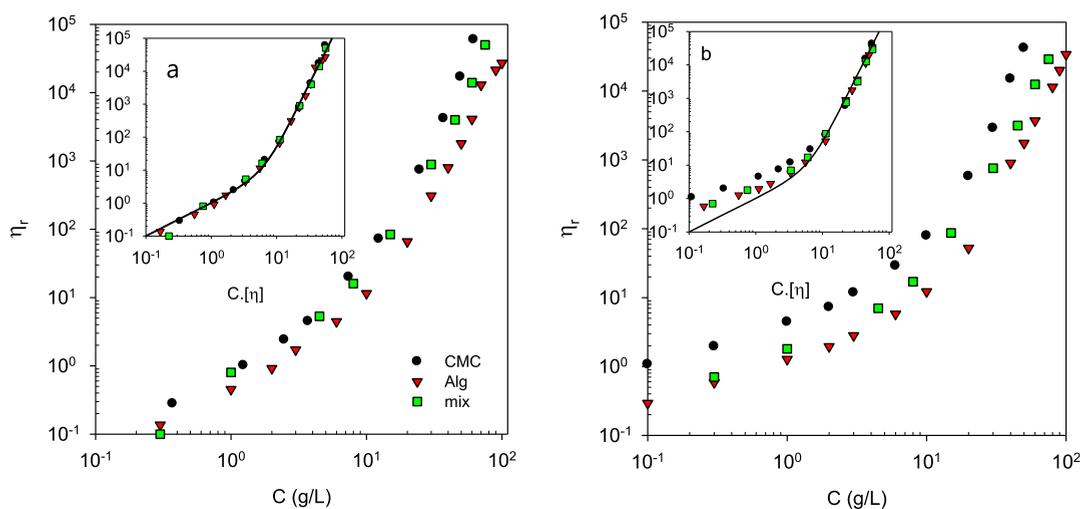


Figure 8. Concentration dependence of the viscosity of pure Alg and CMC solutions as well as 50/50 mixtures in 0.1 M NaCl (a) and in pure water (b). The insets show the same data as a function of $C \cdot [\eta]$, with the solid lines representing eq 7 as in Figure 2. Mixtures of neutral and charged polysaccharides.

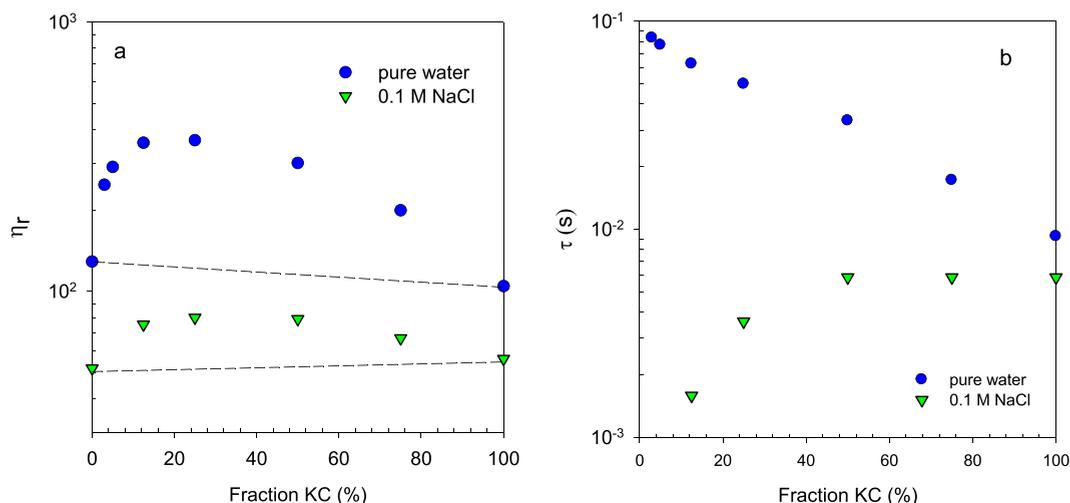


Figure 9. Dependence of η_r (a) and τ (b) on the weight fraction of KC in mixtures of 10 g/L KC and Dex at 180 g/L in pure water and 140 g/L in 0.1 M NaCl. The lines in (a) represent the prediction from the logarithmic mixing law.

fractions as low as 3% already had a significant effect on the viscosity.

All mixtures were transparent, which indicates the absence of phase separation or formation of large dense complexes. In order to check for subtler specific interactions between Dex and KC, we compared the light scattering intensity of a Dex solution at $C = 180$ g/L before and after addition of 1 or 2 g/L KC. The difference was found to be less than 10%, showing that the influence of KC on the structure of the Dex solution was negligible and that no significant complexation had occurred.

For these mixtures, the shear rate dependence of the viscosity differed strongly at different compositions. In the presence of 0.1 M NaCl, the effect of shear thinning increased with increasing fraction of KC, as might be expected (Figure 10). However, in salt-free water, the onset of shear thinning moved to larger shear rates as the fraction of KC increased (Figure 11). Stretching and alignment of the KC chains caused a decrease of η_r of the mixtures with increasing shear rate, but

η_r does not decrease below the value of the pure Dex solution at the concentration in the mixture. This can be clearly seen at low KC fractions for which η_r of the corresponding pure Dex solution is still close to that of the sample without KC. Obviously, master curves could not be obtained, but the dependence of τ on the fraction of the KC solution could still be determined and is shown in Figure 9b. In the presence of salt, we find that τ increased sharply at small fractions of the KC solution and stagnated above a fraction of 50%. This behavior is qualitatively similar to that found for the HPMC/MC mixtures except that for these mixtures, τ was very small for the pure Dex solution. In pure water, the behavior was remarkably different. τ decreased with increasing KC fraction starting from a relatively large value in mixtures with only 3% of the KC solution.

We investigated the strong effect of relatively small amounts of KC on the viscosity of concentrated Dex solutions further by measuring the viscosity of mixtures with a fixed Dex concentration (160 g/L, $\eta_r \approx 60$) as a function of the KC concentration (Figure 12). Both with and without 0.1 M NaCl, the addition KC led to an increase of the viscosity, but at lower KC concentrations the increase was stronger in pure water than in 0.1 M NaCl. Even addition of only 0.1 g/L led to a significant increase of the zero shear viscosity. At higher KC concentrations, η_r increased more sharply in 0.1 M NaCl and approached that in water at 10 g/L. This behavior is similar to that observed for pure KC solutions shown in Figure 3a. However, comparison between Figures 3a and 12 shows that the relative increase of η_r in the Dex solution was weaker than in the absence of Dex, which means that the Dex solution does not simply act as a viscous solvent for the KC chains.

The mixtures in the presence of salt showed shear thinning similar to that of pure KC that started at smaller shear rates when more KC was added (see Figure S7 in the Supporting Information). However, in salt-free water, shear thinning was visible for the mixtures already at very low KC concentrations where it was not observed for pure KC in water. In this case, the onset of shear thinning did not change much with the KC concentration ($\tau \approx 0.022$ s), which means that the decrease of τ with increasing KC concentration shown in Figure 9b can be attributed to the decrease of the Dex concentration that was concomitant with the increase of the KC concentration. It

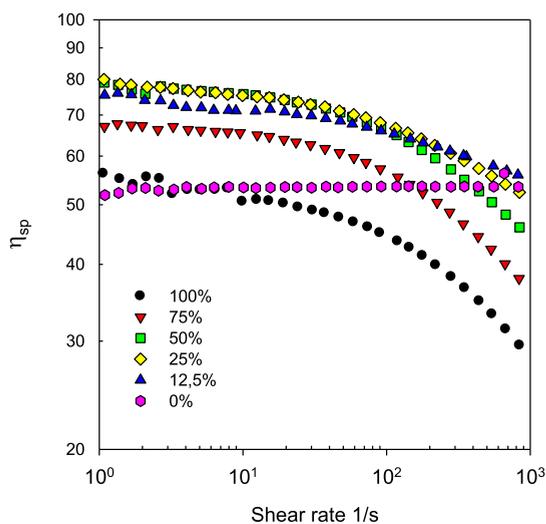


Figure 10. Shear rate dependence of η_r for mixtures of 10 g/L KC and 140 g/L Dex solutions in 0.1 M NaCl at different weight fractions of the KC solution indicated in the figure.

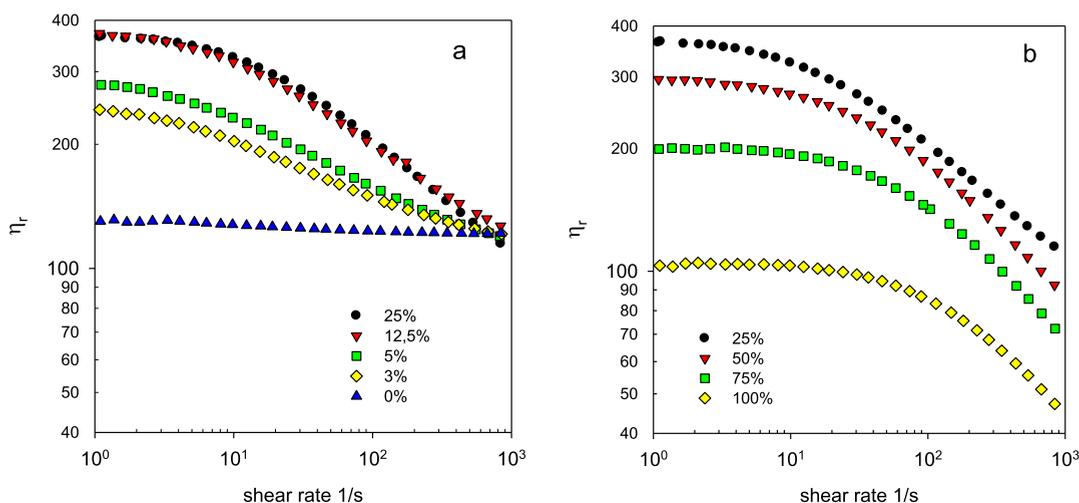


Figure 11. Shear rate dependence of η_r for mixtures of 10 g/L KC and 180 g/L Dex solutions in water at different weight fraction fractions of the KC solutions indicated in the figure. For clarity, the results at lower and higher KC fractions are plotted in separate graphs.

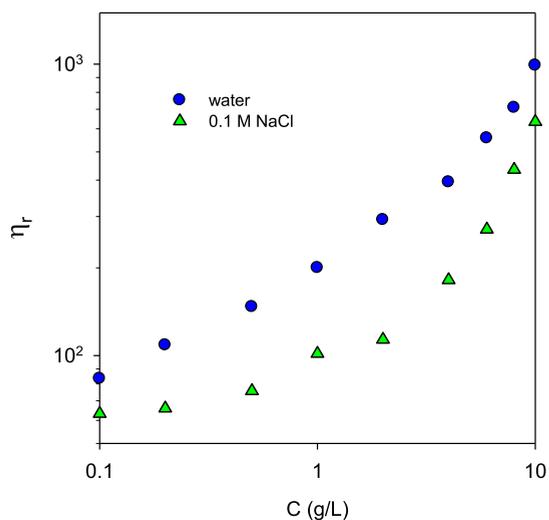


Figure 12. Relative viscosity as a function of the KC concentration in mixtures with 160 g/L Dex in salt-free water and in 0.1 M NaCl.

appears therefore that the shear thinning in salt-free water is at lower KC concentrations dominated by the interaction between KC and Dex and that the interaction of KC chains with each other is relatively small. Here also it is clear that the decrease of η_r with increasing shear rate stops when the viscosity of the pure Dex solution is reached, which was independent of the shear rate. The difference between the results with and without salt show that electrostatic repulsion plays an important role also in a concentrated Dex solution.

Finally, we have studied a 50/50 mixtures of Dex (400 g/L) and KC (25 g/L) solutions with approximately the same viscosity at different dilutions. A master curve could be obtained when η/η_0 was plotted as a function of $\tau \cdot \dot{\gamma}$, see Figure S8 of the [Supporting Information](#), but the superposition was not as good as for pure KC. η_r of the undiluted mixture ($\eta_r \approx 1.1 \times 10^4$) was significantly larger than that of the pure solutions ($\eta_r \approx 5 \times 10^3$). The deviation decreased with decreasing concentration, and for $C = 10$ g/L, the mixture had the same η_r as calculated with the logarithmic mixing law. For $C < 10$ g/L, the experimental viscosities were systematically about 20% smaller than the calculated values. The concen-

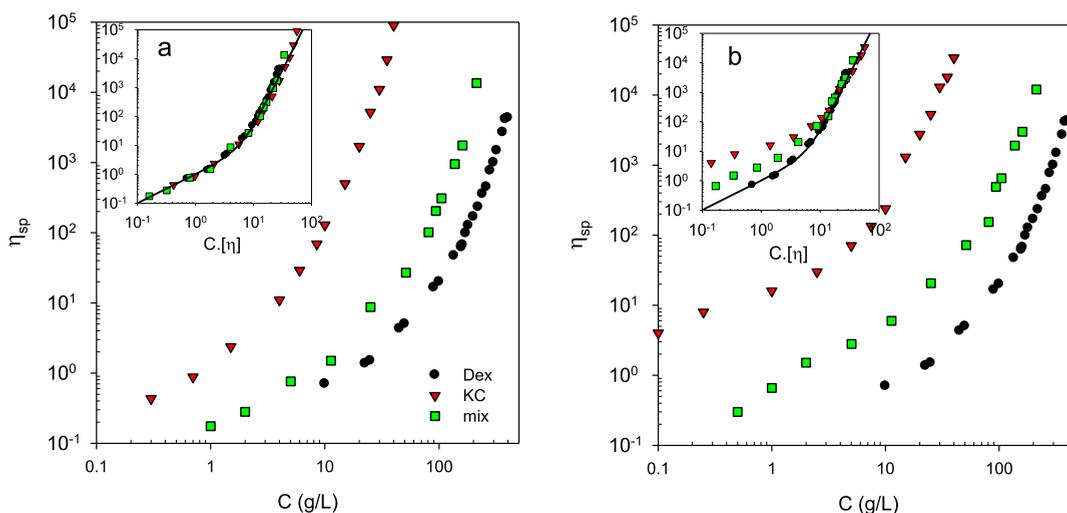


Figure 13. Concentration dependence of the viscosity of pure KC and Dex solutions as well as 50/50 mixtures in 0.1 M NaCl (a) and in pure water (b). The insets show the same data as a function of $C \cdot [\eta]$. The solid lines represent eq 7 as in Figure 2.

tration dependence of η_r is compared in Figure 13 with that of pure Dex and KC solutions. As might be expected, the viscosity of the mixtures was intermediate between that of pure KC and Dex solutions at the same concentrations. In the presence of 0.1 M NaCl, the data superimpose over the whole concentration range when plotted as a function of $C \cdot [\eta]$ with $[\eta] = 0.16$ L/g. In salt-free water, they superimpose for $C \cdot [\eta] > 10$ g/L using the same value of $[\eta]$, demonstrating that the effect of electrostatic interaction is screened by counterions at higher polysaccharide concentrations. The polyelectrolyte effect on η_r at low concentrations is still clearly visible, but it was smaller for the mixture than for pure KC.

The concentration dependence of the Newtonian viscosity of mixtures of a neutral and a charged polysaccharide can be described as a single polysaccharide solution with an intermediate intrinsic viscosity as we found for mixtures of two neutral or two charged polysaccharides. However, there is a striking non-linear effect of the zero-shear viscosity on the composition for this type of mixture that merits further investigation. Mixing charged and neutral polysaccharides in salt-free water allows one to exploit the polyelectrolyte effect for viscous solutions. A high concentration of the neutral polysaccharides does not impede the electrostatic interactions between added charged polysaccharides, whereas a high concentration of charged polysaccharides leads to screening of the interactions.

5. CONCLUSIONS

The Newtonian shear viscosity of the neutral polysaccharides Dex, MC, and HPMC as well as anionic polysaccharides KC, CMC, and Alg in 0.1 M NaCl has a universal dependence on $C \cdot [\eta]$. Theoretical predictions that assume dominating hydrodynamic interactions or that assume dominating topological interactions can describe the universal behavior equally well. The effect of electrostatic interactions was visible for anionic polysaccharides in salt-free water at low concentrations, but at high concentrations, it was screened by the counterions. Shear thinning was observed at higher concentrations and data obtained at different concentrations superimpose when using horizontal and vertical shift factors. The master curves could be well described by eq 9 with parameters that depended on the type of the polysaccharide. Shear thinning was almost the same in salt-free water and in 0.1 M NaCl because it was mostly observed at concentrations where counterions screened the electrostatic interactions. The time that characterized the onset of shear thinning had a power law dependence on the concentration with exponent 3 except for CMC for which the exponent was 4.

The viscosity of binary mixtures of concentrated solutions of two neutral polysaccharides with the same viscosity was independent of the composition. The viscosity of mixtures of solutions with different viscosities varied continuously with the composition, but deviated slightly upward from a simple logarithmic mixing law. The concentration dependence of the viscosity of the mixture was the same as that of a pure polysaccharide with an intermediate intrinsic viscosity. Shear thinning behavior of the mixtures was also intermediate between that of the individual polysaccharide solutions. Similar behavior was observed for mixtures of two anionic polysaccharides except in salt-free water at low concentrations where intermediate effects of electrostatic interactions were observed. Mixtures of an anionic and a neutral polysaccharide showed significant synergy in salt-free water. Mixing solutions

with the same viscosity led to an increase of the viscosity by up to a factor of 3. Strikingly, the onset of shear thinning started at smaller shear rates when less of the anionic polysaccharide was added to a concentrated neutral polysaccharide solution in salt-free water, demonstrating the importance of electrostatic interactions even in dense suspensions of neutral polysaccharides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.0c02157>.

Molar mass distributions of the polysaccharides; master curves of the shear thinning behavior and characteristic times for pure MC, pure HPMC, and mixtures as well as for pure CMC, pure Alg, and mixtures; viscosity and the characteristic time for mixtures CMC and Alg; shear rate dependence of the viscosity for mixtures of Dex and KC; and concentration dependence of the characteristic time for pure KC and mixtures with Dex (PDF)

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Notes

The authors declare no competing financial interest.

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