Tunning the solution organization of cationic polymers through interaction with bovine serum albumin

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Supplementary information

Comparison with Hayter-Penfold structure factor

We have compared our results (model of equations 5-7) with the one of the analytical solution from Hayter and Penfold. We used the excel spreadsheet calculation [1] which uses the approximations of Hayter, Penfold, Hansen and Ginoza to obtain the rescaled mean squared approximation (RMSA) structure factor of charged colloids in dilute solutions.



Figure S1: Structure factors from equations 5 and RMSA for QIm-PCMS1.

The structure factor $S_F(q)$ of equation 5 is extracted using the fitted parameters from the SANS profiles (figure S1). In figure S1 the Hayter-Penfold (RMSA) structure factor that best fits our extracted structure factor is also shown.

Table S1: Extracted parameters from structure factor of interacting charged hard spheres.

NaCl	0	М	0.	01M
Parameter	eq. 5	Hayter- Penfold	eq. 5	Hayter- Penfold
η	0.031	0.0025	0.028	0.0032
σ (nm)	5.4	2.8	6.1	3.1
$\langle R \rangle$ (nm)	13.9	16.6	16.2	16.9
$r_{D}(nm)$	4.1	6.1	2.4	2.7

Z 8.0 13.0 9.4 14.0

In table S1 the extracted parameters from the $S_F(q)$ of equation 5 are compared to the RMSA calculation. Equation 5 underestimated the electrostatic effects i.e. Debye length and particle charge are found higher in the RMSA calculation. It has to be noted though that equation 5 correctly follows the trend of the RMSA calculations upon addition of salt. The hard-sphere diameter σ is found lower in RMSA approximation. Similarly to the approximation of equation 5, σ remains fairly unchanged upon addition of salt. Remarkably the hard-sphere volume fraction η in the RMSA approximation obtains values so that the mean distance $\langle R \rangle = [6\eta/(\pi\sigma^3)]^{-1/3}$ between interacting particles is roughly the same between the two models (table S1). Since in this work we are interested in capturing the comparative effect of salt content and polymer conentration we present our results using the simple analytical form of equations 5-7. We conclude that the approximate equations where the electrostatic interactions are treated as perturbation provide overestimate the effect of the hard-sphere diameter and underestimate the electrostatic interaction.

Justification of using the model of equations 3-7

In figure S2 the data from QIm-PCMS1 are shown as an example of the fits in the absence of measurable interactions (0.15 M NaCl). The red line is the fit with equation 4 without any

structure factor i.e. $I_F(q) = G_F \cdot \left(1 + \frac{2}{3D}q^2 R_{gF}^2\right)^{-D/2} \cdot e^{-\frac{1}{3}q^2 R_g^2}$ as in the main article discussion. The dotted blue line is fitting with the function $I_F(q) = G_0 \cdot e^{-\frac{1}{3}q^2 R_g^2}$ which shows that a model

with a single characteristic size cannot fit the data and an additional length scale R_{gF} is needed. The dotted black line is the fractal scattering without the cut-off $I_F(q) = G_F \cdot \left(1 + \frac{2}{3D}q^2 R_{gF}^2\right)^{-D/2}$ which proves that the scattering from the building blocks of

the fractal aggregate has to be taken into account.



Figure S2: Fitting the data from QIm-PCMS1 at 16 mg/ml at 0.15M NaCl. The continuous and dashed line are explained in the main text.



Figure S3: Fitting the data from QIm-PCMS1 at 16 mg/ml at 0M NaCl. The continuous and dashed line are explained in the main text.

In figure S3 the use of the structure factor of equations 5-7 is demonstrated (red line). Using the structure factor for hard-spheres (with no electrostatic interactions) is shown with the blue line. The structure factor of Percus-Yevick has been used [2]. This hard-sphere structure factor produces an acceptable fit although it cannot follow the scattering suppresion at low q. More importantly it produces a somehow large value for σ (~9 nm) instead of ~5 nm in the case of the finally used $S_F(q)$ where $\sigma^2 2R_{gF}$. Moreover the changes caused by the increase of salt are followed by a decrease in the hard-sphere volume fraction i.e. ϕ =0.14 (0 M) to ϕ =0.07 at (0.01M). Since the position of the maximum does not change notably (figure 2) while only the suppression at low q is compromised by the addition of salt and because it is more plausible to expect ionic strength to interfere with the range of electrostatic interactions than with the hard-sphere radius we believe that this decrease in ϕ for purely hard-sphere interaction is the effect of the decrease in Debye length which is explicitly captured by the S_F(q) of equations 5-7.

References:

- [1] Wu C, Chan D, Tabor RF, J. Colloid Interface Sci. 15, 80-82, 2014.
- [2] Pedersen JS, Adv. Colloid Interface Sci., 1997, 70, 171–210.