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Solution Properties of Partially Hydrolysed Polyacrylamide and Chitosan Mixed Solutions

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Summary: In this paper, the properties of a partially hydrolysed polyacrylamide with a low charge density and chitosan mixtures were evaluated in an aqueous acid solution. The formation of a soluble complex was followed by conductometry and potentiometry, and the stoichiometry at the titration endpoint was investigated as a function of the polyanion added. The influence of salts on the titration endpoint and on the rheological behavior of the mixed solutions was also studied. The mixture of equal concentration of both polymers, in the absence of salt, presented synergy, with a significant viscosity increase. Nevertheless, in the presence of salts, this mixture presented minimum viscosity. These results were discussed as a function of the polymers structural features and the environment used in the study.

Keywords: blends; chitosan; cooperative effects; polyacrylamide; viscosity

Introduction

Polyacrylamides have exhaustively been used especially in the petroleum industry due to their high viscous power.[1,2] These polymers can be obtained by free radical polymerization of acrylamide in an aqueous medium[3] and subsequent hydrolysis, which transforms the essentially neutral polyacrylamide in a strong anionic molecule, due to the partial conversion of the amide groups to carboxylate;[4] or by copolymerization of acrylamide with sodium acrylate.[5] These synthetic polymers present solubility in water in all concentrations, temperatures, and pH values.[3] In an aqueous medium, the partially hydrolyzed polyacrylamides present a polyelectrolyte behavior. The effect of salts in their solution properties has been studied,[6] showing a decrease in viscosity due to the interactions between the cations with the anionic sites in the polyacrylamide backbone.

Chitosan is a biopolymer that has presented a great potential in several applications, being used by the chemical, pharmaceutical and biomedical industries.[7,8] It is a linear polysaccharide, which can be produced in nature by microorganisms (fungi)[8–10] or obtained by alkaline deacetylation of chitin.[11,12] Its chemical structure consists of a copolymer of β-(1 → 4)-*N*-acetyl-D-glucosamine and β-(1 → 4)-D-glucosamine units. The physical and chemical properties depend on the *N*-acetylation degree (DA) as well as the kind of *N*-acetyl groups distribution along the polymeric chain.[13,14] This biopolymer is soluble in dilute acids, such as acetic acid, formic acid, hydrochloric acid,[15,16] and insoluble in a neutral and alkaline medium.[17] In an aqueous acid medium, the amine group of chitosan is easily protonated, and the polymer behaves like cationic polyelectrolyte.[15,18]

In general, mixtures of two neutral polymers in solution present thermodynamic incompatibility, and phase separation occurs when the polymer concentration

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increases in the medium, and the different phases formed will be rich in one of the two components.[19,20] Phase separation can also occur when polyelectrolytes with the same charge and similar charge density are mixed.[20] Nevertheless, when the two polymers present opposite charges, electrostatic interactions will be established between them, giving rise to polymeric complexes, and when macroscopic phase separation occurs, one phase rich in the two polymers and other in the pure solvent are obtained.[19,20]

It is of great importance to know the mechanisms of the complexation and the effects of varying conditions for the formation as well as the solubility and stability of the complexes. Intensive research has been widely done in this field.[12,20–31] Several variables affect the formation mechanisms and the stability of the polyelectrolyte complexes in water, such as the strength of the polyelectrolytes as an acid or base, molecular weight, presence of low molecular weight salt, charge density of the polyelectrolytes, flexibility, and the presence of hydrophilic or hydrophobic moieties in the polymers. During the complexation, the polyelectrolytes can either coacervate or form a hydrogel. However, if ionic interactions are too strong, precipitation can occur, which is quite common.

In the present investigation we show that soluble polyelectrolyte complexes can be formed through chitosan and a low charge density partially hydrolysed polyacrylamide, with synergistic viscosity increase, depending on the ionic strength. Polymeric complexes based on chitosan and several polyanions, such as heparin, carboxymethylcellulose, sodium alginate and carrageenan have been studied,[24,28,30,32] and the polymer matrix formed, as hydrogel or precipitate, have been used in controlled delivery systems of ionic drugs. Nevertheless, just a few papers were found concerning soluble polyelectrolyte complexes based on chitosan and weak polyacids.[7,12] In a general way, the polyelectrolyte complex solubility in water has been approached by using nonionic hydrophilic block or graft copolymers,[21,31] or hydrophobic moieties in the backbone of strong polyelectrolytes.[20,29] The blends studied is this paper are expected to find practical applications in the stimulation of petroleum wells operations, where high viscosity in acid solutions are required sometimes.[33]

Experimental Part

Materials

The partially hydrolysed polyacrylamide in the salt form and chitosan were kindly supplied by SNF FLOERGER (France) and POLYMAR S.A. (Brazil), respectively.

Methods

NMR Spectroscopy

Polyacrylamide: The ^{13}C NMR spectroscopy was used to determine the degree of hydrolysis of the polyacrylamide, in a Varian INOVA 300 spectrometer, at room temperature, and at 40% polymer concentration in H_2O/D_2O.

Chitosan

The chitosan was dissolved in deuterated water containing a small amount of HCl, at a polymer concentration of 10 $mg \cdot mL^{-1}$. The solution was freeze dried and the polymer obtained was again solubilized by adding deuterated water. The ^{1}H NMR spectroscopy analysis was used to determine the degree of *N*-acetylation (DA) of the chitosan, in a Brucker AC200 spectrometer, at 80 °C.

Intrinsic Viscosity and Viscosity Average Molecular Weight

The intrinsic viscosity was determined by using a Schott Ubbelohde capillary viscosimeter of automatic dilution (cappilary diameter = 0.46 mm for chitosan and 0.53 mm for polyacrylamide), at 25 ± 0.01 °C. The stock solution of chitosan was prepared in the polymer concentration of 1 $g \cdot L^{-1}$ by using an aqueous solution containing 18 $g \cdot L^{-1}$ acetic acid and 27 $g \cdot L^{-1}$ sodium acetate as a solvent. The stock solution of polyacrylamide was prepared in the polymer concentration of 0.3 $g \cdot L^{-1}$, using an aqueous solution of 30 $g \cdot L^{-1}$ NaCl as a solvent. Both solvents and solutions used in this work were previously filtered through Millipore membrane of pore size 0.45 μm.

The viscosity average molecular weight for both polymers were obtained by the Mark-Houwink equation, $[\eta] = KM^a$, using K and a values equal to 0.00719 and 0.77 for polyacrylamide,[34] and 0.074 and 0.76 for chitosan,[35] respectively.

Preparation of Solutions for Rheological Measurements

Both polyacrylamide and chitosan were dissolved in the following media: (a) 20 $g \cdot L^{-1}$ acetic acid (HOAc 20 $g \cdot L^{-1}$), (b) 20 $g \cdot L^{-1}$ acetic acid containing 40 $g \cdot L^{-1}$ sodium acetate (HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$) and (c) 20 $g \cdot L^{-1}$ acetic acid in formation water (HOAc 20 $g \cdot L^{-1}$-FW). Formation water is that which is found in the oil reservoir. In this paper it had the following composition: 0.055 $g \cdot L^{-1}$ Ca^{2+}, 0.007 $g \cdot L^{-1}$ Mg^{2+}, 0.316 $g \cdot L^{-1}$ Na^{+} and 0.019 $g \cdot L^{-1}$ K^{+}. Polymer solutions in the range of concentration 0.50–20.0 $g \cdot L^{-1}$ were prepared by dispersion of the powder in the solvent under constant magnetic stirring for 24 h, at room temperature.

Mixed solutions of chitosan and polyacrylamide were made at room temperature from stock solutions of each polymer at 2 $g \cdot L^{-1}$.

Rheological Measurements

The rheological measurements were performed in a RheoStress RS 150 Haake rheometer, using a DG41 coaxial cylinder sensor, in the shear rate range from 0.1 to 100 s^{-1}, at 55 °C.

Titration Experiments

The formation of chitosan-polyacrylamide complex was followed by using a combination of potentiometry and conductometry. Defined volumes of the anionic polyacrylamide (2 $g \cdot L^{-1}$ in HOAc 20 $g \cdot L^{-1}$) were slowly added (flow rate about 5 $mL \cdot h^{-1}$) under stirring to 50 mL of an aqueous chitosan solution (2 $g \cdot L^{-1}$) prepared by solubilization of the polymer in HOAc 20 $g \cdot L^{-1}$. The changes in pH and conductance were automatically registered as a function of the titrant's volume in a pH-Meter B474 Micronal and in a Conductivity Meter MC226 Mettler Toledo, respectively. The same experiments were made in the presence of sodium acetate.

Results and Discussion

Degree of Hydrolysis of Polyacrylamide

The ^{13}C NMR spectrum of the partially hydrolysed polyacrylamide presented absorptions at 182.5 and 185.5 ppm, that were attributed to the amide and carboxylate groups, respectively, and the peaks around 38 and 45 ppm were attributed to the secondary and the tertiary C linked to the amide group, respectively. Therefore, the degree of hydrolysis (DH, 14%) was determined by Equation (1), where Area_{COO^-} means the area below the peak at 185.5 ppm (COO^-) and Area_{CONH_2} corresponds to the area below the peak at 182.5 ppm ($CONH_2$).[5,6]

$$\text{DH} = \frac{\text{Area}_{COO^-}}{(\text{Area}_{CONH_2} + \text{Area}_{COO^-})} \times 100 \tag{1}$$

Degree of N-acetylation of Chitosan

The degree of *N*-acetylation (DA) of chitosan was determined by the ^{1}H NMR spectrum through the following equation:

$$\text{DA} = \frac{\text{Area}_{CH_3}}{(3 \times \text{Area}_{H_1})} \times 100 \tag{2}$$

where Area_{CH_3} corresponds to the area below the peak at 1.9 ppm, attributed to the methyl of the *N*-acetyl group; and Area_{H_1} corresponds to the area below the peak at 3.0 ppm, attributed to the anomeric proton of glucosamine unit. Therefore, the DA

Table 1.
Intrinsic viscosity and viscosity average molecular weight of the polyacrylamide and chitosan.

Sample	$[\eta]$	$M_v \times 10^{-4}$
	$mL \cdot g^{-1}$	$g \cdot mol^{-1}$
HPAM (DH = 14%)	1 290	665.6
Chitosan	220	3.7

obtained for the chitosan sample was 17.8%.

Intrinsic Viscosity and Viscosity Average Molecular Weight

The intrinsic viscosity $[\eta]$ of the polyacrylamide and chitosan was obtained by extrapolating the reduced viscosity to zero concentration (with the polymer concentration in $g \cdot mL^{-1}$).[36] Table 1 shows the $[\eta]$ and M_v values to both polymers.

Chitosan is a polyelectrolyte with positive charges along the chain in acid solution, but a good linear relation between reduced viscosity and polymer concentration was obtained using 18 $g \cdot L^{-1}$ of acetic acid and 27 $g \cdot L$ of sodium acetate in the aqueous medium. This result is attributed to the sodium acetate, which can screen the electrostatic repulsion forces very well between the ionic groups (NH_3^+) on the polymer chain.[35]

Partially hydrolyzed polyacrylamide also presents polyelectrolyte character due to the anionic carboxylate groups (COO^-) along the polymeric chain, and a good linear relation between reduced viscosity and polymer concentration was obtained using an aqueous solution of 30 $g \cdot L^{-1}$ NaCl. The NaCl screens the anionic charges in the molecule, eliminating the polyelectrolytic effects. The intrinsic viscosity and viscosity average molecular weight values to the polyacrylamide were higher than that of chitosan.

Polymer Rheological Behavior

Figure 1 shows the relative viscosity of chitosan in different aqueous media as a function of the shear rate. For the determination of the chitosan relative viscosity, solvent viscosities showed in Table 2 were used. The solutions presented pseudoplastic behavior, in the range of the shear rate used. The rheological properties of polymers in solution are a consequence of the deformation and orientation of the macromolecules in flow. Therefore, when a polymer solution is sheared, the macromolecules are deformed and orientated in the flux direction,[37] decreasing their hydrodynamic volume and their viscosity. For high concentrations of chitosan, the differences of viscosity due to the three

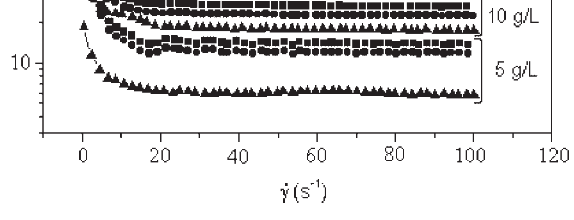

Figure 1.
Relative viscosity in function of shear rate to chitosan at different concentrations and solvents: (■) HOAc 20 $g \cdot L^{-1}$; (▲) HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$; (●) HOAc 20 $g \cdot L^{-1}$-FW, at 55 °C.

Table 2.
Viscosity of the aqueous solvents, at 55 °C.

Solvent	η $mPa \cdot s^{-1}$
HOAc 20 $g \cdot L^{-1}$	0.50
HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$	0.61
HOAc 20 $g \cdot L^{-1}$-FW	0.58

different media (HOAc 20 $g \cdot L^{-1}$, HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$ and HOAc 20 $g \cdot L^{-1}$-FW) were not as significative as for low polymer concentrations. As the polymer concentration decreases, the macromolecules become distant from each other, improving electrostatic interactions between the polymers and the ions, and diminishing the interactions between the polymers.

The lower viscosity for chitosan in HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$ can mean a better screening of the charges than in the formation water. On the other hand, the chlorides present in the formation water can also contribute to chitosan aggregation leading to the increase of viscosity, as previously demonstrated by Rinaudo et al.[35] In the case of polyacrylamide solutions (Figure 2), no significant difference of viscosity was observed among the media used. This is probably due to the low degree of polyacrylamide dissociation in low pH.

Figure 3 shows the viscosity behavior of chitosan, polyacrylamide and chitosan-polyacrylamide mixtures in the different media. Additive curves were introduced as the sum of the curves of the pure polymers. In Figure 3(a), it is observed that the mixtures in HOAc 20 $g \cdot L^{-1}$ presented larger relative viscosities than would be expected by the contribution of each polymer individually (additive curves). This synergy could be explained by the electrostatic interactions between the cationic chitosan and the partially anionic polyacrylamide molecules. Nevertheless, this synergistic effect was not observed in chitosan-polyacrylamide mixed solutions in the presence of salt, as shown in Figure 3(b) and (c). Besides, the viscosity curves of the mixed solutions were found below the additive curves. The lowest viscosity for the chitosan-polyacrylamide mixtures can indicate a more intensive coacervation process, with formation of polyelectrolyte complexes of compact structure.[25,31] The hydrodynamic volume of the polymers in the salt solution was decreased due to the simultaneous salt-polymer and polycation-polyanion interactions, in the form of polyelectrolyte complex.

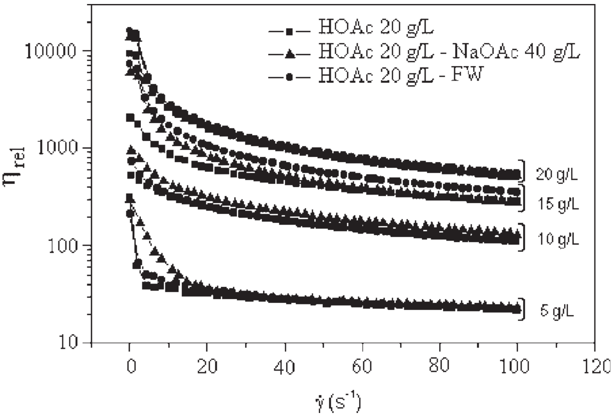

Figure 2.
Relative viscosity in function of shear rate to polyacrylamide at different concentrations and solvents: (■) HOAc 20 $g \cdot L^{-1}$; (▲) HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$; (●) HOAc 20 $g \cdot L^{-1}$-FW, at 55 °C.

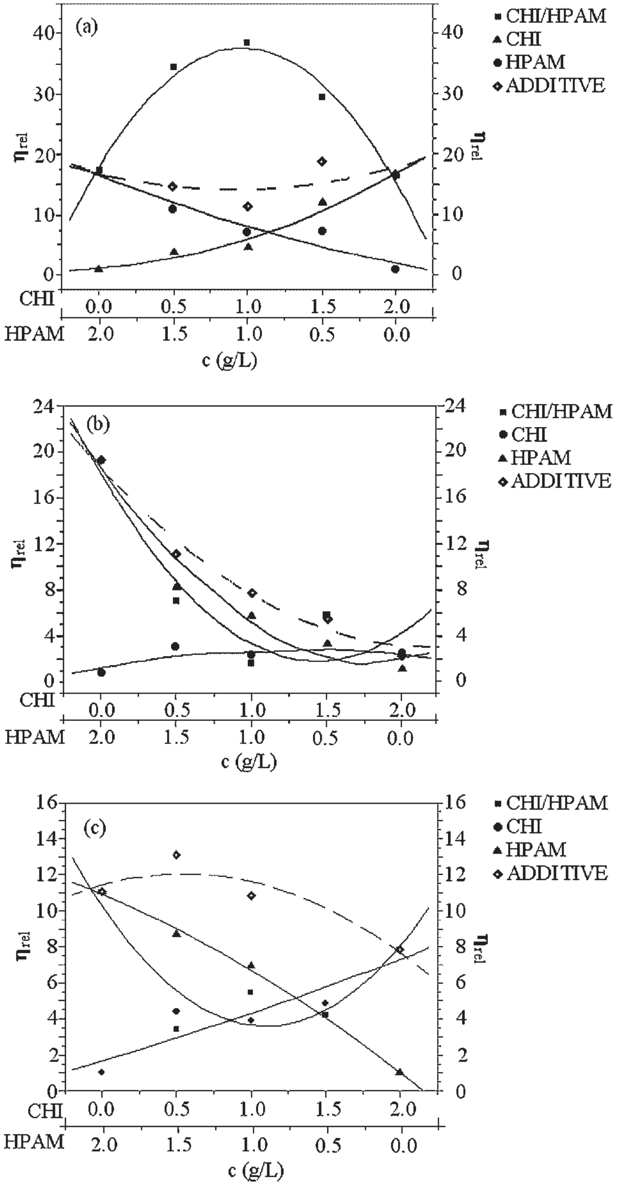

Figure 3.

Relative viscosity for chitosan, polyacrylamide and chitosan-polyacrylamide mixed solutions, in (a) HOAc 20 $g \cdot L^{-1}$, (b) HOAc 20 $g \cdot L^{-1}$-NaOAc 40 $g \cdot L^{-1}$ and (c) HOAc 20 $g \cdot L^{-1}$-FW, at 55 °C and shear rate of 7 s^{-1}.

Polyelectrolyte Titration

To get a further understanding on the rheological behavior of the chitosan–polyacrylamide mixed solutions, titration experiments were carried out following conductivity and pH during the addition of polyacrylamide to the chitosan solutions.

Figure 4 shows the conductivity variation of 2 $g \cdot L^{-1}$ chitosan solutions in titration by 2 $g \cdot L^{-1}$ HPAM in HOAc and HOAc-NaOAc aqueous solutions. In both cases, the addition of the anionic polyelectrolyte HPAM to the cationic polyelectrolyte chitosan led to a decrease

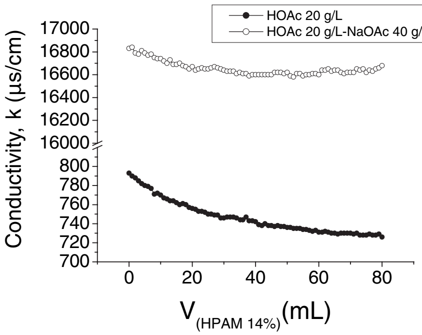

Figure 4.
Conductivity variation of 2 g · L^{-1} chitosan solutions in titration by 2 g · L^{-1} HPAM in (●) HOAc 20 g · L^{-1} and (○) HOAc 20 g · L^{-1}-NaOAc 40 g · L^{-1} aqueous solutions.

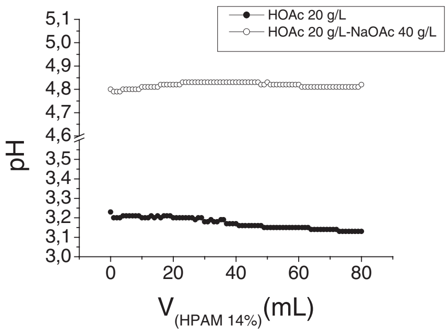

Figure 5.
pH variation of 2 g · L^{-1} chitosan solutions in titration by 2 g · L^{-1} HPAM in (●) HOAc 20 g · L^{-1} and (○) HOAc 20 g · L^{-1}-NaOAc 40 g · L^{-1} aqueous solutions.

in the conductivity solution, due to the electrostatic attraction between the polymers and the reduction of charges in the medium. Nevertheless, in the presence of NaOAc, the conductivity was maintained constant after addition of a smaller volume of HPAM (40 mL) than for the HOAc aqueous solution (60 mL). The titration end point was indicated by the minimum solution conductivity, which means that the polymer charges were compensated. Considering the volume of HPAM solution at the titration end point and the charge density of each polymer (HPAM: degree of hydrolysis = 14%; chitosan: degree of deacetylation = 82%), the complex stoichiometry (represented by COO^-/NH_3^+ ratio) was about 0.5 in HOAc, while the corresponding value in the presence of NaOAc was about 0.3. This difference in complex stoichiometry probably reflects the reduction of interaction sites in the polyelectrolytes, induced by the charge screening effect of NaOAc.

Figure 5 shows the pH variation of 2 g · L^{-1} chitosan solutions in titration by 2 g · L^{-1} HPAM in HOAc and HOAc-NaOAc aqueous solutions. In the case of HOAc aqueous solution, the pH presented a small decrease during the HPAM addition, from 3.20 to 3.13, probably due to a progressive deprotonation of the carboxylic sites during the formation of chitosan-HPAM complex.[14] On the other hand, in the presence of NaOAc, a buffer solution was formed at pH about 4.8. At pH 3, all the amino groups of chitosan protonize while the carboxylic groups of HPAM slightly dissociate. With increasing pH value (4.8), the degree of protonation of chitosan decreases and the degree of dissociation of HPAM enhances. Therefore, in this case, an enhanced inter-polyelectrolyte attraction, with a higher COO^-/NH_3^+ ratio could be expected. However, the effect of screening charges of sodium acetate would probably be larger than that of pH.

Comparing the polymer composition of the titration curves with those of rheological curves, it can be concluded that the maximum viscosity of chitosan-HPAM in HOAc as well as the minimum viscosity in HOAc-NaOAc occurred in the corresponding titration end points, therefore, at the average point of compensation charges. Nevertheless, the rheological responses were different. This result can be attributed to the balance of Coulombic forces between the polyelectrolytes and the salt molecules, and the hydrogen bonds. In the presence of salts, it is possible to have all NH_3^+ and COO^- associated by Figure 4. Coulombic forces between the polyelectrolytes and between the polyelectrolytes and the salts. This network free of charges induces new hydrogen bonds between the polar groups of chitosan (–OH, –$NHCOCH_3$) and polyacrylamide (–$CONH_2$), enhancing the intermolecular interactions and the formation of coacervate phases. On the other hand, in the absence of salt, some remaining free charges in the polymer network could be observed, mainly due to difficulties of Coulombic interactions provoked by steric impedance and the statistic distribution of the charges in each polymer. The result could be a looser polyelectrolyte complex matrix, due to electrostatic repulsion between the remaining cationic charges and/or less hydrogen bonds associations.

Conclusion

The results presented in this paper show that partially hydrolysed polyacrylamides with low charge density can form suitable soluble complexes with chitosan in acidic aqueous solutions, with synergistic effect on the viscosity. Nevertheless, in the presence of salts, the effect is the opposite, with diminished viscosity for all mixtures. The conductometric and potentiometric titrations of chitosan by the polyacrylamide indicated that the polyelectrolyte complex is also formed in the presence of salts, but the interactions between the polymers and the electrolytes of small molecular weight screens the charges of the polyelectrolytes, and the result is a polyelectrolyte complex with all the charges screened, resulting in a minimum viscosity in solution. In the absence of salt, some cationic sites of the chitosan are probably maintained free of interaction with the polyanionic polyacrylamide, giving enhanced viscosity of the complex in solution due to the electrostatic repulsion between the cationic charges and/or less hydrogen bonding polymer associates, resulting in an increased hydrodynamic volume of the polymeric complex.

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