IONIC STRENGTH DEPENDENCE OF THE PERSISTENCE LENGTH OF A NATURAL MODEL SEMIRIGID POLYELECTROLYTE : AGREEMENT WITH THE OSF MODEL.

E. Buhler[1], F. Boué[2]

[1]Centre de Recherches sur les Macromolécules Végétales-CNRS, UPR 5301, Joseph Fourier University, BP 53, 38041 Grenoble Cedex 9, France
[2]Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay, 91191 Gif-sur-Yvette cedex, France

Hyaluronan is a bacterial polysaccharide, hyaluronan (poly[(1→3)-b-D-GlcNAc-(1→4)-b-D-GlcA]). It belongs to a class of water-soluble linear polysaccharides (helical structure), bearing charges in water, which can be called semirigid polyelectrolytes. This means that apart from electrostatic effects, the chain backbone is locally stiff enough to correspond to an intrinsic persistence length L_0 much larger than one monomer (of mass 400 g/mol and length 10.2 Å) [1].
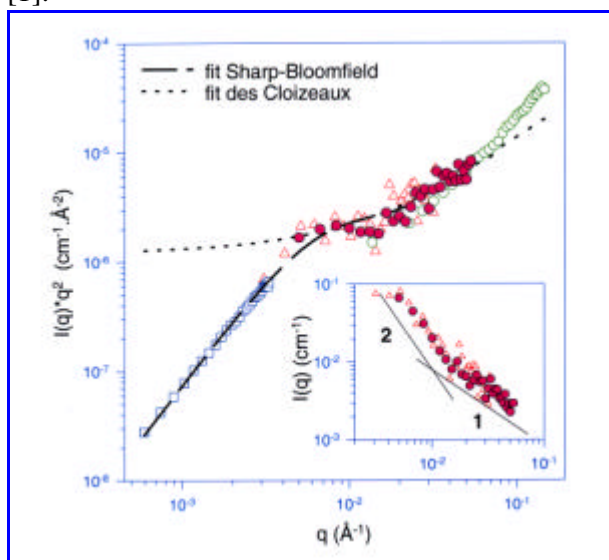

Figure 1. Kratky plot: variation of Iq^2 with q (combined SLS ( ) and SANS (Δ, $\bullet$, and O)) in high ionic strength solution. The log-log representation of the scattered intensity, I, versus q is shown in the insert (SANS). [NaCl]=0.1 M and c=1.5×10^{-3} g/cm^3. The solid line fits the wormlike chain model.

When electrostatic repulsions between the charges along the semirigid chain in aqueous solutions are not screened, they will tend to make even larger the local rigidity and increase the global size of the polyion. An additional electrostatic persistence length, L_e, due to electrostatic repulsions increases the effective persistence length, L_0. Then, following the simplest model, the total persistence length L_T is [2]

$$L_T = L_0 + L_e \qquad (1)$$

The total persistence length L_T would represent the effective rigidity of the polyelectrolyte as the sum of two contributions: the intrinsic persistence length L_0 of the corresponding uncharged chain and the electrostatic persistence length L_e, which would depend on the screening, i.e., on ionic strength due to external salt concentration. In our case, L_0 is easily larger than L_e (at least for external salt concentration larger than 3×10^{-3} M), a situation for which Odijk[1], and Skolnick and Fixman[2], found

$$L_e = \frac{\kappa^2}{4\kappa^2 l_B} \qquad \text{(OSF relation)} \qquad (2)$$

(in absence of condensation, which is the case here) where l_B=7.13 Å in water is the Bjerrum length and κ^{-1} is the Debye-Hückel screening length related to the concentration of the counterions ($\kappa^2 = 4\pi l_B c_f$ in dilute polyelectrolyte solutions).

Using SANS, **we have shown that hyaluronan, a natural product is a model semirigid polyelectrolyte, as good as a synthetic one** when it is well purified and controlled, a know how of CERMAV laboratory. Moreover **we have checked the Odijk law for the first time for a covalent polymer** t our knowledge (it was observed already for composite giant micelles).

In this aim, we have first directly determined the chain conformation at high ionic strength, where Le is naught. We have been able to fit SANS data to the "wormlike" chain model[3,4] (Figure 1). The scattered intensity crosses over, when decreasing q, from a q^{-1} rod variation to a q^{-2} as predicted for a wormlike chain; the analysis yields the backbone, intrinsic, persistence length: L_0=86.5 Å.

Then we have worked at low ionic strength. In this case, we have not been able to measure the whole form factor at low q

because, conversely, intensity crosses over from a q^{-1} to a q^{-4} variation, characteristic of polymer associations(Figure 2). But the larger q measurements allow to claim that the q-1 range is extended at low q (Figure 2 again). This means that L_e is increased ; we find the increase to be at least the amount predicted by OSF, this being the highest predicted by theory. This lower bound at low ionic strength, plus all values measured at
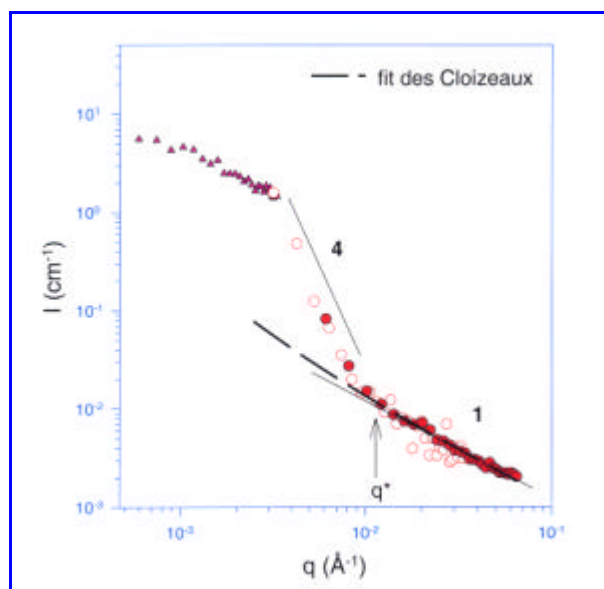
different ionic strength I fits the OSF law, $L_e \sim \kappa^{-2} \sim I^{-1}$ (Figure 3).

Conversely, for the flexible polyelectrolyte case, studied in LLB[5], led to $L_e \sim \kappa^{-1} \sim I^{-1/2}$ or even a lower exponent of I ($I^{-1/3}$). Accepting the failure of OSF law for very flexible chain[6-8] reconciliates the results.

Figure 2. Variation of the scattered intensity with q (SLS (▲) and SANS (o, and ●)) in low ionic strength solution: $[NaCl]=10^{-3}$ M and $c=1.5 \times 10^{-3}$ g/cm^3.
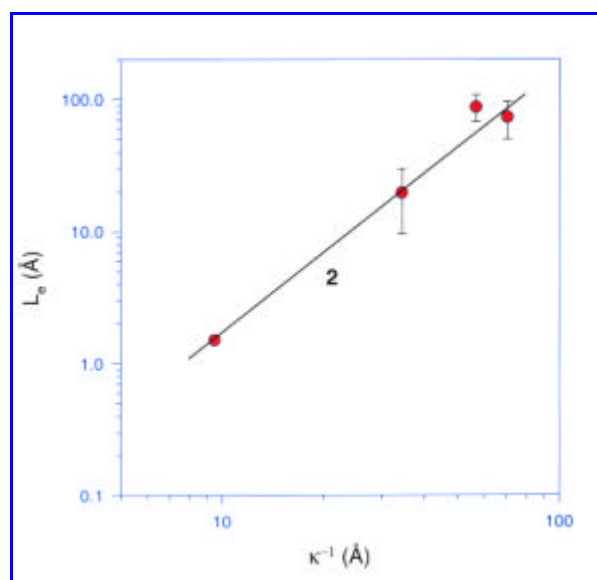

Figure 3. Dependence of the electrostatic persistence length on the Debye screening length. For [NaCl]=0.1 M, we used $L_e=1.5$ Å (cf OSF eq 2).

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