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Viscometric behaviour of polyelectrolytes in the presence of low salt concentration

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The purpose of this paper is to draw a general picture for viscometric behaviour of polyelectrolytes. The polymers tested are hyaluronan ($\lambda = 0.7$) and sodium polystyrene sulfonate ($\lambda = 2.8$) with different molecular weights. The viscometric behaviour in isoionic dilution is examined and one demonstrates that $k'[\eta] \sim C_s^{-3/2}$. Dilution in water or with solvent of low salt concentration causes the reduced viscosity to pass through a maximum for a given polymer concentration. The position of the maximum and the amplitude of this maximum is analyzed for the low molecular weight samples in the dilute regime. The electrostatic contribution dominates and the treatment adopted gives good agreement between calculated and experimental data. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyelectrolyte viscosity; electrostatic effect; maximum reduced viscosity)

INTRODUCTION

The viscometric behaviour of charged molecules is still under discussion for linear chain[1–5] or latex particles[6,7]. Especially the reduced viscosity as a function of polymer concentration passes through a maximum $(\eta_{sp}/C)_{max}$ for a polymer concentration (C_{max}) imposed by the external salt (1–1 electrolyte) content of the solution (C_s). It is usually admitted that the position of this maximum (i.e. C_{max}) is independent of the molecular weight for a considered polymer[2,8], i.e. just imposed by the ionic concentration due to the salt in solution. In that respect, it is important to also consider the contribution of the polymer to the ionic concentration.

The purpose of this work is to draw a general picture for the polyelectrolyte behaviour whatever is the charge parameter (λ), the chemical structure and the molecular weight.

Experimental

Hyaluronan (HA) is a bacterial polysaccharide produced by *Streptococcus zooepidemicus*; commercial samples were obtained from ARD, Pomacle (France). We used a selective C-6 alcohol oxidation process[9] to obtain an oxidized HA, named HAO. All the samples (HA and HAO) were purified under their sodium form as usually[10].

The weight-average molecular weights of the different polymers investigated were HA (I) $M_w = 1500\,000$, HA (II) $M_w = 500\,000$, HA (III) $M_w = 100\,000$, HA (IV) $M_w = 30\,000$, HAO $M_w = 510\,000$, and the polydispersity index was around 1.3. These characteristics were obtained using a multidetection steric exclusion chromatograph[11]. The polystyrene sulfonates under sodium form (PSS-Na) were from Pressure Chemical (DS$\sim$1); their characteristics were the following: $M_w = 484\,000$; $212\,000$; $41\,300$; $M_w/M_n = 1.15$, 1.04 and 1.12 respectively.

The charge parameter for HA is $\lambda = 0.7$, for HAO $\lambda = 1.14$ and for PSS-Na $\lambda = 2.8$.

The viscometric measurements were performed at 25 ± 0.01°C using a capillary Ubbelohde viscometer from Fica (France) (inner diameter $\phi = 0.5$ mm) when no shear rate effect was observed; otherwise, a Low Shear 30 viscometer from Contraves was used.

RESULTS AND DISCUSSION

Isoionic dilution

Isoionic dilution was realized on the different polymers investigated; the basis is to dilute the polyelectrolyte solution prepared in pure water with a 1–1 electrolyte which ionic concentration $C_{s,o}$ is just equal to the effective ionic concentration of the polyelectrolyte solution such as to preserve the electrostatic interactions (i.e. κ^{-1}, the Debye length) and the conformation of the polyelectrolyte; then, the reduced viscosity gives a linear dependency with the polymer concentration in the dilute regime. The intrinsic viscosity $[\eta]$ is determined at low ionic concentration as well as the Huggins constant k'[12–14].

The constant k' decreases largely when the salt concentration increases due to the decrease of the long range electrostatic interactions.

Isoionic dilution implies to fix the contribution of the polyelectrolyte to the ionic concentration of the solution; the concentration $C_{s,o}$ of the salt solution used for dilution of the polyelectrolyte solution is such as:

$$(C_{p,o}/\lambda) = C_{s,o} \tag{1}$$

or

$$(C_{p,o}/2\lambda) = C_{s,o} \tag{2}$$

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depending on the contribution of the polyion–counterions system introduced; λ is the charge parameter but λ is imposed to 1 for low charge parameter ($\lambda < 1$). $C_{p,o}$ is the initial polymer concentration expressed in equiv l^{-1}.

Relation equation (1) implies that the polyelectrolyte behaves as a simple electrolyte when $\lambda \leq 1$ or as the equivalent electrolyte corresponding only to the uncondensed charges when $\lambda > 1$.

Relation equation (2) means that only the uncondensed counterions contribute to the ionic concentration of the polyelectrolyte solution.

From different experiments, one concluded that the relation equation (1) is valid whatever the value of λ is; oxidized guar was investigated[15] as well as hyaluronan[8], sodium polystyrenesulfonate[16] and sodium polygalacturonate[1]. The linear variation of the reduced viscosity (η_{sp}/C) as a function of the polymer concentration (C) for isoionic dilution allows to determine $[\eta]$ at the ionic concentration $C_{s,o}$ and the slope gives k'; this technique is very useful for the low values of $C_{s,o}$.

Following the treatment of Antonietti *et al.*[17], one has previously assumed that the values of η_{sp}/C as a function of the polymer concentration (C) in the dilute regime can be written as an additivity:

$$(\eta_{sp}/C) = [\eta][1 + k'[\eta]C + (\eta_{sp}/C)_{HK}] \tag{3}$$

in which $(\eta_{sp}/C)_{HK}$ represents the increase of the reduced viscosity due to electrostatic long range interactions.

This electrostatic contribution was admitted previously as well predicted in a first approach by the general relation proposed by Hess and Klein[18], which can be expressed by:

$$(\eta_{sp}/C)_{HK} = \Phi(C_p/(C_{p,\mathrm{red}} + C_s)^{3/2}) \tag{4}$$

with $C_{p,red} = C_p$ when $\lambda \leq 1$ or C_p/λ when $\lambda > 1$,Φ is a constant taking into account the conversion of C_p in g ml^{-1} and that of C_T to κ; C_T is the total ionic concentration with $C_T = C_{p,red} + C_s$.

Then,for isoionic dilution, the total ionic concentration is constant and equal to $C_{s,o}$; the slope of the curve giving (η_{sp}/C) as a function of C will give, in fact, an apparent k' (k'_{app}), which may be identified to:

$$k_{app}' = k' + k_{es}' \text{ with } k_{es}'[\eta]C = (\eta_{sp}/C)_{HK} \text{ and}$$

$$k_{es}'[\eta] = \Phi(m_e^{-1} \times 10^3)C_{s,o}^{-3/2} \tag{5}$$

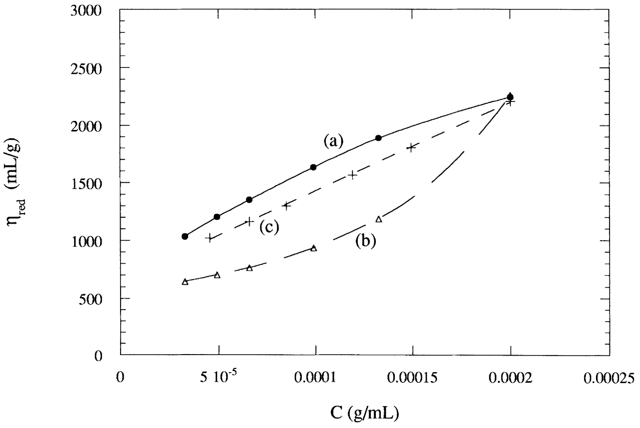

Figure 1 Reduced viscosity as a function of polymer concentration for different salt concentrations used for dilution: (a) $\varphi = 0.7$ ($C_{s,o} = 3.5 \times 10^{-4}$ M); (b) $\varphi = 2$ ($C_{s,o} = 10^{-3}$ M); (c) $\varphi = 1$ ($C_{s,o} = 5 \times 10^{-4}$ M); isoionic dilution HA $M_w = 100\,000$ $C_{p,o} = 0.2$ g l^{-1} or 5×10^{-4} equiv l^{-1}

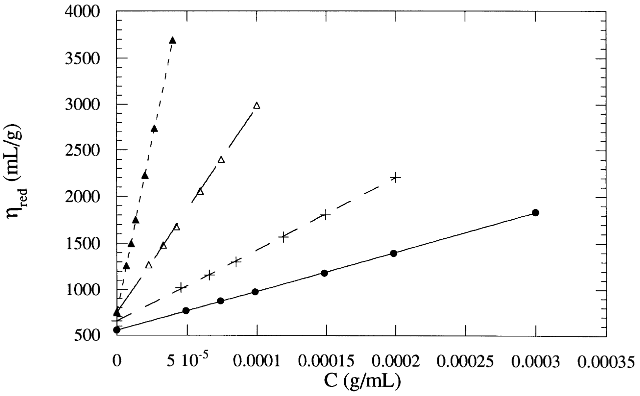

Figure 2 Isoionic dilution for different initial concentrations of a salt free polymer solution. HA $M_w = 100\,000$. (▲) $C_{s,o} = 10^{-4}$ M; (△) $C_{s,o} = 2.5 \times 10^{-4}$ M; (+) $C_{s,o} = 5 \times 10^{-4}$ M; (●) $C_{s,o} = 7.5 \times 10^{-4}$ M

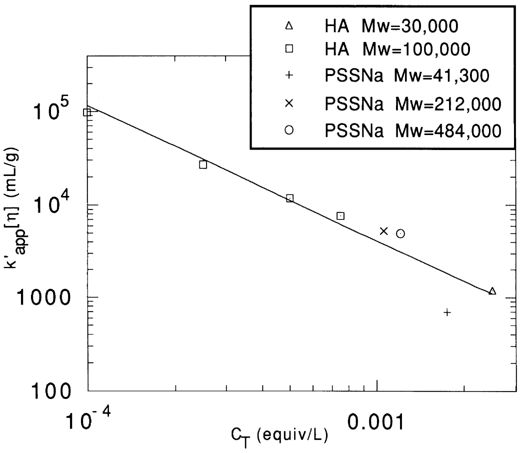

Figure 3 Dependence of the factor k'_{app} $[\eta]$ as a function of the total ionic concentration C_T in a log–log plot (data from *Table 1*)

In this relation, m_e represents the mass per equivalent charge unit.

The Huggins constant k' should be related to the absence of electrostatic contribution (or large excess of salt) and be negligible compared to $\Phi(m_e^{-1} \times 10^3)[\eta]^{-1}$ $C_{s,o}^{-3/2}$ in the range of $C_{s,o}$ tested. Then, one should predict in a first approach:

$$k_{app}'[\eta] \sim C_{s,o}^{-3/2} \tag{6}$$

Nevertheless, the data from the literature give very dispersed k' values and no exact dependency with C_s nor eventually λ was established before.

In *Figure 1*, the condition for isoionic dilution is represented; when the salt solution used for dilution of the polyelectrolyte corresponds to the effective initial polyelectrolyte concentration (expressed in equiv l^{-1}), the reduced viscosity is linear when plotted as a function of polymer concentration. To determine the isoionic conditions, different values are imposed for the fraction of counterions φ which contributes to the ionic concentration; the value of φ giving the linear variation represents the fraction of charge which play a role in electrostatic properties. For HA, one found $\varphi = 1$ corresponding to $\lambda < 1$ and absence of condensation. This result confirms previous data[1] and is in agreement with relation equation (1). In *Figure 2*, isoionic dilution is performed for different initial concentrations of

Table 1 Isoionic dilution. Comparison between calculated and experimental values of intrinsic viscosity

System tested	$[\eta]_{exp}$ (ml g^{-1})	$[\eta]_{calc}$(ml g^{-1})	k'_{app}
HA			
$M_w = 100\,000$			
$\varphi = 1$			
$C_{s,o} = 10^{-4}$	750	2240	130
$C_{s,o} = 2.5 \times 10^{-4}$	744	1840	40.1
$C_{s,o} = 5 \times 10^{-4}$	653	1594	18.1
$C_{s,o} = 7.5 \times 10^{-4}$	552	1446	13.9
HA			
$M_w = 30\,000$			
$\varphi = 1$			
$C_{s,o} = 2.5 \times 10^{-3}$	135	211	8.8
PSS-Na			
$M_w = 484\,000$			
$\varphi = 0.25$			
$C_{s,o} = 1.21 \times 10^{-3}$	800	1690	6.2
PSS-Na			
$M_w = 212\,000$			
$\varphi = 0.25$			
$C_{s,o} = 1.06 \times 10^{-3}$	310	640	17
PSS-Na			
$M_w = 41\,300$			
$\varphi = 0.37$			
$C_{s,o} = 1.75 \times 10^{-3}$	41	56	17

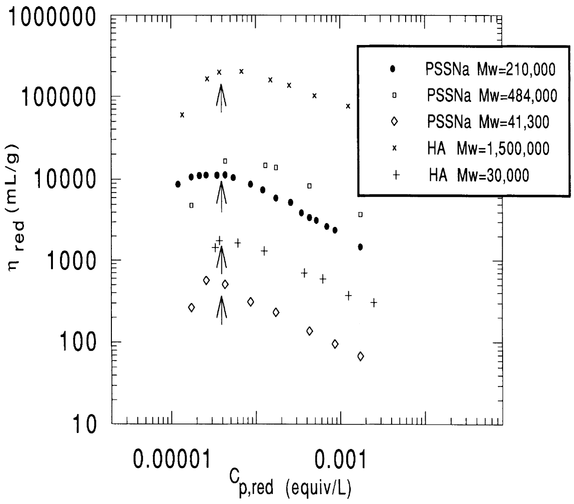

Figure 4 Reduced viscosity as a function of dilution in water for the different polyelectrolytes. The polymer concentrations are expressed as the reduced concentration $C_{p,red}$ (equal C_p or C_p/λ for $\lambda \leq 1$ and $\lambda > 1$ respectively)

the polyelectrolyte. A series of experimental data is given in *Table 1*; data are obtained on sodium hyaluronate (HA, $\lambda < 1$ and $\varphi = 1$) and sodium polystyrene sulfonate (PSS-Na). In this last case, φ was found equal to 0.25 or 0.37; the values are in agreement with λ^{-1}, the fraction of uncondensed counterions ($\varphi = \lambda^{-1} = 0.35$)[16].

In *Figure 3*, the k'_{app} values obtained by isoionic dilution in a large range of external salt concentration is represented (*Table 1*).

Up to $C_{s,o} = 2.5 \times 10^{-3}$ M a linear behaviour in log–log plot is obtained with a slope -1.45 in good agreement with our prediction $-3/2$ (relation equation (6)). For higher $C_{s,o}$, k'_{app} levels off to values in agreement with that of neutral polymers ($0.3 < k' < 0.5$) (*Table 2*).

In *Table 1*, the experimental values obtained for the intrinsic viscosity in different conditions are compared with that calculated using our usual approach[1,19]. The calculated values are always largely overestimated (nearly a ratio of 2 compared with the experimental values). This may be related to the limitation of the model adopted in the range of large κ^{-1} values. At the present time, no better prediction was found in the literature.

Dilution with low salt content solvent

When the polyelectrolytes are solubilized and diluted in an aqueous salt solution at low salt concentration (i.e. $C_s < 10^{-3}$ M), the reduced viscosity first increases then passes through a maximum and then decreases again. This behaviour is directly related to the existence of long range electrostatic repulsions. The position of the maximum was previously predicted from the Hess and Klein treatment[18]; the polymer concentration corresponding to the maximum $(C_p)_{max}$ is given by $(C_{p,red})_{max}/C_s = 2$. This prediction was recently discussed for HA[8] and sodium polygalacturonate[1]. In this paper, one extends this analysis for different polyelectrolytes with low or large charge parameter. The data are given in *Table 3* and *Figures 4* and *5*.

First of all, one confirms that the position of the maximum in reduced viscosity occurs for a polymer concentration nearly independent of the molecular weight. In addition, when solvent is pure water (assuming that the ionic impurity contents are the same in the different

Table 2 Intrinsic viscosity determined from dilution with a salt concentration C_s used as solvent

(a) Low C$_s$ ($C_s = 10^{-4}$ M)

Systems investigated	$[\eta]_{exp}$ (ml g^{-1})	$[\eta]_{calc}$ (ml g^{-1})	C^* (g ml^{-1})
HA			
$M_w = 100\,000$	800	2 240	$\sim 1.2 \times 10^{-3}$
HAO			
$M_w = 510\,000$	26 000	26 800	$\sim 4 \times 10^{-5}$
HA			
$M_w = 1\,500\,000$	43 000	95 560	$\sim 2 \times 10^{-5}$

b) Higher C$_s$

Systems investigated	$[\eta]_{exp}$ (ml g^{-1})	$[\eta]_{calc}$ (ml g^{-1})	k'_{app}
HA			
$M_w = 500\,000$			
$C_s = 0.01$ N	2 220	2 750	0.14
$C_s = 0.1$ N	1 116	1 275	0.26
$C_s = 0.3$ N	780	1 000	0.47

Table 3 Position of the maximum in the reduced viscosity

System tested	C_s (M)	$(C_p)_{max}$ (equiv l^{-1})	$[\eta]_{calc}$ (ml g^{-1})	$(\eta_{sp}/C)_{max}$ (ml g^{-1})	Φ
HA					
$\lambda = 0.7$					
$M_w = 100\,000$	10^{-4}	3×10^{-4}	2 240	2 100	$(0.0422)^a$
$M_w = 1\,500\,000$	10^{-4}	2.75×10^{-4}	95 580	90 000	–
HAO					
$\lambda = 1.14$					
$M_w = 510\,000$	10^{-4}	2.32×10^{-4}	26 800	31 500	7.75×10^{-4}
HA					
$\lambda = 0.7$					
$M_w = 1\,500\,000$	H_2O	5×10^{-5}	208 900	200 000	–
$M_w = 30\,000$	H_2O	3.75×10^{-5}	370	1 760	0.0418
PSS-Na					
$\lambda = 2.8$					
$M_w = 41\,300$	H_2O	7.27×10^{-5}	78	565	0.0209
$M_w = 212\,000$	H_2O	7.27×10^{-5}	1 190	11 270	0.028
$M_w = 484\,000$	H_2O	12×10^{-5}	5 060	16 680	1.89×10^{-3}

[a] Calculated with $[\eta] = 800$ ml g^{-1}

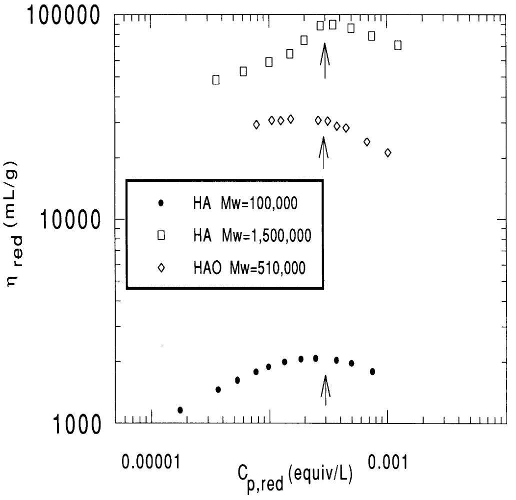

Figure 5 Reduced viscosity as a function of dilution in NaCl 10^{-4} M solvent (same representation as *Figure 4*)

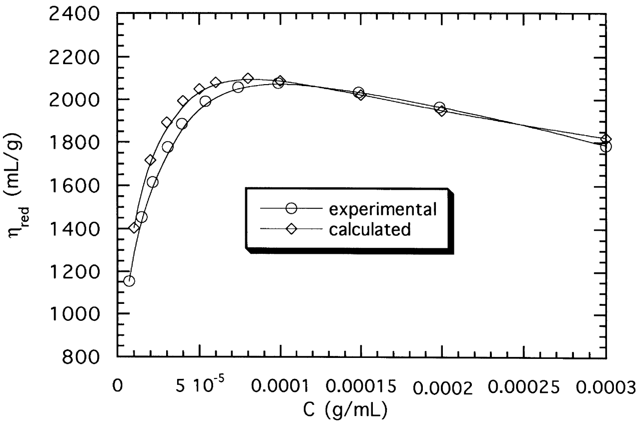

Figure 6 Reduced viscosity as a function of polymer concentration in NaCl 10^{-4} M; HA $M_w = 100\,000$; $C_{p,o} = 0.3$ g l^{-1}. Comparison of the experimental values (○) and calculated values (◇)

experiments) the maximum is shown to be located at the same position when the reduced viscosity is plotted as a function of a reduced polymer concentration $C_{p,red}$ for the different polymers. The curve giving (η_{sp}/C) as a function of C for low salt concentration C_s (10^{-4} M) also passes through a maximum independent of the molecular weight and of the charge parameter in the same type of representation. These curves extrapolate to zero polymer concentration at a value $[\eta]$ corresponding to the salt concentration C_s. The values were obtained and compared with the values calculated as previously developed (*Table 2a*); the experimental values are also usually lower than the calculated values. Nevertheless, for $M_w = 100\,000$ when the range of polymer concentration covered is in the dilute regime, the extrapolated value (800 ml g^{-1}; *Figure 6*) is in good agreement with that obtained for $C_s = 10^{-4}$ M by isoionic dilution (750 ml g^{-1}; *Table 1*). For higher molecular weight, isoionic dilution was not performed and the data cannot be compared; in addition, the domain covered is the semi-dilute regime for the higher molecular weight samples.

The last point one examines is the amplitude of the reduced viscosity at this maximum. Following the treatment of Antonietti *et al.*[17] one has previously assumed that the curve (η_{sp}/C) (C) is described by the additivity expressed by relation equation (3) in the dilute regime[20].

This relation can be expressed as the sum of three terms:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + k_{es}'[\eta]^2C \qquad (7)$$

or

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C + \Phi[\eta]C_p/C_T^{3/2} \qquad (8)$$

The second term $k'[\eta]^2C$ is usually negligible compared with the electrostatic one. Considering the calculated values of $[\eta]$ at the corresponding ionic concentration C_s, one has calculated the numerical values of Φ for the different polymers. Nevertheless, these values of $[\eta]$ are overestimated compared with the experimental extrapolation as previously mentioned.

In addition, the curves reflect the dilute regime only for the lower molecular weight samples of HA and PSS-Na. In these conditions, Φ are in the same range of values and agree

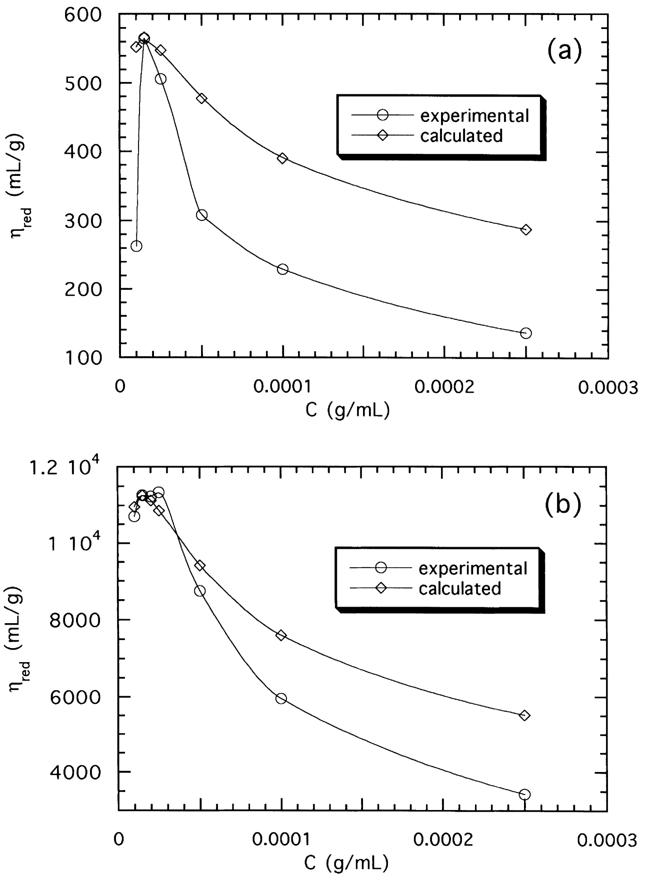

Figure 7 Reduced viscosity as a function of PSS-Na concentration in water. Comparison between experimental data and calculated values. (a) $M_w = 41\,300$; (b) $M_w = 210\,000$

with those determined previously (*Table 3*)[20]. The values are $\Phi \cong 0.042$ and 0.023 for HA and PSS-Na respectively. From these data, it comes from relation equation (5):

$$(\Phi/m_e \times 10^{-3}) \cong \text{const.} \cong 0.105 \pm 0.005$$

This parameter is independent of the polyelectrolyte and allows to recalculate the complete η_{sp}/C (C) curve. The calculated values are shown on *Figure 6* in which one has considered for $[\eta]$ the experimental extrapolation 800 ml g^{-1} which is the only case where determination is valid. For the two samples of PSS-Na, the calculated values were considered (*Figure 7*). The agreement is good in the range of the maximum but the decrease of η_{sp}/C observed in experience is larger than the prediction when the polymer concentration increases. This result may be related to the large flexibility of this molecule whose hydrodynamic volume is largely modified when the ionic concentration increases due to the progressive increase of the polyelectrolyte concentration.

CONCLUSION

In this paper, the viscometric behaviour of different polyelectrolytes is discussed in the same line as presented before. Considering that the electrostatic contribution (as predicted by Hess and Klein) dominates, one predicts the dependence of the apparent Huggins constant during isoionic dilution; it is demonstrated that:

$$k_{es}'[\eta] = \text{const.}C_{s,o}^{-3/2}$$

where $C_{s,o}$ is the ionic concentration maintained constant during dilution.

For dilution with pure water or with a solvent at low ionic concentration, the reduced viscosity as a function of the polymer concentration passes through a maximum which is independent of the molecular weight as usually admitted in the literature. One demonstrates that the position of the maximum is imposed by the external salt concentration but is independent of the charge parameter as soon as only the uncondensed charges are considered, i.e. that the ionic concentration is expressed by $C_{p,red}$.

The position of the maximum in the reduced viscosity is well predicted even if the experimental data are frequently very difficult to obtain with a good precision as these experiments are very delicate to perform.

At the end, the amplitude of the maximum is predicted following the same model. The constant Φ introduced to reflect the different parameters relating the reduced viscosity to the ratio ($C_p/C_T^{3/2}$) depends on the molar mass of the equivalent charge unit (m_e) and the parameters relating the Debye length and C_T.

As a conclusion, this paper gives new experimental data on the viscosity of polyelectrolytes and a tentative interpretation of the long range electrostatic interaction only valid in the dilute regime.

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