Elements of Polyelectrolyte scaling theory

In dilute solutions, polyelectrolytes can be seen as stretched electrostatic blobs, as schematically shown in figure A1.

The electrostatic blob is defined as the typical size at which the conformation of the chain starts to be perturbed by the electrostatic interactions between monomers. In order to be quantitative as far as possible, we will take into account the flexibility of the PAA chain by using the equivalent Kuhn chain.

In a Θ solvent, the blob is Gaussian so its size ξ_e is $n^{1/2}b$ where n is the number of monomers in a blob and b the Kuhn length ($n^{3/5}b$ in a good solvent). Finally, the size of the chain scales with the number of Kuhn segments N and the size of a blob, so:

$$R = \frac{N}{n}\xi_e \qquad \text{(A1)}$$

In the blob, the electrostatic energy between all monomers is roughly of the order of the thermal energy k_bT, so n can be estimated as a function of b, l_b (the bjerrum length, which is 7,1 $\AA$ in water) and f the number of charges carried by a Kuhn segment.

$$n \approx \left(\frac{l_b}{b} f^2\right)^{-2/3} \qquad \text{(A2)}$$

which leads for R to:

$$R = \frac{N}{n}\xi_e \approx bN\left(\frac{l_b}{b} f^2\right)^{1/3} \qquad \text{(A3)}$$

However, the electrostatic interactions also cause a crossover from dilute to semidilute solution at lower concentrations than for neutral chains. Polyelectrolyte chains start to overlap

when the distance between them become of the order of their size, and as the dilute chain is in a stretched state, this occurs for really lowl polymer concentrations.

The overlap concentration c^* is given by equation

$$c^* \approx \frac{N}{R^3}, \text{ with } R \text{ calculated as before} \quad \text{(A4)}$$

For higher concentrations than the overlap concentration, the important length scale becomes the correlation length ξ which is the average mesh size of the semidilute solution (see figure 2).

On length scales larger than this correlation length, the conformations of the chain are assumed to be Gaussian, because the other chains and the counterions screen the electrostatic interactions. In consequence, the chain in a semidilute salt-free polyelectrolyte is a random walk of correlation blobs. Thus we have:

$$R_e = \xi\left(\frac{N}{G_\xi}\right)^{1/2} \quad \text{(A5)}$$

where R_e is the chain size of the polyelectrolyte in a semi-dilute solution, and G_ξ the number of Kuhn monomers in a correlation blob.

The mesh size can be estimated by assuming that in the correlation volume ξ^3, the chain has a dilute conformation: its size is the same that a whole chain of the same size at c^*. In consequence[48,49]:

$$\xi \approx b^{-1} c^{-1/2} \xi_e^{1/2} \quad \text{(A6)}$$

where c is the polymer concentration

and G_ξ is given by

$$G_\xi = b^{-3} c^{-1/2} \xi_e^{3/2} \quad \text{(A7)}$$

Finally,

$$R_e \approx b^{1/4} c^{-1/4} N^{1/2} \left(\frac{l_b}{b} f^2\right)^{1/12} \qquad \text{(A8)}$$

for a polyelectrolyte in a semidilute solution.

This equation shall be valid only for a range of chain concentrations

$$c^* < c \leq \frac{\left(\frac{l_b}{b} f^2\right)^{1/3}}{b^3} = c^{**} \qquad \text{(A9)}$$

(c^{**} is the polymer concentration at which electrostatic blobs begin to overlap). For higher concentrations, we will simply assume that the polyelectrolyte chain has a Gaussian conformation $R_e \approx b\, N^{1/2}$.

To estimate the Kuhn segment length b, we refer to the literature[43]: poly(acrylic acid) with a molar mass M of 567000 g/mol in a θ-solvent has a radius of gyration $R_g = 227$ Å (values obtained by viscometry and confirmed by SAXS measurements).

In consequence, the Kuhn length b and the Flory characteristic ratio C_∞ for poly(acrylic acid) can be estimated:

$$6R_g^2 = 2\frac{M}{M_0} C_\infty l^2 \qquad \text{(A10)}$$

with M_0 the molar mass of an acrylic acid monomer unit = 72g/mol and l the length of a C-C bond ($l = 1.54$ Å)

which gives

$C_\infty \approx 8.3$ $\quad$ $b \approx 15.7$ Å

(The contour length of the chain is given by $R_{max} = Nb = a l \sin(\theta/2)$ where θ is the tetrahedral angle = 109°28 and a the number of C-C bonds)

We assume that these values are the same for the poly(acrylic acid) in its salt form.

In the following, the effective charge f_* due to Manning counterion condensation[12] near the chain will be taken into account instead of f. In consequence, the effect of the charges on the chain conformation is less important than accounted for fully charged polyelectrolytes (roughly $f^* = 1/3\, f$).

We can estimate f^* using these data: we consider m, the fraction of charged real monomers. As expressed before, $m = 1$ in our system. However, the condensation threshold is given by $l_b\, m_* / L = 1$ with L the distance between two monomers, roughly $2\, l \sin(54{,}6) \approx 2.5$Å in the zigzag conformation, which gives $m^* \approx 0.35$. In consequence, we have $f^* = b\, m^* / L \approx 1.8$.

Coming back to equation (3), it appears that for our system (and for every systems in the highly charged limit) $R > Nb$ which is physically meaningless. Thus we will use $R = Nb$ (3bis) in the following.

Consequently, we will consider that:

$$c^* \approx \frac{1}{N^2 b^3} \qquad \text{(A4bis)}$$

$$c^{**} = \frac{1}{b^3} \qquad \text{(A9bis)}$$

Using this scaling polyelectrolyte theory, we can try to estimate the typical size of a chain with N_c Kuhn monomers between two crosslinks for our system. To calculate N_c in the gels, we use results from our previous work[34]: titration and rheological measurements gave us the average number of effective crosslinks (-C-S-R-S-C- bonds) for the PAA10db gels, as presented in table 2. The results are presented in terms of percentage of "active" double bonds, i.e. double bonds which gave an effective chemical crosslink (and not an intramolecular loop or a dangling chain). Since, there is on average one double bond each ten

monomers, it is easy to estimate the molar mass between crosslinks M_c for all gels, and in consequence, N_c the related average number of Kuhn segments:

$$N_c = \frac{2M_c}{M_0 C_\infty}. \quad \text{(A11)}$$

For the 5% hydrogel, a gel is formed even if less than 2% of double bonds give an effective crosslink. Since M_n is 35kg/mol and the average number of monomeric units $n_m \sim 500$ for the PAA before gelling, we estimated that M_c is the whole chain.

The values of N_c are summarized in table 1.

Table 1. Estimate of the number of Kuhn monomers between two crosslinks for PAA10db hydrogels

C (w/w)	5%	6%	7%	8%
inter -C-S-R-S-C-	<2%	4%	5%	7%
Average number of AA monomeric units between crosslinks n_m	500	250	200	140
M_c	35000	18000	14500	10000
N_c	80	40	32	23

Using equations (4bis) and (11), the overlap concentration c^* is estimated to be close to $0.65\ 10^{-4}$ mol/L $\approx 4.10^{-8}$ Å^{-3} (in terms of Kuhn monomers concentration): polyelectrolyte chains start to overlap when the distance between them becomes of the order of their size, and since the dilute chain is in a stretched state, this occurs for really low polymer concentrations.

A 6% w/w concentration corresponds to a molar concentration of Kuhn segments c_K of $0,159$ mol/L $= 9,6.10^{-5}$ Å^{-3} ($M_{AA10dbNa}$ = 96 g/mol as it is in its sodium salt form, and c_K is the real

monomer concentration divided by the ratio (real monomers/Kuhn monomers) in the whole chain, i.e.

$$c_K = \frac{10^3 C_{(w/w)}}{M_{AA10dbNa}(1-C_{(w/w)})}\frac{2}{C_\infty}\text{ mol/L),}$$

Finally, $c^{**} \approx 3.\ 10^{-4}$ Å^{-3}

In the range of concentrations used, entanglements effects shall be negligible (see also the viscosity solutions experiments in paper 1):

Kavassalis et al.[48] established experimentally that at the entanglement onset, the chain overlap with n other chains, with $5 < n < 10$, and this gives for the concentration of entanglements

$c_{ent} \approx n^4\, c^*$

This gives in our case $c_{ent} \approx 10^{-4}$ mol/L

Figure 1: Polyelectrolyte chain in a dilute solution

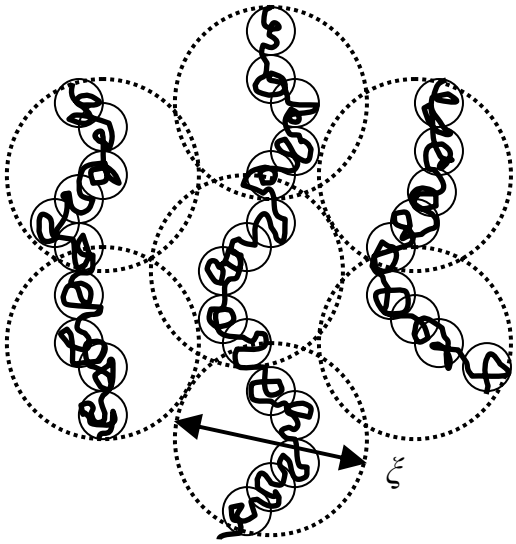

Figure 2: Polyelectrolyte chains in semidilute solutions

References

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