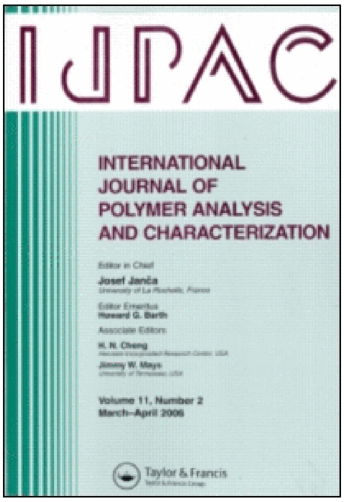

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Electrostatic Interactions in Aqueous Solutions of Ionic Polysaccharides

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This paper describes the interpretation of the variation of the reduced viscosity as a function of polyelectrolyte concentration in the absence of an external salt or in the presence of a low salt concentration. Based on the Hess and Klein model developed for two low-molecular-weight polymers, good agreement was found between the calculated and experimental values. The position of the maximum in the reduced viscosity vs concentration curve was located at a polymer concentration c_p (expressed in equiv/L) such that $c_p/c_s = 2\lambda$ or 2 when $\lambda > 1$ or $\lambda \leq 1$, respectively, where c_s is the external salt concentration and λ is a charge parameter. The amplitude of the maximum reduced viscosity corresponds to the sum of two terms: one being equal to the reduced viscosity of the equivalent neutral polymer and the second one reflects the electrostatic long-range interactions.

Keywords: Electrostatic interactions, viscometry, polyelectrolytes, ionic polysaccharides

INTRODUCTION

We have been interested in the role of electrostatic effects on viscosity measurements on ionic polymer solutions, which are also involved in steric exclusion chromatography, as discussed previously.[1,2] When a solution of polyelectrolyte is diluted with water or a low salt-content aqueous solvent, the reduced viscosity increases as the polymer concentration is decreased. It then passes through a maximum whose position is imposed by the ionic

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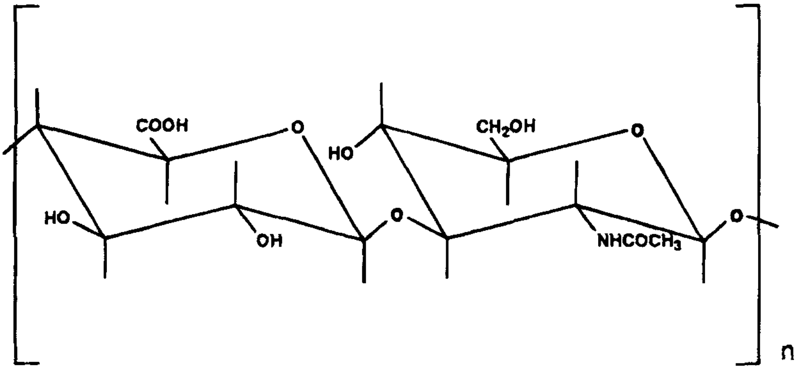
concentration of the solvent. This effect is also observed for rigid, spherical particles such as latex and other flexible polyelectrolytes.[3–6]

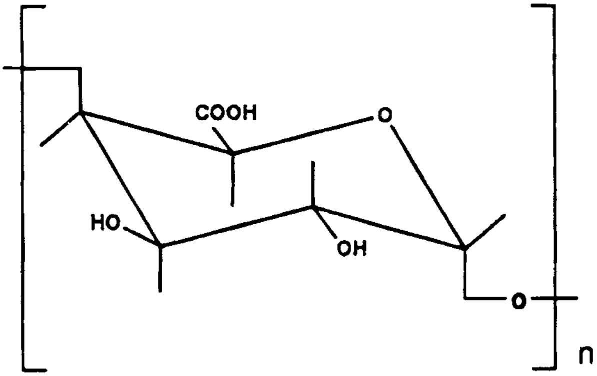
The role of chain stiffness on this behavior was investigated and the general trends are discussed in this paper. A tentative quantitative interpretation of the electrostatic contribution on the reduced viscosity is introduced.

EXPERIMENTAL

The polymers investigated were hyaluronic acid, sodium salt form (HA) produced by ARD Cy (Pomacle, France) (Scheme 1) and poly(galacturonic acid) sodium salt form (PGA) (Genu Pectin, Medium Rapid Set, Type A, Copenhagen, Denmark) (Scheme 2). They were purified by ethanol reprecipitation. The main characteristics of these polymers are given in Table I: the weight-average molecular weight M_w, the contour length of the molecule L, the charge parameter $\lambda = \nu e^2/DLkT$, the intrinsic viscosity calculated for the fully extended molecules $[\eta]$(mL/g), and the minimum critical overlap concentration c_o^* $\left(c_o^* = M_w / \frac{4}{3}\pi\left(\frac{L}{2}\right)^3 N_a\right)$ calculated for a stiff chain rotating freely about the center of mass, and the mass per ionic group, me, where ν is the number of ionic groups per chain, e the electronic charge, D the dielectric constant of the solvent, kT the Boltzman term, and N_a Avogadro's number.



Scheme 1



Scheme 2

The viscosity was investigated with a capillary Ubbelohde viscometer from FICA (Paris, France) at 25° ± 0.01°C for concentrations where no shear rate effect was observed; for extrapolation to zero shear rate, when necessary, a low shear viscometer model LS 40 from Contraves (Zurich, Switzerland) was used.

RESULTS AND DISCUSSION

Dilutions in salt-free solutions or in the presence of low salt concentrations ($c_s = 10^{-5}$ to 7×10^{-4} M) were performed. Plots of reduced viscosity η_{red} (mL/g) as a function of polymer concentration (g/mL) are given in Figures 1 and 2. The curves pass through a maximum that is independent of the molecular weight in a series of homologous polymers,[5] but is influenced by the external salt content c_s (mol/L).[3] The maximum is characterized by

TABLE I Characteristics of the polyelectrolytes: weight-average molecular weight M_w, contour length L, overlap concentration c_o^*, calculated intrinsic viscosity for the fully extended molecules [η], charge parameter λ, and mass per ionic group *me*.

Samples	M_w	L(Å)	c^*_o (g/mL)	$[\eta]_{ext}$ (mL/g)	λ	me (g/charge)
HA	100,000	2,500	2×10^{-5}	1,970	0.7	400
PGA	25,500	580	4.16×10^{-4}	155	1.4	200

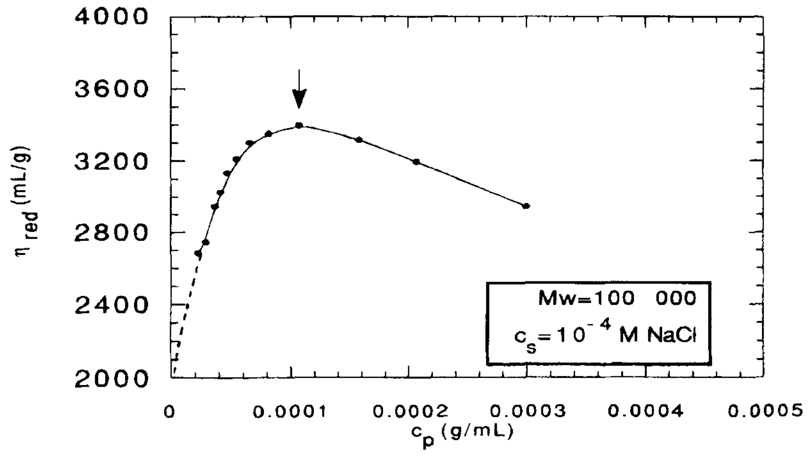


FIGURE 1 Reduced viscosity of sodium hyaluronate in 1 × 10^{-4} M NaCl.

a value of the reduced viscosity $(\eta_{red})_{max}$, which decreases sharply with salt concentration, and by the polymer concentration c_{max} which increases when c_s increases.

Theoretical approach

It was previously demonstrated[3] that the maximum in the viscosity curve can be described using the Hess and Klein approach.[7] On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following relation:

$$\frac{\eta_{sp}}{c} \sim \frac{c_p}{K^3} \tag{1}$$

where c_p is the polyelectrolyte concentration expressed in equiv/L and K^{-1} is the Debye length. Considering this relation, we previously demonstrated[3] that one can assume:

$$\frac{\eta_{sp}}{c} \sim \frac{c_p}{(c_p/\lambda + c_s)^{3/2}} \text{ or } \frac{c_p}{(c_p + c_s)^{3/2}} \tag{2}$$

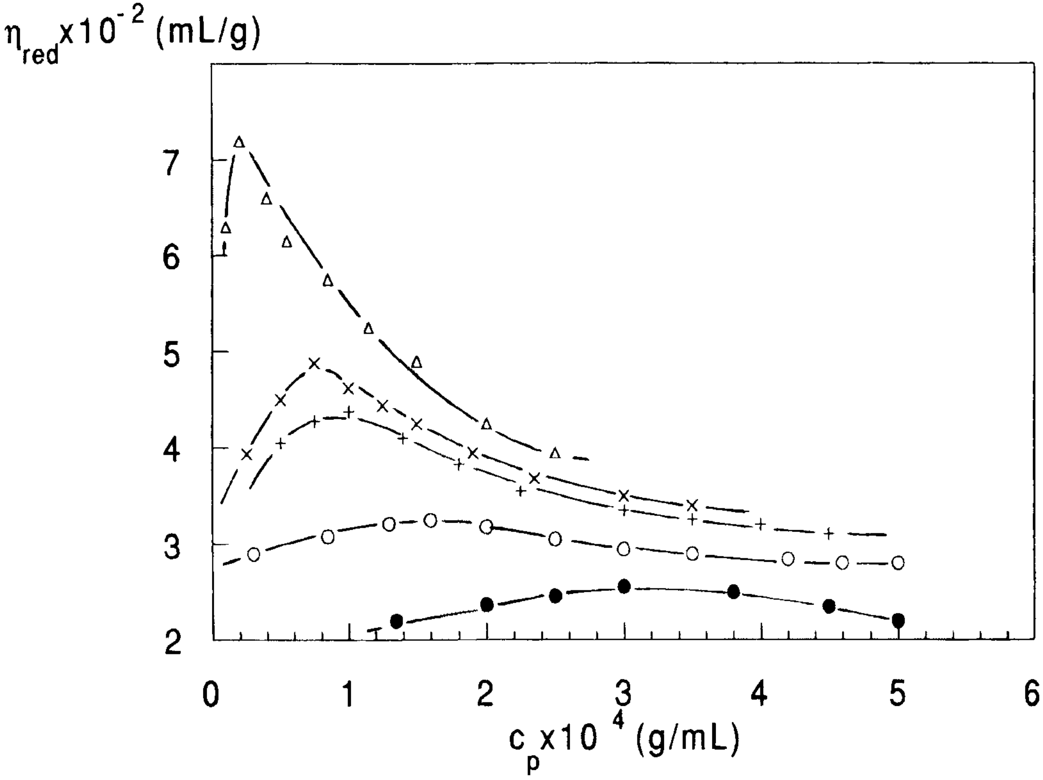


FIGURE 2 Variation of the reduced viscosity of sodium polygalacturonate as a function of polymer concentration at different NaCl concentrations, (●) 5×10^{-4} M; (○) 2×10^{-4} M; (+) 1×10^{-4} M; (×) 5×10^{-5} M; (Δ) 1×10^{-5} M.

when $\lambda > 1$ or $\lambda \leq 1$, respectively. It was verified that the polymer concentration corresponding to the maximum of the reduced viscosity corresponds to $c_p/c_s = 2\lambda$ or 2· when $\lambda > 1$ or $\lambda \leq 1$, respectively. It must be mentioned that the linear dependency of η_{red} (c) during isoionic dilution implies that K^{-1} is a constant which is also justified by Equation (1).[3]

Recently, Antonietti *et al.*[6] expressed the reduced viscosity for charged latex particles as:

$$\frac{\eta_{sp}}{c} = [\eta]\left[1 + k'[\eta]c + \left(\frac{\eta_{sp}}{c}\right)_{HK}\right] \tag{3}$$

in which $(\eta_{sp}/c)_{HK}$ represents the electrostatic contribution expressed in Equation (1). The increase of reduced viscosity in the low polymer concentration range, especially in the dilute regime, can be considered as the sum of two terms [A] and [B]:

$$[A] = (1 + k'[\eta]\,c)[\eta] \tag{4}$$

and

$$[B] = \left(\frac{\eta_{sp}}{c}\right)_{HK}[\eta] \tag{5}$$

Experimental Data Analysis

The term $[A]$ is easily calculated at the maximum when $[\eta]$ at the considered ionic concentration, is known. For PGA, having a low $[\eta]$ for the fully extended chain, the term k′ c $[\eta]$ is negligible (k′, the Huggins constant, is 0.5; for $c_s = 7 \times 10^{-4}$, k′ c $[\eta] = 2.96 \times 10^{-2} \ll 1$); then, [A] is equal to $[\eta]_{ext}$. The term [B] at the maximum, equals $\Delta\eta_{sp}/c_p = (\eta_{sp}/c)_{max} - [\eta]_{ext}$, in which the polymer concentration c is converted in terms of c_p equiv/L using the values of the mass per ionic group, *me*. For HA having a higher molecular weight, k′ $[\eta]$ = 0.1045 which must be taken into account to estimate $\Delta\eta_{sp}/c_p$. The values of $\Delta\eta_{sp}/c_p$ were calculated and compared with the theoretical prediction $c_p/(c_p/\lambda + c_s)^{3/2}$ or $c_p/(c_p + c_s)^{3/2}$; a prefactor ϕ discussed previously[6], has to be introduced to relate [B] or $(\eta_{sp}/c)_{HK}$ to c_p/K^3 and especially to take into account the change in the hydrodynamic volume of the molecule with salt concentration; this point will be discussed later. The experimental data $(\Delta\eta_{sp}/c_p)$ and the calculated values (c_p/K^3) obtained for PGA are given in Table II and Figure 3, which shows good agreement between experimental and calculated values. The variation of the maximum reduced viscosity and that of the position of the maximum are predicted well by the model. The best agreement is obtained for $c_s > 10^{-5}$ mol/L neglecting the role of salt impurity traces.

For the two polyelectrolytes, we also calculated the radius of gyration at the maximum of the curves (total salt concentration, $c_T = (2\lambda + 1)\,c_s$ and $3c_s$ respectively for $\lambda > 1$ and $\lambda \leq 1$ and for the extrapolated zero polymer concentration (salt concentration c_s). The data are obtained applying the treatment for a wormlike chain described previously[8,9] and are given in Table III. These values are used to calculate the critical overlap concentration c^*:

$$c^* = \frac{M}{\frac{4}{3}\pi\, R_g^3\, \mathrm{N}a} \tag{6}$$

which must be adopted for the wormlike chain when c_o^*, as expressed previously for the fully extended molecule, is no longer valid. In the case of PGA, it is very important to point out that all the viscosity data in the range of the maximum of the reduced viscosity involve a polymer concentration lower than c^*, in agreement with the Hess-Klein model. Considering the calculated radius of gyration for HA, one can conclude that the polymer concentration for the maximum is also in the dilute regime.

The electrostatic persistence length L_e calculated from Odijk's treatment[10] is also given. For PGA, it is shown that at least for $c_s < 5 \times 10^{-4}$ M, the persistence length is larger than the contour length of the molecule which suggests that the molecule is fully extended. For the range of tested ionic concentrations, the radius of gyration calculated remains nearly unchanged and for first approximation, equal to the radius of gyration of the fully extended molecule ($R_g \simeq 170$ Å).

In the case of HA, the extrapolation of experimental values for $c_s = 10^{-4}$ and $c \rightarrow 0$ gives a $[\eta]$ that is very near to the calculated values and equal to 2000 mL/g[8,9] (Fig. 1). The calculated values (Equation (2)) for the electrostatic contribution are represented in Figure 4 for $c_s = 10^{-4}$ mol/L and $\lambda_{eff} = 1$ (as $\lambda = 0.7$ lower than 1).

Another example of the variation of $c_p/(c_p + c_s)^{3/2}$ (as a function of c_p) is given in Figure 5 for HA and $c_s = 2 \times 10^{-4}$ mol/L showing the very dilute

TABLE II Comparison Between Experimental and Calculated Values for PGA and HA, from Figures 1 and 2

	c_s (*M*)	$c^{max} \times 10^5$ (g/mL)	$c_p^{max} \times 10^5$ (equiv/L)	$c_p^{max,\,calc} \times 10^5$ (equiv/L) Equation (2)	$(\eta_{sp}/c)^{max}$ (mL/g)	$\left(\frac{C_p}{K^3}\right)_{calc}$ Equation (2)	$\Delta\eta_{sp}/c_p$ (L/equiv)
PGA	H_2O	0.65	2.59	–	1178	–	–
	1×10^{-5}	1.91	9.55	3	720	170	113
	5×10^{-5}	5.4	27.0	14	485	76	66
	10^{-4}	7.94	39.7	28	440	59	57
	2×10^{-4}	12.72	63.6	56	320	38	33
	5×10^{-4}	23.8	119	150	255	24	20
	7×10^{-4}	38.2	191	195	219	20	12.8
HA	1×10^{-4}	11	27.5	20	3400	37.5	560

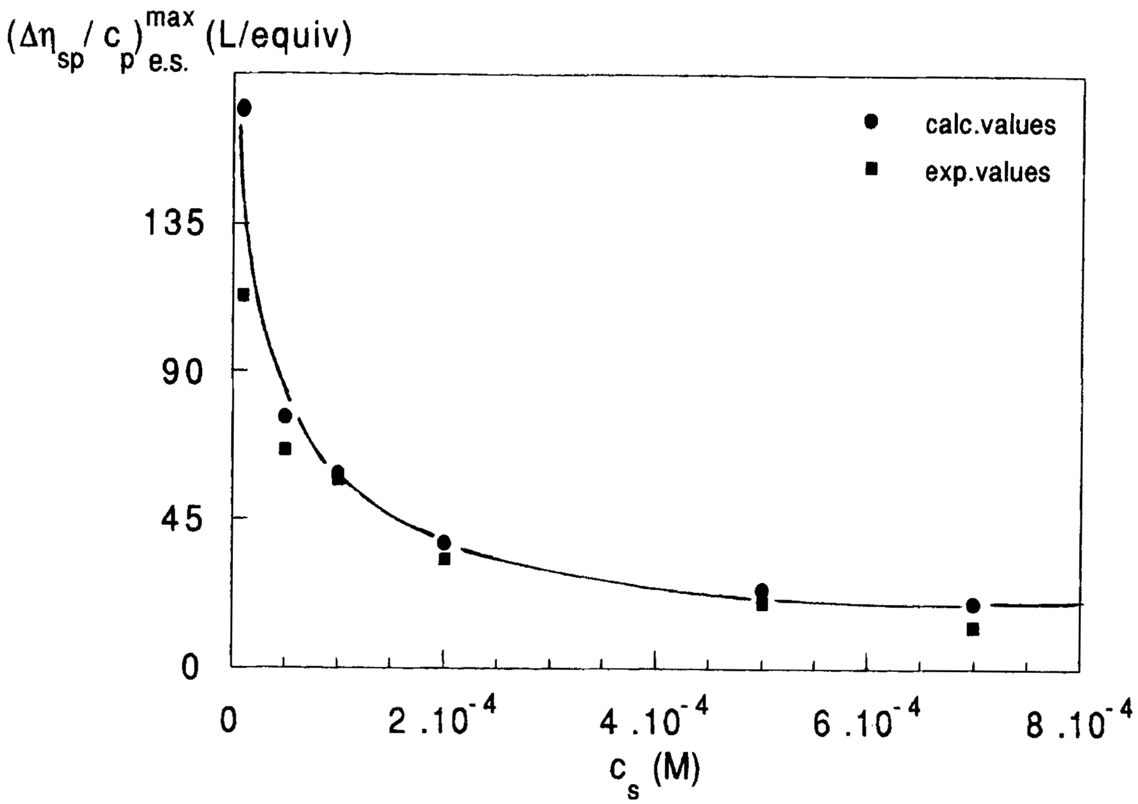


FIGURE 3 Comparison of the theoretical electrostatic contribution to the reduced viscosity $(\Delta\eta_{sp}/c_p)^{max}_{e.s}$ at the maximum (●) with the experimental one (■) as a function of NaCl concentration for PGA.

TABLE III Radius of gyration R_g and electrostatic persistence length L_e calculated at the maximum of η_{red} vs c curves (c_T) and at zero polymer concentration (c_s). Calculated critical overlap concentration c* is at c_T (Equation (6))

	$c_s \times 10^4$ (M)	R_g (c_s) (Å)	R_g (c_T) (Å)	L_e (c_s) (Å)	L_e (c_T) (Å)	c* (c_T) g/mL
PGA	0.1	174	166	1180	1080	2.2×10^{-3}
	0.5	164	157	1040	790	2.6×10^{-3}
	1	161	152	930	607	2.66×10^{-3}
	2	157	150	775	425	3×10^{-3}
	5	151	145	530	227	3.31×10^{-3}
	7	150	143	445	184	3.56×10^{-3}
HA	1	640	574	1080	435	2.1×10^{-4}

range for polymer concentrations. It is clear that no simple exponents can be applied in the range of the maximum for $c_p < c_s$ (*i.e.*, $\eta_{sp}/c \sim c^1$) nor for $c_p > c_s$ ($\eta_{sp}/c \sim c^{-1/2}$) and that the exponent –½ predicted by Fuoss is never found for these conditions.

From Equation (3), one can also write the viscosity maximum as:

$$\left[(\eta_{sp}/c)_{max} - [A]\right][\eta]^{-1} \sim \left(\frac{\eta_{sp}}{c}\right)_{\mathrm{HK}}^{\max} = \frac{c_p}{(c_p/\lambda + c_s)^{3/2}}\phi \qquad (7)$$

These relations together with the values given in Tables I and II, can be used to estimate the prefactor ϕ and to compare the two polyelectrolytes. The data are given in Table IV. One can see that the prefactor ϕ is nearly constant ($\phi \sim 0.024$) and independent of the polymer studied, which helps support our approach.

TABLE IV Electrostatic Contribution; Estimation of the Prefactor ϕ

	c_s (M)	$[(\eta_{sp}/c)_{max} - [A]][\eta]^{-1}$	ϕ
PGA	10^{-5}	3.64	0.0214
	5×10^{-5}	2.13	0.0279
	10^{-4}	1.84	0.0310
	2×10^{-4}	1.064	0.0277
	5×10^{-4}	0.645	0.0261
	7×10^{-4}	0.413	0.0191
HA	1×10^{-4}	0.7	0.0182

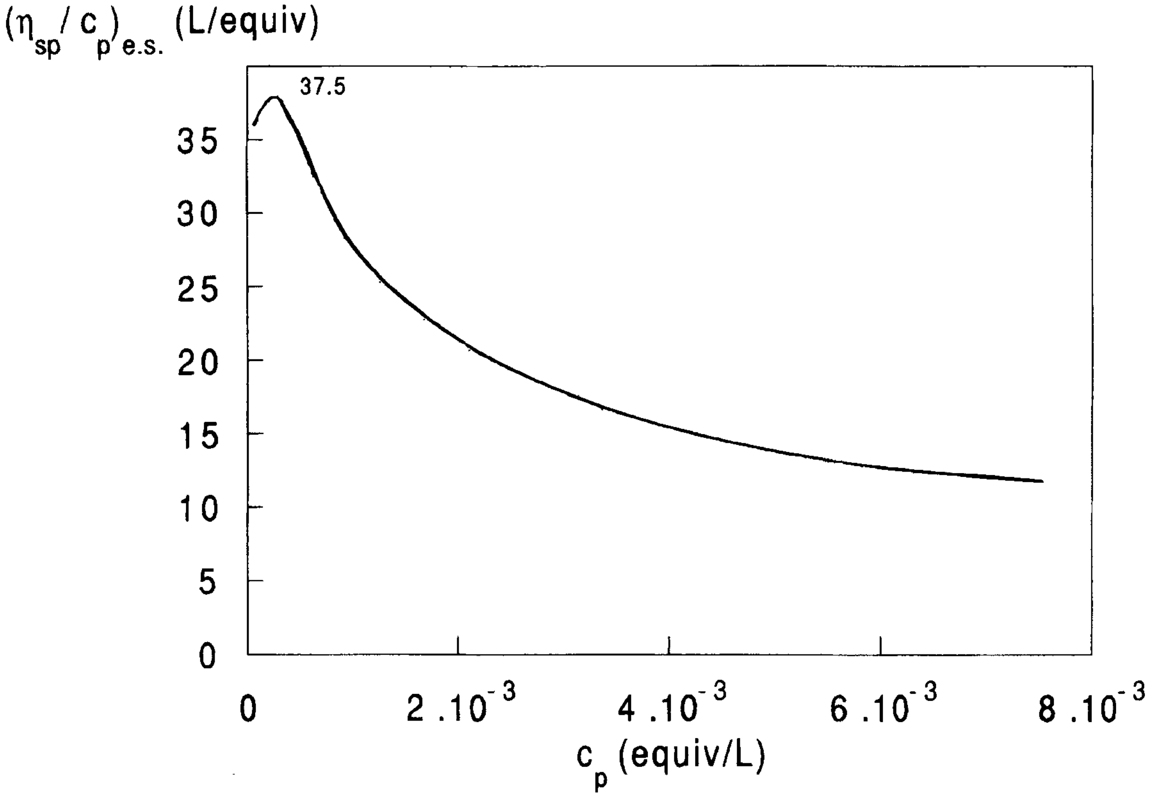


FIGURE 4 Variation of the theoretical electrostatic reduced viscosity $(\eta_{sp}/c_p)_{e.s}$ versus polymer concentration (in equiv/L) (Equation (2)) for HA at 10^{-4} M NaCl.

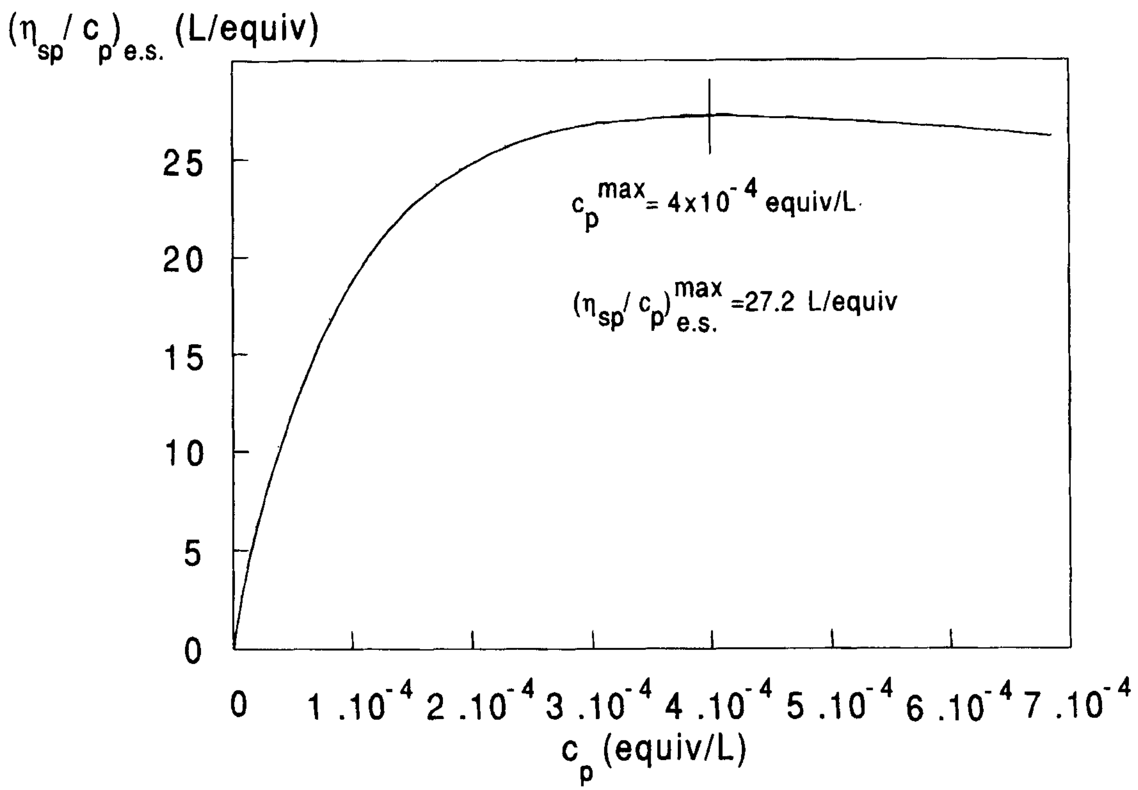


FIGURE 5 Variation of the theoretical electrostatic reduced viscosity $(\eta_{sp}/c_p)_{e.s}$ versus polymer concentration (in equiv/L) (Equation 2) for HA at 2×10^{-4} *M* NaCl. Extrapolation to very low polymer concentrations. + maximum of the curve obtained for the values given in the figure.

CONCLUSION

This preliminary analysis gives good agreement between predicted variation of the reduced viscosity and the polymer concentration in very dilute solutions. The position and the amplitude of the maximum in the reduced viscosity is, for the first time, well predicted by the approach proposed for polyelectrolytes in the dilute regime.

In the case of HA, considered as a wormlike chain, it should be convenient to consider the expansion of the chain during dilution in the range covered by Figure 1. The radius of gyration and the intrinsic viscosity were calculated following the model of wormlike chain taking into account electrostatic contribution.[8,9] The expansion of the chain, as reflected by these two characteristics, increases continuously during dilution; this factor should be also considered to fit Equation (3) in which we assumed as a first approximation that the dimensions were nearly constant. Nevertheless, this contribution remains low compared with the electrostatic term B.

The validity of our approach is limited to moderate molecular weight polymers for which the dilute regime is accessible in experimental investigations.

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