Influence of polyeclectrolyte concentration and metallic ions on viscosity of soft colloidal polysaccharides

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Abstract: *Viscosity of carboxymethyldextran (CMD), a charged and well-defined polysaccharide, was evaluated in the presence and in the absence of divalent cations (calcium and cadmium) in aqueous $NaNO_3$ solution. The data collected in the absence of metallic ions clearly indicates that CMD viscosity is almost independent on polymer concentration at sufficiently high ionic strength while an influence of polyelectrolyte concentration occurs on viscosity at low salt concentrations, reflecting stretched polymer chains and the overlap of their electrical double layers. At high electrolyte background concentration where electrostatic effects are minimized, the presence of metal ions leads to a significant decrease of CMD viscosity, pointing out a structural modification following complexation of metal ions with CMD carboxylicreactive sites.*

Keywords: *carboxymethyldextran, reduced viscosity, soft particle, overlapping, interparticle spacing.*

I. INTRODUCTION

In polar solvent, attractive and repulsive interactions between chain segments affect on soluble polysaccharide hydration and so its molecular hydrodynamic volume. The changes in molecular hydrodynamic volume, conformation and macromolecular associations can be illustrated by any change in viscosity. A number of studies showed that viscosity measurements in dilute solution regimes, in which individual polysaccharide coils are well separated from one another, and are free to move independently, are important in providing information on how molecules behave in solution and how structure and property of biopolymers are related [1-3]. In particular, intrinsic viscosity provides deep insight on the fundamental molecularproperties of macromolecules in solution [4,5]**.** For the polymers with ionisable groups, as known as polyelectrolytes, the viscosity results from hydrodynamic polymer and polyion charge effects [6].

Also, the flow behavior differs from that of neutral polymers. This difference is ascribed in general to the electroviscous effects**.** [7,8]**.** The first one, the primary effect electroviscous arises from additional dissipation due to the distorted ion cloud by the imposed flow. The secondary effect results from the interchain electrostatic interactions, ie interactions between double layers of different particles that

change the polyelectrolyte configuration. The former, the tertiary effect is due to the change in chain conformation caused by the intrachain electrostatic repulsions. These three effects are coupled for flexible polyelectrolytes because the deformed ion cloud can modify both intra- and interchain electrostatic interactions. In the present paper, an experimental investigation of the viscosity of carboxymethyldextran (CMD), a soft, anionic polysaccharide [9] is presented and the influence of the ionic strength and polymer volume fraction on the viscosity of this polyelectrolyte is analysed.

II.   EXPERIMENTAL SECTION

2.1. Experimental Material

The chemicals listed below were from analytical grades and were used as received: $NaNO_3$ and $Ca(NO_3)_2$ from Prolabo (Merck, USA); HNO_3, NaOH, $ClCH_2COOH$ and $\{Cd(NO_3)_2, 4H_2O\}$ from Aldrich (St. Quentin Fallavier, France). Ultrapure Milli-Q water was used to prepare polymer solutions. Carboxymethyldextran was obtained by carboxymethylation of native Dextran T500 purchased from Amersham Biosciences (Uppsala, Sweden) with monochloroacetic acid under alkaline conditions as detailed elsewhere [10-12].

2.2. Material Characterization

The degree of substitution (DS), i.e. the amount of carboxymethyl groups per 100 glucopyranosidic units, and the volume charge density (ρ_0/F) of the synthesized CMD are determined by potentiometric titration at 100 mM $NaNO_3$ ionic strength and pH7 (complete dissociation of the carboxylic sites). The hydrodynamic diameter (D) of the synthesized CMD and native Dextran T500, and their weight-average molar mass Mw were measured at 25.0 ± 0.1 C using a Zetasizer Nano ZS instrument (He–Ne red laser (633 nm), Malvern Instruments) and the multi angle laser light scattering coupled to steric exclusion chromatography (SEC–MALLS), respectively. Table 1 lists several properties of the native Dextran T500 and the functionalized carboxymethyldextran (CMD).

Table 1. Values of the degree of substitution (DS), volume charge density (q_0/F), hydrodynamic diameter (D) and weight-average molar mass (Mw) of the Native Dextran T500 and CMD at pH 7 in 100 mM $NaNO_3$.

Polymer	DS (%)	q_0/F (mol/m3)	D (nm)	Mw (g/mol)
Dextran T500	–	–	40	634,800
CMD	49	38	58	794,000

2.3. Sample preparation

Polysaccharide solutions were prepared 24 h prior to experiments in $NaNO_3$ electrolyte solution and stored at 4 C to ensure the complete dispersion of polymers. All measurements were carried out at a temperature at 25 ± 0.1 C.

2.4. Experimental method

Viscosity measurements were carried out at 25.0 ± 0.1°C and initiated after approximately 10 min equilibrium time, using a Viscologic TI.1 – Version 3.0 viscometer (Sematech) with type capillary ''Ostwald Biology'' model (capillary diameter of 0.46 mm), which is suspended in a thermostatic water bath under precise temperature control. An exact volume of 3ml is added in the tube and absorbed through the capillary by a pump. As this latter stops, the flow time of sample solution is automatically measured by the viscosimeter. The flow times were determined from an average of eight readings, in order to check the reliability of the data. Variation between consecutive readings was lower than 1.5% and typically around 0.5%. The specific viscosity, η_{sp} was obtained, from the ratio of the flow time of the solution t to the flow time of solvent t_0 according to the equation

$\eta_{sp} = (t - t_0)/t_0$ and the reduced viscosity η_{red} was deduced from the following ratio $\eta_{red} = \eta_{sp}/C_p$ where C_p is the polymer concentration.

III.   RESULTS AND DISCUSSION

The reduced viscosity of the Carboxymethyl dextran is plotted against its polymer concentration at three ionic strengths 1mM, 10 mM and 100 mM NaNO₃ in Fig. 1. Two trends may be observed. At ionic strength of 100 mM, the polymer concentration has very little influence on the reduced viscosity since this former varies from 0.15 to 0.17 L.g^{-1}, an increase of 15% in the whole range of CMD concentration studied. In contrast, viscosity is a function of polymer amount in the same range of CMD concentration for 10mM and 1mM NaNO₃.
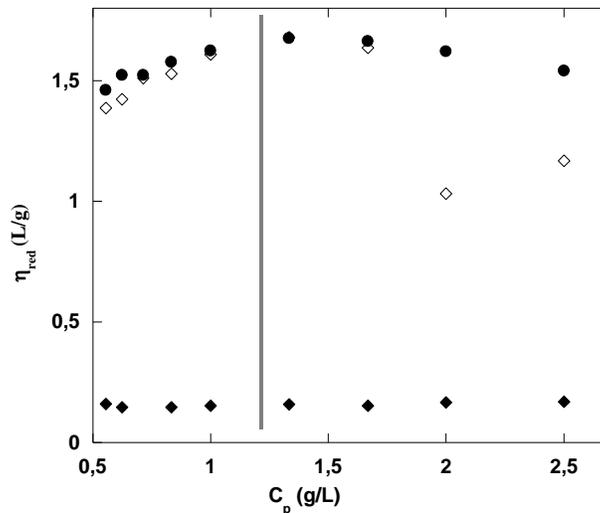

Fig. 1. The observed reduced viscosity η_{red} as a function of CMD polymer concentration C_p for in various salt concentrations: (●) 1 mM NaNO₃; (◊) 10 mM NaNO₃; (♦) 100 mM NaNO₃.

These features are related to the change in the hydrodynamic volume of macromolecules, which is determined by several types of interactions, including polymer-solvent interaction and polymer-polymer interaction [13]. Also, the situation in which the polymer concentration has almost no effect on the viscosity can be assigned to the fact that at high-salt concentration , the charges on the CMD chains are significantly screened due to the excess amount of counter ions present in solution. Intramolecular repulsive interactions are negligible and the polymer-solvent interaction is weak, resulting in macromolecular shrinking as previously observed [12]. In these conditions, the polyelectrolyte behavior would be similar to that of an uncharged polymer. However, the collected viscosity values are still higher than those measured by Rotureau *and al.* [14] on the native dextran macromolecule in the same concentration range. This clearly indicates that the grafting of the carboxylate functions leads to a significant increase in the viscosity of the polysaccharide firstly due to the increase in molar mass which varies from 638 kDa to 794 kDa (table 1), and on the other hand due to solvent hydrodynamic effects on the polyion in presence of these functions. Fuss and Strauss [15,16] show moreover many years ago that viscosity behaviours of polyelectrolyte solutions are significantly different than those of neutral polymers.

From the intersect with the *y*-axis, we can extract the intrinsic viscosity. This extrapolation of the viscosity data towards vanishing polymer concentrations lead to value of 0.15 L/g. A non-zero value of viscosity at such high salt concentrations was described as typical microgel behavior and attributed to the build-up of an electrostatic shell where counterions are mutually coupled and act cooperatively also from a hydrodynamic point of view [17] .

The independence on viscosity to polyion concentration at sufficiently high salt concentration was also observed for others systems as suspensions of sodium salt of partially sulfuric acid-esterified poly (vinyl alcohol) macromolecules by Nishida *et al.* [18], who explained the physical meaning of the constant by the hydrodynamic contribution of an isolated chain into the reduced viscosity. Plots on Fig.1 clearly show that for sufficiently low ionic strengths, the trends of viscosity variation depart from that of high ionic strength. Indeed, in comparison to 100 mM $NaNO_3$, the value of reduced viscosity of the suspension at 1 mM and 10 mM $NaNO_3$ is at least seven times higher, meaning that other features are added to the effect of the hydrodynamic permeability between the particle and the solvent. This discrepancy is attributed to the contribution of intermolecular part to the reduced viscosity [18].

In conditions of low ionic strengths, the electrostatic potential is non-zero in the macromolecule. Thus, the particles are swollen due to significant electrostatic repulsions between adjacent carboxylic groups. Therefore, the particles have sufficiently larger sizes to give rise to hydrodynamic interactions between themselves as the polyion concentration increases. Such configurations are accompanied by an overlap of their electric double layers as shown previously our results [19, 20]. Furthermore, this increment to the overall viscosity is also due to the additional contribution of secondary and tertiary electroviscous effects between neighbor particles and intrachain respectively.

In order to expand the discussion, the extend of electrical double layers is estimated and compared to the interparticle spacing (IPS). This former is defined as the distance from the surface of one particle to that of another and evaluated on the base of equation derived by Hao and Riman [21] by assuming the cell model proposed by Kuwabara [22]. In this configuration, each of soft particles, schematically shown in Fig. 3, consists of the particle core of radius *a* covered with a polyelectrolyte layer of radius *b*. Kuwabara cell model [22] is used to take into account the particle interaction: each sphere is surrounded by a concentric

spherical shell of an electrolyte solution, having an outer radius c such that the particle/cell volume ratio in the unit cell is equal to the particle volume fraction, $\phi = (b/c)^3$.
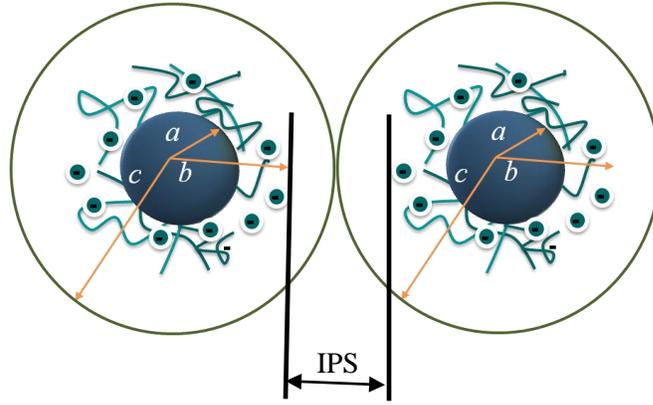
Fig 2. Illustration of IPS in a system of soft particles of radius b in a cavity of radius c and a hard core of radius a.

According to the assumption proposed by Hao and Riman [21], the IPS should be zero when particles reach the maximum particle packing fraction, ϕ_m, because particles contact one another *(c ~ b)* and when the particle volume fraction is less than φ_m, there is free volume not occupied by particles. By supposing the maximum packing fraction for random dense packing and random loose packing are 0.63 and 0.59 respectively, the IPS was written in the term:

$$\text{IPS} = 2b\left(\left(\frac{\phi_m}{\phi}\right)^{1/3} - 1\right)$$

To evaluate this IPS, knowledge of the particle size is required. For sake of simplicity and to reduce the complexity of the problem as connected to swelling and segment distribution heterogeneity in low ionic strengths where the polymer chains are likely stretched as a result of significant electrostatic repulsions between adjacent carboxylic groups, the macromolecular size at 100 mM $NaNO_3$ is considered. Indeed, CMD macromolecule can be considered as a random coil with a uniform segment distribution at sufficiently high strength [12]. At 100m mM, a constant diffusion coefficient of 8×10^{-12} m²/s is obtained, which would correspond to a hydrodynamic diameter of 58 nm on the basis of Stokes–Einstein's relation [23].

Table 2. Values of the Debye screening length (κ^{-1}), the extend of electrical double layer thickness ($3\kappa^{-1}$) and the sum of these extends for two particles $2.(3\kappa^{-1})$ in 1, 10 and 100 mM $NaNO_3$.

$NaNO_3$ (mM)	κ^{-1} (nm)	$3\kappa^{-1}$ (nm)	$2.(3\kappa^{-1})$ (nm)
1	10	30	60
10	3.1	9.3	18.6
100	1	3	6
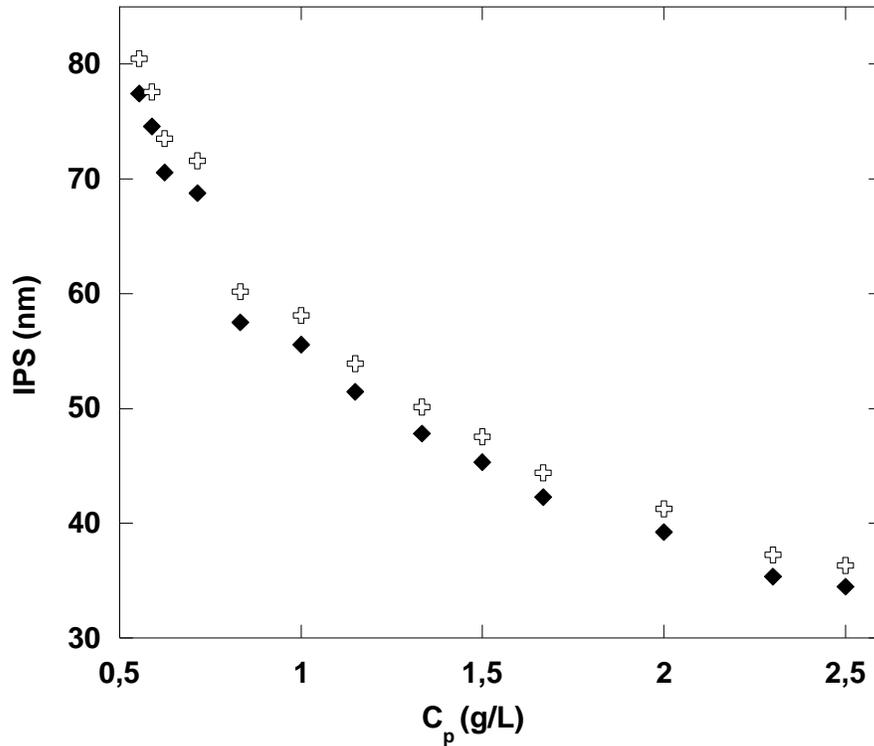
Fig. 2. Interparticle spacing (IPS) as a function of CMD macromolecules volume fraction (C_p) for both random dense and random loose packing structures at a hydrodynamic diameter of 58 nm.

Figure 2 presents the evolution of IPS evaluated according to equation proposed by Hao and Riman [21]. As can be seen, the IPS decreases as the polymer concentration increases in background. The comparison of these IPS to the sum of extends of electrical double layer thickness for two particles at 1mM $NaNO_3$ indicates values of IPS lower than 60 nm from 0.8 g/L despite the minimum CMD size is considered to estimate the IPS. This trend is likely increased with particle swelling, favoring also an overlap of electric double layers of neighbor particles.

This assumption is supported by a previous study [12] in which it was evidenced that electrical double layer polarization effects induce an important electrical for CMD macromolecules in similar region of ionic strengths. In situation of lower ionic strengths, the thickness of the electrical double layers is maximum. The increase of particle volume fraction thus favors their overlapping, the hydrodynamic interactions between particles being more significant at such salinities.

It is of interest to see if soft particles viscosity is modified upon adsorption of a non hydrolyzable metal ion such as Cd^{2+} and Ca^{2+}. In order to reduce the complexity of the problem as connected to swelling and segment distribution heterogeneity (electrostatic, electrical double layers overlapping effects), the following developments are derived for measurements are limited to CMD suspensions in 100 mM $NaNO_3$ solution.

Table 3. Reduced viscosity η_{red} (L/g) for different CMD macromolecules solutions (g/L) at 100 mM $NaNO_3$ in the presence or absence (indicated) of Ca^{2+} or Cd^{2+} ions.

Sample	Reduced viscosity (L/g)				
	0.62 g/L	1 g/L	1.33 g/L	2 g/L	2.5 g/L
$NaNO_3$	0.15	0.15	0.16	0.16	0.17
$NaNO_3 + Ca^{2+}$ at 2.47 mM	0.11	0.11	0.11	0.12	0.13
$NaNO_3 + Cd^{2+}$ at 2.47 mM	0.038	0.048	0.057	0.075	0.091

Table 2 reports reduced viscosities for several CMD concentrations at 100 mM $NaNO_3$ in the absence and presence of divalent cations. Inspection of these data reveal a difference in the presence of cations. Even in the presence of high concentrations in sodium nitrate, adding divalent cations at high background ionic strength leads to a decrease further of viscosity of CMD macromolecules. This difference being more marked with Cd^{2+}, which reveals the rather high affinity of Cd^{2+} ions for deprotonated carboxylate groups located within CMD.

IV.   CONCLUSION

We have conducted experiments to examine the effect of polyeclectrolyte concentration and metallic ions on the viscosity of soft colloidal polysaccharides in aqueous $NaNO_3$ solution. It appears that viscosity is almost constant and independent on polyion concentration at sufficiently high salt concentration but is increased for lower ionc strengths as intra- and intermolecular contributions as evidenced to electrical double layers overlapping. Addition of metallic ions at high ionic strength induces viscosity decreasing as a result of complexation of metallic ions with the carboxylic charges. To extend the range of measurements, new techniques of precise viscosity determination will have to be developed, which will allow a still more detailed look into the theoretical and experimental description of soft colloidal polysaccharides behavior.

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