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The influence of mono and divalent cations on dilute and non-dilute aqueous solutions of sodium alginates

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ABSTRACT

A broad study of the viscous behavior of three different sodium alginates in dilute and non-dilute solution in the presence of different electrolytes has been performed. In dilute solutions, we have determined the molecular weight of three different samples of sodium alginate from the same source through the Mark–Houwink–Sakurada equation. We have confirmed for the three chains the Pals–Hermans relation in a wide range of ionic strength. The quality of the solvent in this range of ionic strength has also been studied. For non-dilute systems, we have evaluated the behavior of alginates not only in salt-free conditions but also with the addition of monovalent and divalent cations. The transition from Newtonian to non-Newtonian behavior and the variation of the viscosity have been found to be profoundly affected by the addition of these electrolytes.

1. Introduction

Alginate is a broad term which includes alginic acid and its monovalent salts. It is a structural biopolymer, obtained from brown seaweeds, with a wide range of applications in the food industry, pharmacy, agriculture and environmental science (Paul, 2008), due to its natural source and non-toxic characteristics. From a chemical point of view, alginate is a heteropolymeric chain composed by two kinds of monomers: manuronate and guluronate (see Fig. 1), which can be arranged in either homopolymeric or heteropolymeric blocks. It is well known that the conformational properties of the chain are strongly dependent not only on the ratio of these monomers but also on their distribution in the chain (Hartmann, Dentini, Draget, & Skjåk-Bræk, 2006; Sime, 1990). Experimental and theoretical studies conclude that polyguluronate blocks (GG) are stiffer than the polymanuronate (MM), while the heteropolymeric blocks (MG) are the most flexible (Mackie, Noy, & Sellen, 1980; Smidsrød, 1970; Whittington, 1971). The water soluble sodium salt of alginic acid is one of the most common types of alginates studied and used and it can be consider as a semiflexible polymeric chain (Braccini, Grasso, & Pérez, 1999).

In dilute systems, one of the most relevant aspects of sodium alginate is its polyelectrolytic nature. Polyelectrolytes are macromolecules which can become ionised when they are dissolved in aqueous media. These charges along its skeleton provoke changes in the conformational properties of the polymer which can be tuned by the presence of inorganic salts. A high ionic strength leads to a decrease in the viscosity of the solution when compared with salt-free conditions. This is attributed to the expansion of the polymer chain due to the intrachain electrostatic repulsion when electrolytes are absent or present only at low concentrations; when an inert salt is added a screening of the charges takes place, the electrostatic interactions decrease and the conformation of the chain becomes more compact. Despite this simplified picture, polyelectrolytes in solution are considered one of the least understood systems, especially compared to neutral polymer solutions (Yethiraj, 2009). In this paper, we focus on determination of intrinsic viscosity as a conformational parameter in order to evaluate how the polymer chain is affected by the ionic strength. We have set the ionic strength with sodium chloride which is an inert, inorganic and widely used electrolyte. The electrolytic nature is also an aspect which can affect the conformational properties of the polyelectrolyte (Volk, Vollmer, Schmidt, Oppermann, & Huber, 2004).

In non-dilute solution, the transition from the Newtonian to the non-Newtonian behavior depends on the concentration of the polymer. A higher concentration of polymer enables more interchain interactions resulting to occur, resulting in more pronounced non-Newtonian behavior. In this case, the conformation of the chain plays a secondary role in the properties of the solution, because the interchain interactions prevail over polymer–solvent interactions. One of the most important aspects of non-dilute alginate solutions, due to the huge number of applications, is the capacity of forming gels in the presence of divalent cations (Clemente, Manzini, & Moresi, 1998; Liu, Qian, Shu, & Tong, 2003). The addition of cations like Ca^{2+} generates three-dimensional

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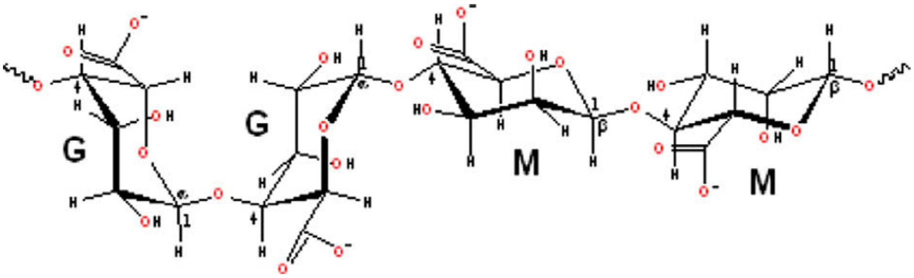

Fig. 1. Chemical structure and conformation of the two alginate monomers, guluronate (G) and manuronate (M).

hydrogels which have been evaluated by the aid of rheological techniques in this work. This kind of gel follows the so called egg-box model (Morris, Rees, & Welsh, 1980). However, despite the numerous studies of semiconcentrated solution of alginates in water (Morris, Cutler, Ross-Murphy, Rees, & Priece, 1981; Morris et al., 1980) and in presence of divalent cations (such as calcium or copper) (Ouwerx, Velings, Mestdagh, & Axelos, 1998; Zheng, 1997), the addition of a monovalent salt, as sodium chloride, to concentrated solutions has gone almost unnoticed. It has been demonstrated (Mackie et al., 1980) that a high concentration of monovalent salt in the media can lead to the formation of the egg-box gel in dilute and semidilute alginate solutions. In the present work, two types of alginates with high and moderate molecular weight have been studied at different values of ionic strength. The effect of the addition of cation Ca^{2+} has also been evaluated for the alginate of moderate molecular weight.

2. Experimental

We have studied three commercial samples of sodium alginate with different molecular weight acquired from Sigma–Aldrich. These polymers are extracted from the alga *Macrocystis pyrifera* and have an M/G ratio of 1.56. References are A2158, A2033 and A7128, from the lowest molecular weight to the highest. Dilute solutions of sodium alginate were prepared by dispersing the polymer in distilled water and stirring for one day at room temperature. NaCl was added in order to set the ionic strength of the solution. These solutions were filtered by 0.22 μm filters to remove impurities. We have determined the intrinsic viscosity, $[\eta]$, by the traditional technique of capillary viscometry. Solutions were prepared by isotonic dilution (Morris et al., 1980, 1981) and measured using Ubbelhode viscometers (model AVS 310 from Schott Geräte) with capillary diameters of 0.53 or 0.63 mm, depending on the flow time of the solution. The size of the capilar are 0.53 and 0.63 mm, depending on the flow time of the solution. All the experiments were done at 298 K and the solution flow times were in the range of 200–900 s. The intrinsic viscosity is calculated by double extrapolation to zero concentration using of Huggins (1942) and Kraemer (1938) equations:

$$\frac{\eta_{sp}}{C} = [\eta]\ (1 + k_H[\eta]C) \tag{1}$$

$$\frac{\ln \eta_r}{C} = [\eta]\ (1 - k_K[\eta]C) \tag{2}$$

where k_H and k_K are the Huggins and Kraemer constants, respectively.

The treatment of the data was done by means of VISFIT, a computer program developed in our research group and available in our webpage http://leonardo.fcu.um.es/macromol. This program allows us to simultaneously fit the data to Eqs. (1) and (2) giving a unique result of $[\eta]$, as detailed in (López Martínez, Díaz, Ortega, & García de la Torre, 2003). The range of employed ionic strength is given by the reproducibility of the experimental data. The upper limit is the ionic strength, I, at which it was possible to totally dissolve the alginate samples (the presence of a high concentration of sodium chloride induced formation of aggregates, giving irreproducible values of viscosity).

For non-dilute solutions, we have performed rheological experiments to obtain both the viscosity and the stress versus shear rate, using the MVI, MVII, MVIII, SVI and SVII geometries on a Haake RV20 viscometer. The samples were dissolved either in water or in presence of the electrolytes and stirred for one or two days, depending on the polymer concentration.

3. Results and discussion

3.1. Dilute solutions

The determination of molecular weight, M_v, from intrinsic viscosity is made through the viscometric equation for that system (Mark, 1938; Houwink, 1940),

$$[\eta] = K_v \langle M \rangle_v^a \tag{3}$$

also known as Mark–Houwink–Sakurada relation, where $\langle M \rangle_v$ is the molecular weight determined by viscometry and K_v and a_v are constants which depend on the polymer–solvent-temperature system. For alginates from *M. pyrifera* in 0.1 M NaCl and 298 K, the values of the viscometric constants are: $K_v = 7.3 \times 10^{-3}$ cm^3/g and $a_v = 0.92$ (Martinsen, Skjåk-Bræk, Smidsrød, Zanetti, & Paoletti, 1991). In the case of alginates A2158 and A2033 (low and medium molecular weight) we have been able to use these parameters; however, for the sample A7128 the calculation of the molecular weight could not be performed because it is not soluble in 0.1 M NaCl. In Table 1 we show the values of $\langle M \rangle_v$ of alginates A2158 and A2033 and an estimation for A7128 which will be carefully explained below. As can be seen from the data, we have verified that A2158 has the lowest molecular weight and A7128 the highest.

It is clear that when the ionic strength decreases, the polyelectrolyte coils expand, because of the decreased screening of intramolecular electrostatic repulsion. Obviously, when the polymer conformation is more expanded, the values of the intrinsic viscosity are higher (Zhang, Wang, Wang, Guo, & Zhang, 2001). The relation between intrinsic viscosity and ionic strength is given by the Pals–Hermans equation (Pals & Hermans, 1950, 1952).

Table 1
Molecular weight and Pals–Hermans parameters for alginates A2158, A2033 and A7128.

Polymer	$M_v \times 10^5$ (g/mol)	$[\eta]_\infty$ (cm^3/g)	S (cm^3 M$^{-1/2}$)	S' (g M$^{-1/2}$)
A2158	1.43 ± 0.01	29.5 ± 0.2	310 ± 5	10.5 ± 1.0
A2033	3.50 ± 0.04	72 ± 2	670 ± 20	9.3 ± 0.6
A7128	4.04 (estimated)	93 ± 5	760 ± 60	8.2 ± 1.2

$$[\eta] = [\eta]_\infty + S \cdot I^{-1/2} \tag{4}$$

where $[\eta]_\infty$ is the intrinsic viscosity at infinite ionic strength and S is a parameter which is related to the flexibility of the chain. $[\eta]_\infty$ can be thought as the intrinsic viscosity of an analogous chain without charges and the behavior is as a flexible coil. This value can be determined from the intercept in the Pals–Hermans plot of $[\eta]$ versus $I^{-1/2}$, and S can be calculated from the slope. We have measured $[\eta]$ in the range of I, as shown in Fig. 2 for our three samples. As expected, the values of $[\eta]$ decrease when I is increased for all polymers. As far as $[\eta]$ can be related to the hydrodynamic volume of the polymer, when a high concentration of NaCl is added to the solution the conformation of the polymer is more compact and the value of the intrinsic viscosity is lower. This is due to the above mentioned effect of the screening of the charges disposed along the chain which leads to a decrease of the repulsive intrachain interactions. We also note the excellent accordance of the experimental data with the Pals–Hermans theory in the range of ionic strength studied, which allows us to determine of the Pals–Hermans parameters for the polymers studied, $[\eta]_\infty$ and S. Both parameters increase (Table 1) with the molecular weight of the polymer. In the case of $[\eta]_\infty$, it is obvious that a higher molecular weight chain occupies a bigger hydrodynamic volume so the highest values $[\eta]_\infty$ belongs to alginate A7128 and the lowest to A2158. Regarding parameter S, we have not seen in the literature an explicit discussion of its molecular-weight dependence. It has been reported that the longer polymer chain, the higher is S due to the increase on the flexibility of the chain (Fixman, 1964), which is related to the molecular weight of the polymer and its counterions (Smidsrød, 1970; Smidsrød & Haug, 1971). Our experimental data in Table 1 show that S increases with M. However, this may be in part due to the obvious fact that the absolute increase in $[\eta]$ and the hydrodynamic volume arising from a given ionic strength is larger in a longer polymer. We consider a more insightful form of the empirical Pals–Hermans equation:

$$\frac{[\eta] - [\eta]_\infty}{[\eta]_\infty} = S' I^{-1/2} \tag{5}$$

where the left-hand-side gives the relative increase in $[\eta]$ or hydrodynamic volume caused by a given ionic strength and the parameter S' is the corrected form of S, defined as:

$$S' = \frac{S}{[\eta]_\infty} \tag{6}$$

Our experimental data in Table 1 indicate that the change of S' with M is quite small. Considering the limited amount of data and the experimental error, the hypothesis that S' could be independent of molecular weight, depending only on intrinsic features of the polyelectrolyte and the added salt (with $S' \sim 9$ g $\mathrm{M}^{-1/2}$ for sodium alginate in NaCl), cannot be discarded.

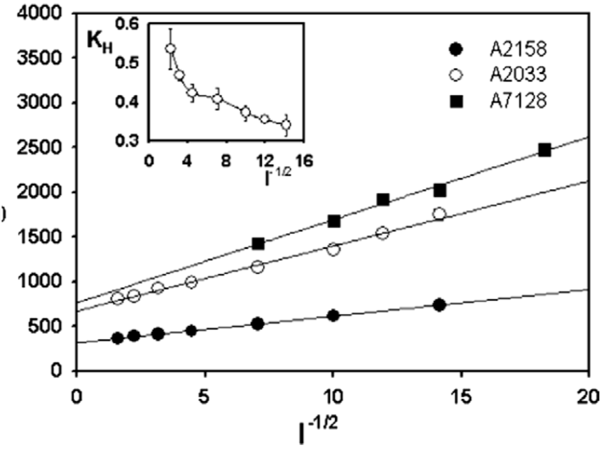

Fig. 2. Pals–Hermans plots for the three alginates studied. The inset plot shows the k_H values (with standard deviations) at different ionic strengths.

One of the aspects which has not been deeply studied for diluted solutions of sodium alginates is the quality of the solvent when the ionic strength is modified. The Huggins constant, k_H, is a useful dimensionless parameter to determine the goodness of the solvent in this kind of systems. k_H is a quantitative measure of the intermolecular interactions which depends on the hydrodynamic interactions between solvent and polymer, so that it is obviously affected by the solvent, the nature of the polymer and the temperature. It has been established that k_H values in the range from 0.3 to 0.5 correspond to good solvent conditions (Handbook of Chemistry and Physics, 1996–1997). The value of this constant decreases when the expansion factor grows, e.g., when the solvent conditions are improved. The inset plot in Fig. 2 shows the behavior of k_H for polymer A2033 at different values of I. As expected, k_H diminishes when $I^{-1/2}$ values grow due to the fact that the solvent quality is improved for lower values of ionic strength. Table 2 shows the values of k_H for the three polymers at different I. There is a general trend to (slightly) higher values of k_H with increasing molecular weight. This surprising effect might be explained by the stiffness of the chain. It is known, that alginates cannot be considered as totally flexible polymers, and their slight stiffness makes the Kuhn length a parameter to be taken into account when evaluating the quality of the solvent. In addition, the longer the polymer the larger amount of GG blocks are present in the chain and the probability for the formation of egg-box microaggregates increases and the system is not in good solvent conditions. Our hypothesis is that this is the case for polymer A7128 and that is the reason why dilute systems of this polymer at high ionic strength give results with a low reliability.

As mentioned above, the intrinsic viscosity of A7128 could not be obtained from experiments in the conditions of the Mark–Houwink equation available in literature ($I = 0.1$ M). However, using the Pals–Hermans equation for this polymer, we can determine the value of $[\eta]$ in NaCl 0.1 M by extrapolation. Therefore, this value can be used, by means of the viscosimetric equation, in order to obtain the molecular weight of this sample. Then, the value shown in Table 1 for this alginate has been estimated by this procedure.

3.2. Non-dilute solutions

Several rheological experiments have been performed on the previously mentioned alginates in the non-dilute regime in absence of any salt and with different concentrations in order to study the differences between Newtonian and non-Newtonian behavior. Solutions of the three polymers with various concentrations were subjected to a shear flow in the rotational rheometer with an increasing shear rate from 0 to 350 s^{-1} in 15 min. We have also made an analogous study of the flow curves of calcium algi-

Table 2
Influence of the ionic strength on the values of k_H for the three studied polyelectrolytes.

I (M)	A2158	A2033	A7128
0.4	0.43 ± 0.01	0.45 ± 0.03	–
0.2	0.49 ± 0.08	0.54 ± 0.03	–
0.1	0.49 ± 0.03	0.47 ± 0.01	–
0.05	0.43 ± 0.06	0.42 ± 0.02	–
0.02	0.375 ± 0.004	0.41 ± 0.03	0.44 ± 0.02
0.01	0.312 ± 0.004	0.37 ± 0.02	0.448 ± 0.008
0.007	–	0.355 ± 0.005	0.402 ± 0.006
0.005	0.41 ± 0.05	0.34 ± 0.03	0.409 ± 0.006
0.003	–	–	0.41 ± 0.02

nates. For solutions of entangled polysaccharide coils, there is a general form of shear thinning (Morris, 1990) given by:

$$\eta = \eta_o/[1 + \dot{\gamma}/\dot{\gamma}_{1/2})^{0.76}], \qquad (7)$$

where η_o is the maximum viscosity at low shear rates and $\dot{\gamma}$ is the shear rate at which η is reduced to $\eta_o/2$. The power of 0.76$^{1/2}$corresponds to the maximum value of the negative slope of log η versus log $\dot{\gamma}$ at high shear rate. It follows (Morris, 1990) from re-arrangement of the equation that plotting η versus $\eta\dot{\gamma}^{0.76}$ gives a straight line with intercept η_o. We have fitted our viscosity curves to Eq. (7) to corroborate if there is a shear thinning effect due to disentanglement of disordered polysaccharides when the behavior of the solutions is not Newtonian. In the case of alginates A2158, Newtonian behavior was found for the lower concentrations and for polymer A2033 the behavior was non-Newtonian in the whole range of concentrations studied following the above mentioned equation. Polymer A7128 showed unexpected behavior which will be explained below. The concentration effect can be seen in Fig. 3(a). As expected, increasing the concentration of the polymer raises the viscosity of the solution. For polymer A2158 at concentration 1 and 2 wt.%, the behavior is typically Newtonian, giving a constant value of the viscosity in the whole range of the applied shear rate. At concentrations higher than 3 wt.%, we have plotted η versus $\eta\dot{\gamma}^{0.76}$ (Fig. 3(b)), finding a linear relationship. Therefore, non-dilute solutions of sodium alginate show the shear thinning phenomena due to the higher number of interchain entanglements that are broken by the application of a shear flow. In addition, with this equation the viscosity at 0 shear rate, η_0, can be calculated. In the inset plot in Fig. 3(b), the dependence of η_0 on concentration is depicted, showing an increase of the viscosity which is in agreement with the previous results. When a comparison between the three alginates at the same concentration of 1 wt.% is made, we can observe (Fig. 3(c)) that the viscosity increases with molecular weight. Non-Newtonian behavior is found for polymers A2033 and A7128 in comparison with the Newtonian behavior of A2158. Using Eq. (7), we have found a linear relation only in the case of polymer A2033 (Fig. 3(d)), while the corresponding plot for the longest polymer (A7128) shows obvious curvature, which implies that the chains are not just entangling with one another. This effect can be ascribed to the presence of impurities in the polymer (possibly divalent cations) leading to stronger interactions. But regarding only to the two polymers with the lower molecular weights, we can conclude that the shear thinning effect is higher for the longer chain, as can be seen in Fig. 3(c). Then, a longer chain length read gives stronger non-Newtonian behavior, due to increase in the extent of entanglement. Obviously, the probability of interchain interactions is higher when the molecular weight and the concentration of the polymer are increased. Therefore, a more intense shear thinning effect is expected because of the higher number of interpolymer interactions can be disrupted by shear flow.

After the separate evaluations of ionic strength effect in dilute solution and concentration in non-dilute solution, we proceed to study the effect of ionic strength on the rheology of non-dilute solutions. Polymer A2033 in presence of NaCl has been studied in the non-diluted regime. The ionic-strength dependence of the viscosity curves for alginate A2033 is depicted in Fig. 4. The concentration was set to 1 wt.% and the ionic strength varied between 0.0 and 0.4 M. As expected (Macosko, 1994), the higher the ionic strength the lower viscosity of the solution in the range of $I = 0$ to 0.1 M. When the concentration of salt is increased, the polymer chain changes into a more compact conformation, as has been demonstrated in the previous section, and a weaker network is formed. At the highest values of I, an unexpected inversion of the trend is observed, with the viscosity now increasing with increasing ionic strength. When we apply Eq. (7) to these data, linear plots are obtained in every case and the viscosity at 0 shear rate, η_0, is calculated. In the inset plot in Fig. 4, we can easily observe the

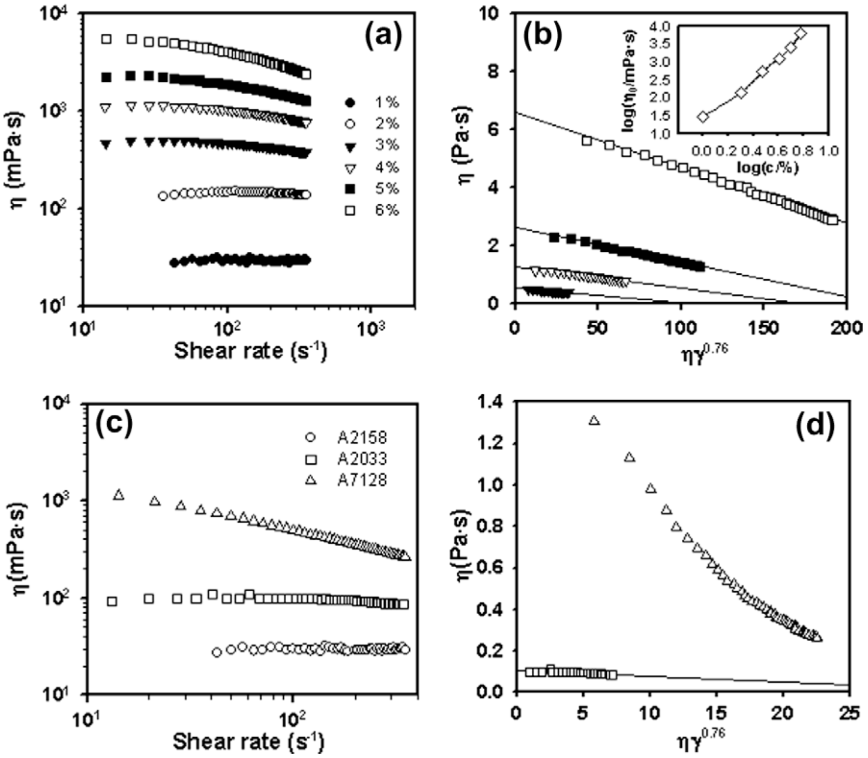

Fig. 3. Viscosity curves for alginate A2158 at several concentrations (a) and shear thinning study for alginate A2158 at 3, 4, 5 and 6 wt.% (b). The inset plot in (b) shows the dependence of η_0 versus concentration. Viscosity curves of alginates A2158, A2033 and A7128 at a set concentration of 1 wt.% (c) and shear thinning curves for A2033 and A7128 (d).

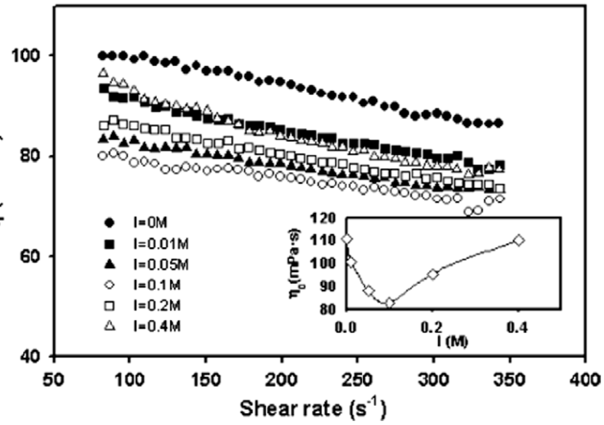

Fig. 4. Viscosity curves of alginate A2033 1 wt.% at different ionic strength. The inset plot shows the variation of the viscosity with the ionic strength 0 shear rate.

trend of η_0 with the ionic strength, where we can observe a decrease in the viscosity of the solution if the ionic strength is raised from 0 to 0.1 M. However, for $I = 0.2$ and 0.4 M an increase of the viscosity is observed, as mentioned above. Therefore, a minimum value of the viscosity is found when the ionic strength is 0.1 M with a reduction in the viscosity in comparison with the salt-free solution. The upturn at higher ionic strength might be due to the formation of intermolecular junctions when the concentration of monovalent salt is high enough (Mackie et al., 1980). In the case of this polymer at a concentration value of 1 wt.%, the critical value for the formation of this type of association seems to be I between 0.1 and 0.2 M.

Finally, we consider the case of the well-defined gelation effect of divalent cations. When Ca^{2+} is added to the solution of sodium alginate, a polymer network is formed. The properties of these networks depend on the type of alginate and the quantity of calcium added. This reversible gelation is induced by the capacity of the divalent ions to link with alginate chains and induce a conformational change. Ca^{2+} ions link with GG blocks according to the egg-box model, although is not the single factor of gelation (Funami et al., 2009). The divalent cations are located between the polymer chains in a tridimensional structure in which the polymers are ordered forming gaps in a similar way to an egg-box where the cations play the role of the eggs.

Fig. 5 shows how $[Ca^{2+}]$ changes the behavior of solutions with a constant concentration value of 0.5 wt.% of polymer A2033. As the calcium content is raised, the probability of cation-mediated association is increased, causing greater resistance to flow. Thus the addition of calcium raises the viscosity. When Eq. (7) is applied, a linear relation is found when $[Ca^{2+}]$ is lower than 3 mM which is the form of shear thinning typical of entangled networks, suggesting progressive formation of small microgel clusters that interact with one another solely by physical entanglement. These fittings appear in Fig. 5 as dashed lines. At higher concentrations of Ca^{2+} (4 and 5 mM), the corresponding plots show a deviation from this equation, indicating further intermolecular association to give a continuous weak gel network with a linear relation of log–log plot of the viscosity curves (Ross-Murphy, 1984). The figure includes the plot for 0.5 wt.% A2033 in 0.12 M NaCl, and we can see that the presence of NaCl at this high concentration does not affecting the viscosity of the solution as much as the addition of $CaCl_2$ at much lower concentrations. This must be due to the greater capacity of calcium to lead to the formation of intermolecular junctions, which is ascribed to its higher charge and we can confirm that alginates form hydrogels with Ca^{2+} more easily than with Na^+.

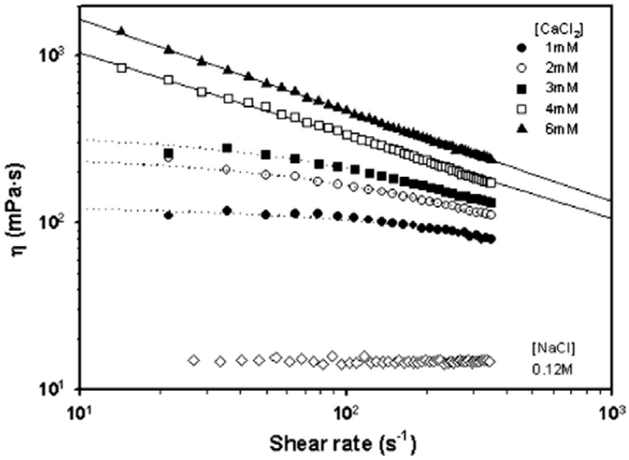

Fig. 5. Viscosity of calcium alginate A2033 at different values of $[Ca^{2+}]$ with a fixed polymer concentration of 0.5 wt.%.

4. Conclusions

In this work we have explored the polyelectrolyte behavior of sodium alginate in dilute solution using the simple technique of capillary viscometry. $[\eta]$ is proportional to $I^{-1/2}$ for our three samples; therefore, we can conclude that sodium alginate follows the experimental relationship of Pals and Hermans. When experimental data are not available, we have shown that it is possible to evaluate the molecular weight by a simple extrapolation from the Pals–Hermans equation, which is the case for alginate A7128 in 0.1 M NaCl at 298 K. This method gives the opportunity to easily characterize the molecular weight of the sample. We have also examined the ionic-strength dependence of k_H, which is related to the quality of the solvent, and found better solvent conditions at low I. We speculate about the constancy or weak dependence of the relative change in solution viscosity with molecular weight for a given polymer/salt system.

We have also made a brief study of the behavior of sodium alginate in non-dilute solution. We show the transition from Newtonian to non-Newtonian behavior of the sample depending on the concentration of the polymer and the length of the chain. A shear thinning effect due to the disentanglement of the chains has been found when the systems deviate from Newtonian behavior, except for the polymer with the longest chain which shows stronger interactions. The longer the chain the greater the shear thinning at a defined concentration. Finally, we have demonstrated that the addition of salts produces big changes in the solutions in the non-dilute regime. The viscosity increases with the addition of small amounts of Ca^{2+} because of the formation of a hydrogel, but this effect is lower when the added salt is NaCl. Indeed, to obtain the formation of these gels it is necessary to raise both critical values in polymer and salt concentration.

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