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# Viscometric Behavior of Dilute Polyelectrolytes. Role of Electrostatic Interactions

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**Key Words:** *Electrostatic Interactions / Hyaluronate / Polyelectrolyte / Solutions / Viscosity*

This paper deals with the investigation of the electroviscous effects on sodium hyaluronate aqueous solutions. Dilution of a polyelectrolyte in water or low salt concentration solvent gives a reduced viscosity passing through a maximum whose position corresponds to a polymer concentration directly related to the ionic concentration. Independently of the molecular weight when isoionic dilution is performed, the conformation is preserved and the intrinsic viscosity corresponding to the adopted ionic concentration is obtained as soon as the concentration range corresponds to the dilute domain.

At end the model previously proposed to take into account the role of the electrostatic interactions on the conformation is adopted to interpret, with a good agreement, the data of intrinsic viscosity versus ionic concentration.

## Introduction

The viscometric behavior of polyelectrolytes is quite original especially in dilute solution and in the presence of low salt concentration. It is well known that the viscosity of polyelectrolytes dissolved in water decreases rapidly when external salt is added. An other characteristic behavior corresponds to the increase of the reduced viscosity during dilution of an aqueous solution of polyelectrolyte in absence of external salt or for low salt content. This increase was previously interpreted by the empirical Fuoss law [1].

But, for very high dilution, usually a maximum appears in the reduced viscosity as discussed first by Pals and Hermans [2] and Goring and Rezanowicz [3]. The position of the maximum depends on the salt content in the solution, at least for low external salt content ( $10^{-5}$ – $10^{-4}$  M).

Then for very low salt concentration, it remains impossible to extrapolate for the intrinsic viscosity. Isoionic dilution, which preserves the ionic atmosphere of the polyelectrolyte, allows to determine the intrinsic viscosity  $[\eta]$  which depends on the total ionic concentration ( $C_T$ ) adopted. In these conditions, it is admitted that the conformation remains unchanged.

The variation of  $[\eta]$  with  $C_T$  is usually assumed to vary as:

$$[\eta]_{C_T} = [\eta]_{\infty} + SC_T^{-1/2} \quad (1)$$

corresponding to a linear variation of  $[\eta]$  with  $C_T^{-1/2}$  at least in a moderate range of salt concentration; the slope  $S$  depends on the molecular weight and on the persistence length of the molecule. This variation was previously discussed [4]. For a wormlike chain,  $[\eta]$  as a function of  $C_T$  can be calculated as proposed by Odijk [5].

This paper will describe the viscometric behavior in the newtonian regime for hyaluronan (sodium salt-HA) in absence or presence of low external salt content. Our objective is to focus on the role of long range electrostatic interactions on the viscosity.

## Experimental

Hyaluronan (HA) is a bacterial polysaccharide produced by *Streptococcus*, *Zoepidemicus*; commercial samples were obtained from ARD, Pomacle (France).

The samples were purified under their sodium form as usually [6]. The weight average molecular weights of the different polymers investigated were (I)  $M_w = 100000$ , (II)  $M_w = 1500000$  and the polydispersity index around 1.3. These characteristics were obtained using a multidetection steric exclusion chromatography [7].

The viscometric measurements were performed at  $25 \pm 0.01^\circ\text{C}$  using a capillary Ubbelohde viscometer from Fica (France) (inner diameter  $\phi = 0.5$  mm) for very low polymer concentrations where no shear rate ( $\dot{\gamma}$ ) effect was observed; for extrapolation to  $\dot{\gamma} \rightarrow 0$  when necessary, a Low Shear 30 viscometer from Contraves was used.

## Results and Discussion

### A) Dilution in Salt Free Solution or Low Salt Concentration

The Fig. 1 gives the variation of the reduced viscosity with polymer concentration obtained in absence of shear rate effect in two different solvents.

For very dilute solution a maximum is obtained for  $\eta_{sp}/C$  as previously discussed for Na-polygalacturonate [8]. In pure water this was interpreted as due to the presence of external salt traces; more, the maximum is shifted to higher polymer concentration when the solvent used for dilution of the polyelectrolyte is a 1-1 electrolyte solution (concentration  $C_s$ ) (see Fig. 1).

Fig. 2 shows that the position of the maximum is nearly independent of the molecular weight.

In a previous paper [8], following Hess and Klein [9] and Cohen et al. [10], one expressed the reduced viscosity by the following relation:

$$\frac{\eta_{sp}}{C} \sim \frac{C_p}{K^3} \sim \frac{C_p}{(C_p/\lambda + C_s)^{3/2}} \quad (2)$$

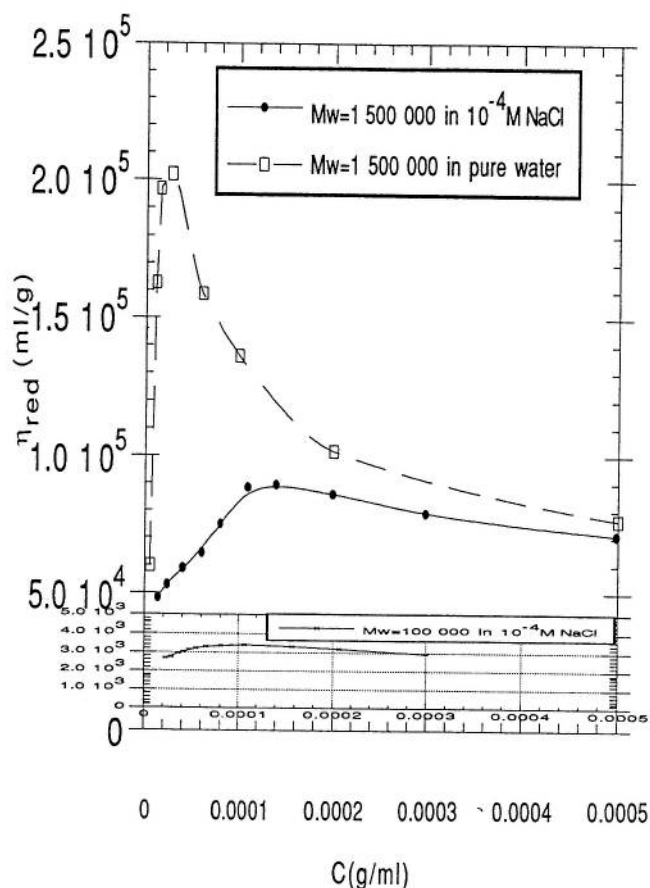


Fig. 1  
Reduced viscosity of HA in water or in NaCl  $10^{-4}$  M as solvents

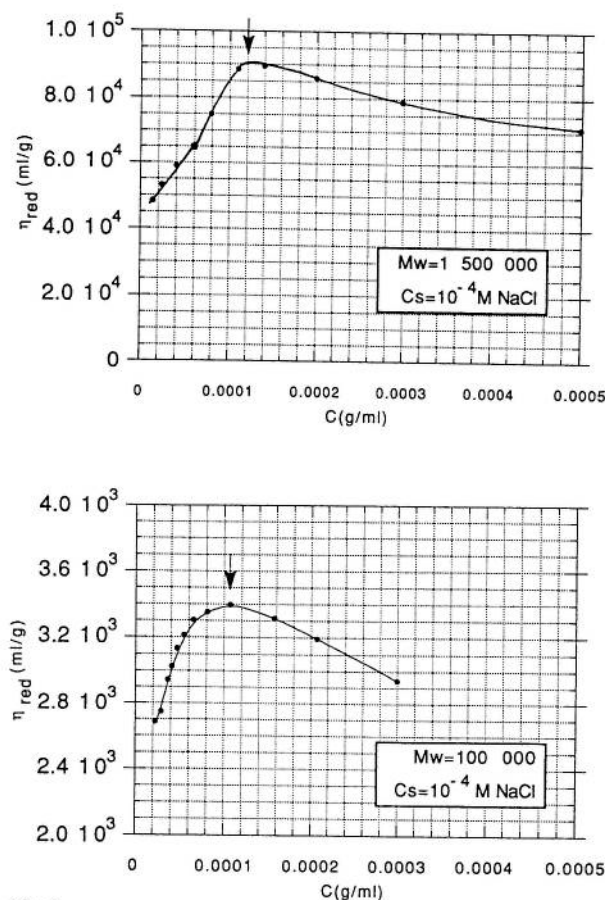


Fig. 2  
Reduced viscosity of HA(I) and (II) in NaCl  $10^{-4}$  as solvent

In this relation, the Debye length  $K^{-1}$  is related to the total ionic concentration and more exactly to  $(C_p/\lambda + C_s)^{-1/2}$  in which  $C_p/\lambda$  is the fraction of free counterions when  $\lambda > 1$  and  $C_s$  the salt concentration;  $C_p$  is the concentration of polymer expressed in equiv./L.

In the case of HA, the charge parameter  $\lambda = 0.7$  is lower than 1 and the relation (2) becomes:

$$\eta_{sp}/C_p \sim \frac{C_p}{(C_p + C_s)^{3/2}} \quad (2')$$

In absence of external salt or when the salt is in very low concentration such as  $C_s \ll C_p$  this relation gives  $(\eta_{sp}/C)^{-1} \sim C_p^{1/2}$  corresponding to the Fuoss relation [1] and giving a curve with no maximum which is usually not the case (see Fig. 1).

In the presence of external salt, the derivative of relation (2') gives the position of the maximum in the reduced viscosity:

$$C_p^{\max} = 2C_s \quad (3)$$

The values obtained are given in Table 1 and confirm that the relation (3) is a good approximation as previously

discussed [8]. In fact the ratio  $C_p^{\max}/C_s$  remains larger than 2 due to the presence of external salt traces.

Then independently of the molecular weight, this viscometric behavior is only controlled by the long range electrostatic interactions reflected by  $K^{-1}$ .

The increase of the reduced viscosity when dilution increases directly reflects the electrostatic interaction between the charged molecules on a short distance as previously discussed [11]. In this domain, a peak in radiation diffusion usually appears and indicates the liquid like correlation between the charged molecules. In the case of HA, this peak was never observed till now even if we have shown it for different polyelectrolytes such as PSSNa [12], xanthan [13] and succinoglycan [14, 15].

Table 1  
Characterization of the position of maximum in reduced viscosity for  $H_2O$  and NaCl  $10^{-4}$  M as solvents

$C_s$ (NaCl)	$C_{\max}$ [g/ml]	$C_p^{\max}$ [equiv/l]	$C_p^{\max}/C_s$
$H_2O$ (HA(II))	$2.0 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	—
$10^{-4}$ M (HA(I))	$1.1 \cdot 10^{-4}$	$2.75 \times 10^{-4}$	2.75
$10^{-4}$ M HA(II)	$1.2 \cdot 10^{-4}$	$3 \times 10^{-4}$	3

## B Isoionic Dilution

Isoionic dilution was proposed to avoid conformational change and to determine intrinsic viscosity at low ionic strength and constant  $K^{-1}$ . The experimental data are given in Fig. 3 for one of the sample; we investigate sample I for which the range of concentration lower than  $C^*$  was accessible.

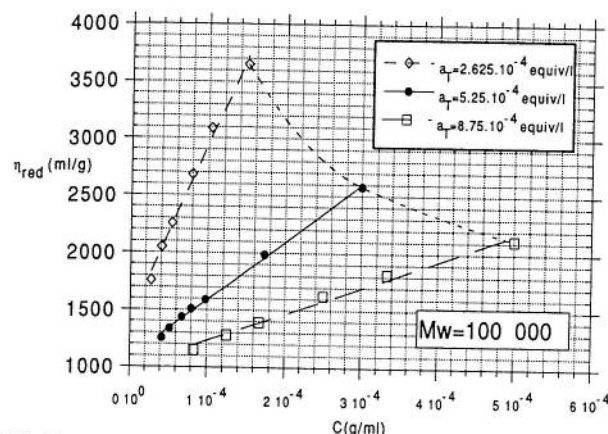


Fig. 3  
Isoionic dilution for HA(I) in NaCl for different total ionic activities

The total ionic activity is expressed as  $a_T = \gamma_s C_s + \gamma_p C_p$  in which  $\gamma_p$  corresponds to the activity coefficient of the counterion in absence of external salt determined previously ( $\gamma_p = 0.7$ ) and  $\gamma_s$  to the activity coefficient of external salt ( $\gamma_s \approx 1$ ) [16].

From this figure, the intrinsic viscosities were determined as well as the slope, or an apparent Huggins constant  $k'$  (Table 2).

Table 2  
Intrinsic viscosities obtained by isoionic dilution on HA(I)  $M_w = 100000$  with NaCl

$a_T$ [equiv/l]	$[\eta]_{\text{exp}}$ [ml/g]	$k'$	$10^3 (a_T^{-3/2}/\text{slope})^*$	$[\eta]_{\text{calc}}$ [ml/g]
$2.625 \cdot 10^{-4}$	1406	7.8	15.25	1790
$5.25 \cdot 10^{-4}$	1080	4.3	16.57	1570
$8.75 \cdot 10^{-4}$	997	2.3	16.9	1380

\*)  $\text{Slope} = k' [\eta]^2$ .

First, it is clear that the dilution corresponds to the dilute regime, the polymer concentration being for HA (I) always lower than the overlap concentration  $C^*$  estimated for the fully extended macromolecule (Table 3).

The intrinsic viscosities obtained are lower than  $[\eta]$  of the extended molecule; the values are compared in Table 2 with those calculated for the model we applied previously [4]; even if the agreement is not perfect, the values move in the good way. The apparent  $k'$  increases when  $a_T$  decreases corresponding to an increase of the electrostatic interaction.

Table 3  
Some characteristics of the two samples used

Samples	$M_w$	$C^*$ extended *) [g/ml]	$[\eta]_{\text{calc}}$ extended
I	100000	$5.07 \cdot 10^{-4}$	1970
II	1500000	$2.99 \cdot 10^{-6}$	334000

\*)  $C^* = [\eta]^{-1} \text{ calc.}$

Isoionic dilution allows the separation of conformational change and electrostatic interchain interaction.

More, the slopes of the linear curves (Fig. 3) obtained when  $a_T$  is maintained constant gives a ratio ( $a_T^{-3/2}/\text{slope}$ ) nearly constant for the different concentrations (Table 2); this can be related with the prediction of relation (2') and points out that perhaps the activity of counterions has to be introduced instead of total ionic concentration in relation (2'). This question is still under discussion.

From these results, it becomes clear that electroviscous effects reflecting interparticle electrostatic interactions control the large increase observed in the reduced viscosity during dilution.

## Conclusion

In this paper, the influence of electrostatic interactions on the reduced viscosity of hyaluronan solution is examined.

When the viscosity is considered in pure water or low salt concentration solution as solvent, the reduced viscosity passes through a maximum whose position is imposed by the actual salt concentration and  $C_p^{\text{max}}/C_s \sim 2$ . The polymer concentration at the maximum is independent of the molecular weight. The global effect which is mainly electrostatic is controlled by the values of  $K^{-1}$ .

Then isoionic dilution was applied to obtain the intrinsic viscosity for very low ionic concentration. This extrapolation is in relatively good agreement with the value calculated with the model previously tested.

It is then confirmed that the large change of the reduced viscosity change with dilution corresponds to the existence of large electrostatic interaction without conformational change. These interactions are directly related with the Debye length.

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