Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for

Highly Stretchable Hydrogels from Complex Coacervation of Natural Polyelectrolytes

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Rheological behavior of HA solutions

The rheological behavior of solutions of HA at 3% (w/v) and 6% (w/v) has been studied at various pH. The storage and loss modulus for the solutions at pH = 2.5 are reported in Fig. SI-1 for an angular frequency ranging from 10^{-1} to 10^{2} rad s^{-1}. The effect of the concentration in the frequency range studied is noticeable; however, at longer times, the two systems behave as solutions and adopt the shape of their containers.

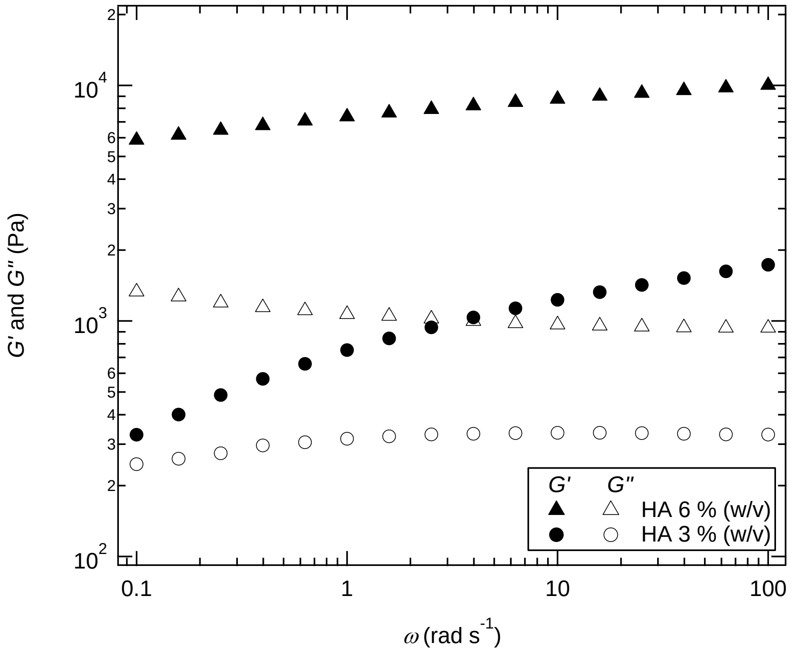

Fig SI-1. Storage (G') and loss (G'') moduli for two solutions of HA at pH 2.5 and of concentrations 3% (w/v) and 6% (w/v).

To compare with the data reported in the main text, the complex viscosities of HA solutions at 3% (w/v) and 6% (w/v) are reported in Fig SI-2 as a function of pH (ω = 10 rad s^{-1}). As expected, the complex viscosities increase with pH. It has to be noted that the evolution as a function of pH remains the same.

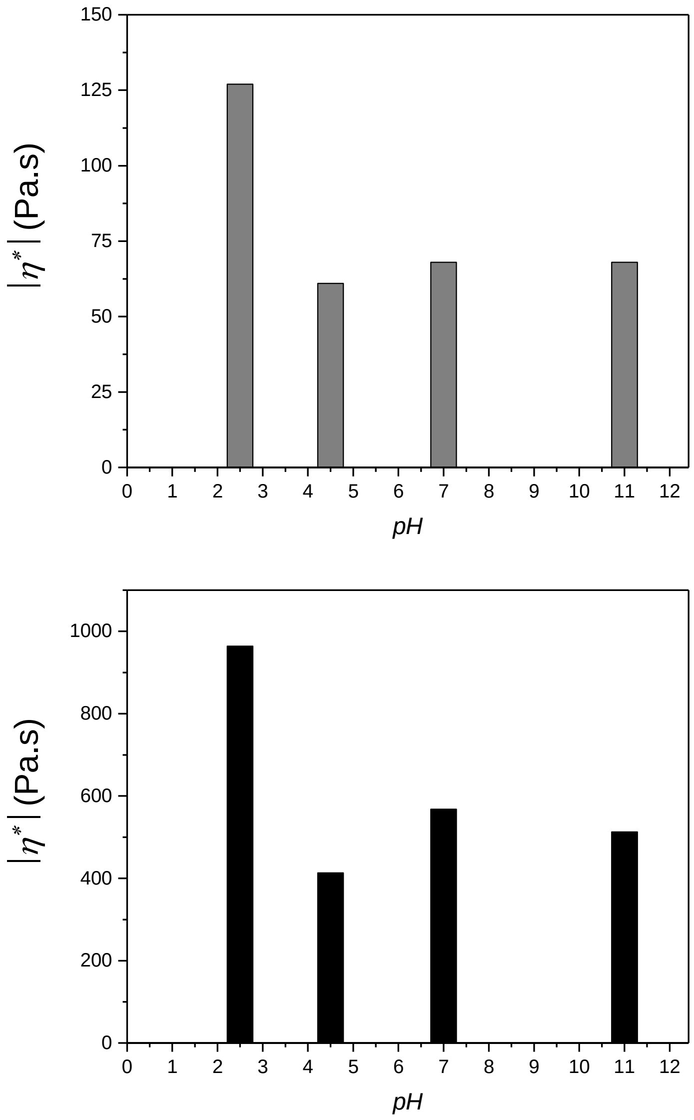

Fig SI-2. Complex viscosities of HA solutions as function of pH for concentrations of 3% (w/v) (top) and 6% (w/v) (bottom).

Scattering length densities of the systems studied by small angle scattering

For chitosan and hyaluronic acid, the neutron SLD has been calculated (see Table SI-1) by supposing that the labile hydrogen atoms (alcohol and amine functions) were replaced by deuterium atoms since the solutions were prepared in deuterium oxide. The specific volume of hyaluronic acid (HA) was approximated to 0.59 $cm^3 g^{-1}$,[1] and that of chitosan (CS) was approximated to 0.58 $cm^3 g^{-1}$.[2]

Table SI-1. Scattering length densities of the components of the systems

Component	X-ray SLD ($\times 10^{10}$ cm^{-2})	Neutron SLD ($\times 10^{10}$ cm^{-2})
Water H_2O	9.40	Not used
Deuterium oxide D_2O	Not used	6.38
Chitosan DA = 15%	14.79	4.31
Hyaluronic acid	15.12	4.04
Sodium hyaluronate	14.94	3.72

Fitting explanation for the SAXS / SANS experiments

To support the fitting choice that has been made in this paper, we have detailed the results of the influence of each term on the fitting on the curves of Fig. 8[a]. The proposed model for these curves contains two main contributions:

$$I_{SAXS}(q) = I_1(q) + I_2(q)$$

The first one corresponds to the model previously used in a previous publication, which consists of two power laws:

$$I_1(q) = \frac{A}{q^\alpha} + \frac{B}{q^\beta}$$

The first power law accounts for the presence of aggregates ($3.5 < \alpha < 4$) and the second power law is used to describe the rod-like associations within the aggregates with $0.5 < \beta < 1$. This model works well for all the systems of low pH (pH < 3.6).

However $I_1(q)$ is not sufficient to fit the intensity scattered by systems with pH > 3.6: a complementary polyelectrolyte peak is expected since hyaluronic acid is in excess and ionized (see Fig. SI-3[B], at pH < 3.6, no polyelectrolyte peak is observed; at pH > 3.6, a polyelectrolyte peak is observed). In this case, we propose the addition of a Lorentzian function and to fix the values of the exponents in $I_1(q)$ ($\alpha = 4$ and $\beta = 1$).

$$I_2(q) = \frac{C}{1 + ((q - q_0)\xi')^2} + I_{bkg}$$

The total intensity can then be written:

$$I_{SAXS}(q) = \frac{A}{q^4} + \frac{B}{q^1} + \frac{C}{1 + ((q - q_0)\xi')^2} + I_{bkg}$$

$I_1(q)$ alone allows to properly fit the low pH systems measured in SAXS and in SANS, as shown on Fig. SI-3[A] in the main text.

However, when using $I_1(q)$ alone for systems with pH > 3.6, the fit is not convincing. By using $[I_1(q) + I_2(q)]$, and taking into account the presence of a polyelectrolyte peak, the obtained fit is more convincing. On Fig. SI-3[A], the measured intensity I(q) is plotted as a function of q, as well as the fits $I_1(q)$ and $[I_1(q) + I_2(q)]$. On Fig. SI-3[B], $I(q)-I_1(q)$ is plotted; then, a peak in the usual q-range of the polyelectrolyte peak is observed and is fitted with $I_2(q)$. The fitting parameters which have been obtained are presented in Table SI-2.

Table SI-2. Fitting parameters for Fig. SI-3.

pH	A	α	B	β	C	q_0	ξ'	I_{bkg}
2.5	4.24×10^{-8}	4	8.86×10^{-3}	0.898				
3.5	4.50×10^{-8}	4	1.03×10^{-2}	0.793				
4.5	1.89×10^{-8}	4	3.41×10^{-3}	1	0.0312	0.0560	22.02	1.73×10^{-2}
6.0	1.95×10^{-8}	4	3.38×10^{-3}	1	0.0363	0.0598	20.12	1.74×10^{-2}
7.5	1.66×10^{-8}	4	2.65×10^{-3}	1	0.0343	0.0625	17.65	8.80×10^{-3}

Extrapolated from Lalevée et al.,[3] the positions found for q_0 would indicate that the residual concentrations of uncomplexed disaccharide units of HA are in the range 4×10^{-2} to 6×10^{-2} mol.L^{-1}.

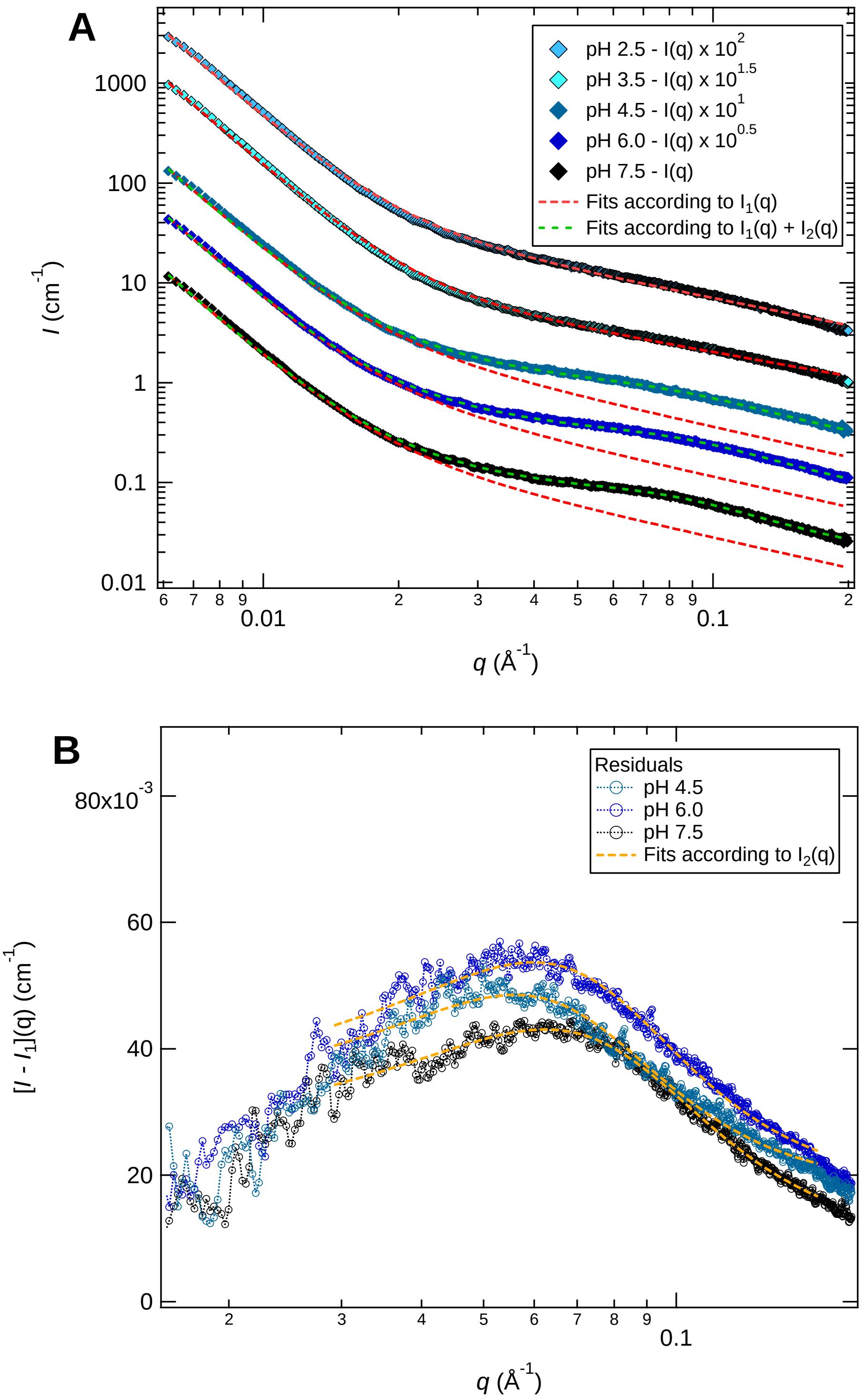

Fig. SI-3. [A] Absolute intensities from SAXS measurements of hydrogels obtained by dialysis (pH of the dialysis bath indicated on the graph) from a HYA/CS/NaCl mixture containing HA at 3 % (w/v), CS at 0.82 % (w/v) and NaCl at 0.65mol/L. The fits using $I_1(q)$ have been plotted for all pH, the fit using $I_1(q) + I_2(q)$ has been plotted for pH > 3.6. For clarity, the intensity at pH 7.5 is has not been modified, the other absolute intensities have been multiplied by successive powers of $\sqrt{10}$. [B] Residuals $[I - I_1](q)$ for the absolute intensity shown in [A] for systems at pH > 3.6; the residuals have been fitted with $I_2(q)$.

The same approach has been attempted on the SANS measurements, using a general form for I(q) as follows:

$$I_{SANS}(q) = I_1(q) + I_3(q)$$

with

$$I_1(q) = \frac{A}{q^{\alpha}} + \frac{B}{q^{\beta}}$$

For the system at pH = 2, the fit according to $I_1(q)$ is sufficient to describe the measured scattered intensity (see Fig. SI-4[A]);

For the system at higher pH, following the same procedure which has been done for the SAXS analysis, the exponents in $I_1(q)$ have been fixed ($\alpha = 4$ and $\beta = 1$). A Lorentzian contribution, to take into account the polyelectrolyte peak expected for HA in excess has been added. As mentioned in the main text, a shoulder is clearly visible in the intermediate q-range (roughly in the *q*-range between 7×10^{-3} and 5×10^{-2} Å^{-1}, see Fig. SI-2). This shoulder has been modeled using a Guinier term.

$$I_3(q) = \frac{C}{1 + ((q - q_0)\xi')^2} + D.\exp\left(-\frac{R_g^2 q^2}{3}\right)$$

The contributions of each term clearly appears on the residuals [$I(q) - I_1(q)$] plotted on Fig. SI-4[B]. The contributions of each fitting term of $I_3(q)$ have been added for clarity.

The fitting procedure has been performed by maintaining the value of q_0 equal to that obtained in the SAXS fitting ($q_0 = 5.98 \times 10^{-2}$ Å^{-1}). The fitting parameters are in Table SI-3. For comparison, the curves obtained in SAXS and SANS for a solution of HA at 3% are given in Fig. SI-5; one can notice that the diffusion at low *q* is approximately 2 orders of magnitude weaker than that of the complexed systems.

Table SI-3. Fitting parameters for Fig. SI-4.

pH	A	α	B	β	C	q_0	ξ'	D	R_g
2.5	3.05×10^{-7}	3.53	3.88×10^{-3}	0.7388					
6.0	6.84×10^{-9}	4	1.04×10^{-3}	1	5.05×10^{-3}	0.0598	7.98	1.32	95.7

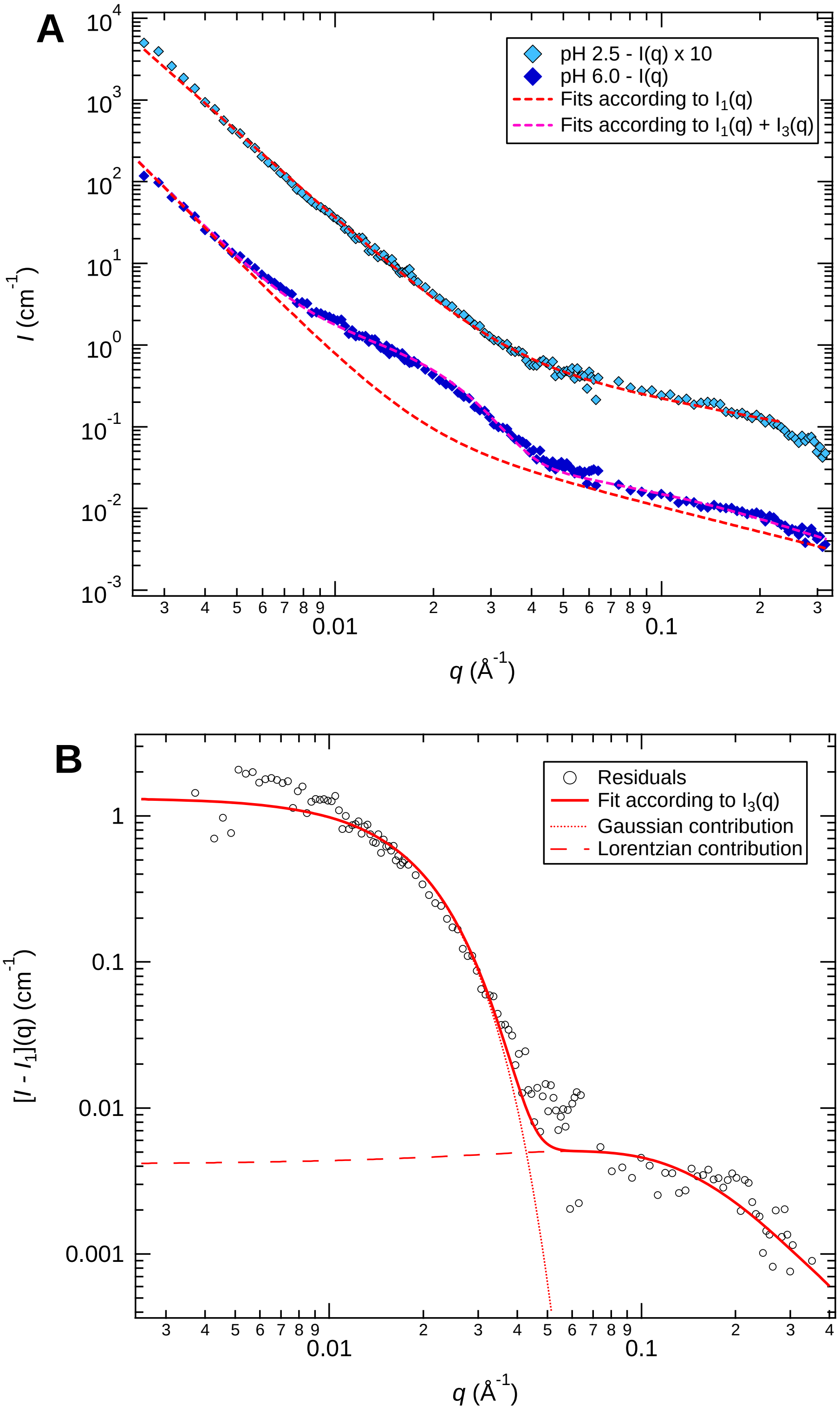

Fig SI-4. [A] Absolute intensities from SANS measurements of hydrogels obtained by dialysis (pH of the dialysis bath indicated on the graph) from a HYA/CS/NaCl mixture containing HA at 3% (w/v), CS at 0.82% (w/v) and NaCl at 0.65 mol L^{-1}. The fits using $I_1(q)$ have been plotted for both pH, the fit using $I_1(q) + I_3(q)$ has been plotted for pH = 6.5. For clarity, the intensity at pH = 6.5 is has not been modified, and the intensity at pH = 6.0 has been multiplied by 10. [B] Residuals $[I - I_1](q)$ for the absolute intensity shown in [A], pH = 6.0; the residuals have been fitted with $I_3(q)$.

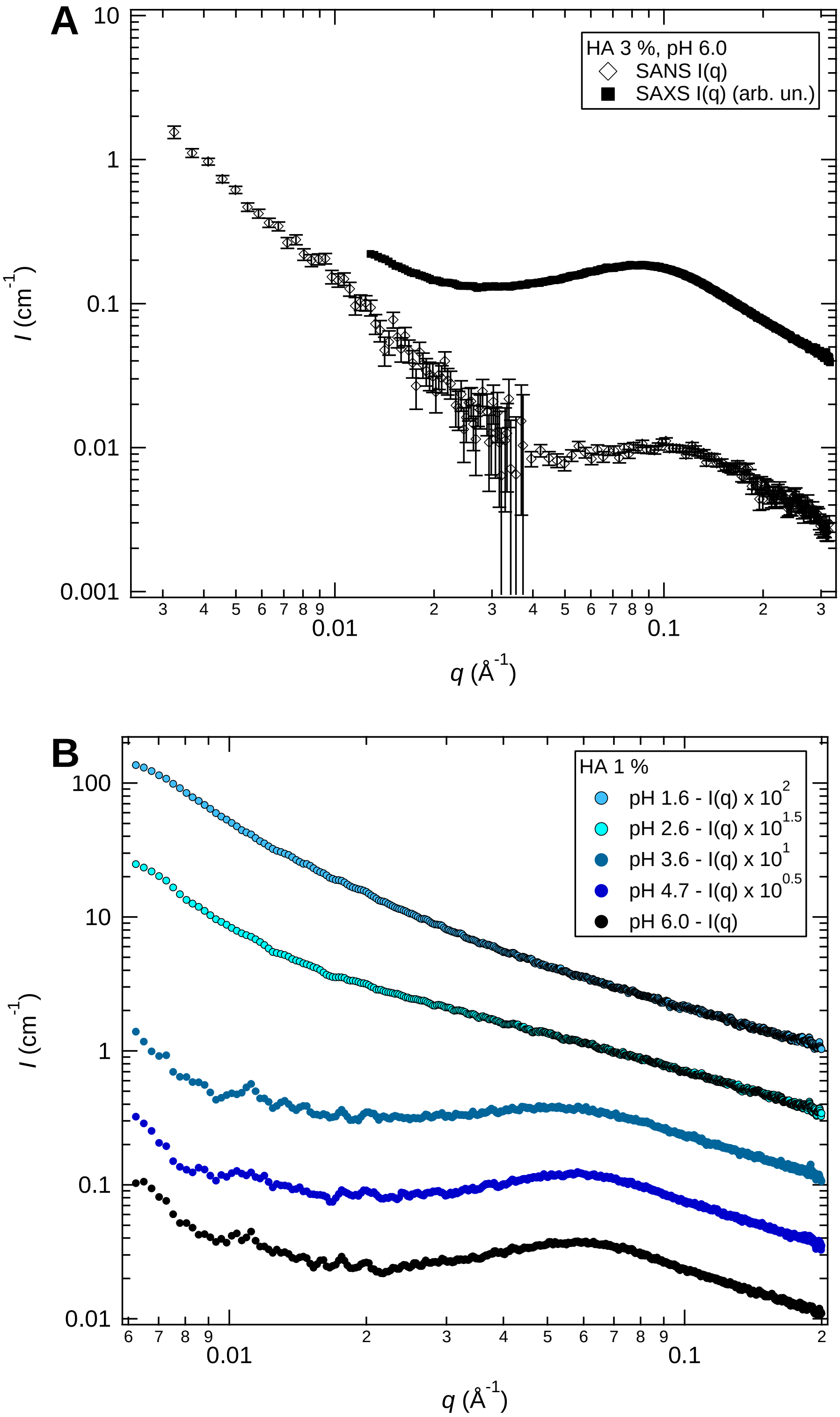

Fig SI-5. [A] Neutron scattering intensity of HA solution at 3% in deuterium oxide and X-ray scattering intensity of HA solution at 3% in water. [B] X-ray scattering absolute intensities for aqueous solutions of HA at 1% for various pH. For clarity, the intensity at pH = 6.0 is has not been modified, the other absolute intensities have been multiplied by successive powers of $\sqrt{10}$.

References

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