

## Supporting Information

### Unravelling Polyethylenimine Mediated Non-Monotonic Stability Behaviour of Silica

#### Colloids: Role of Competing Electrostatic and Entropic Interactions

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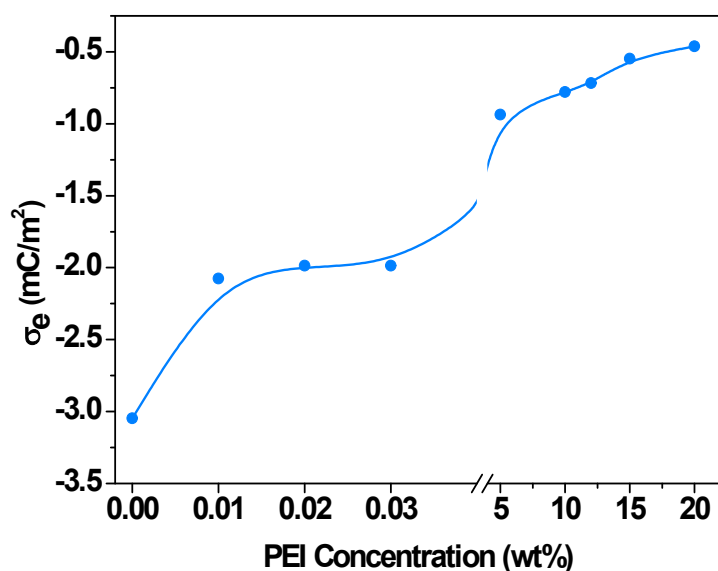
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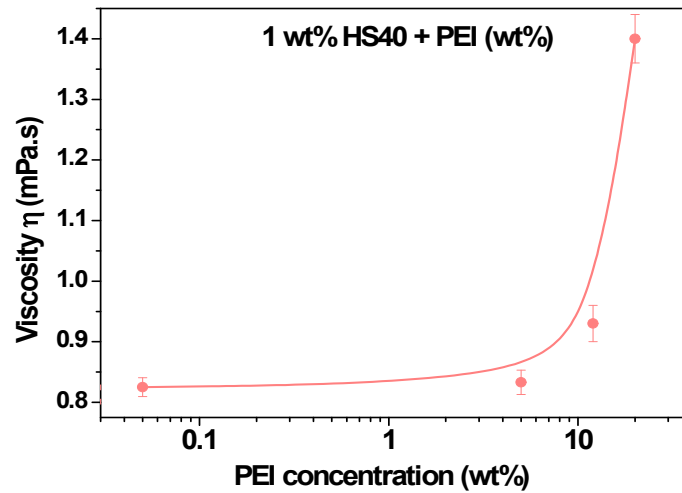


**Figure S1:** Estimated effective surface charge for silica-PEI dispersion as a function of PEI concentration.

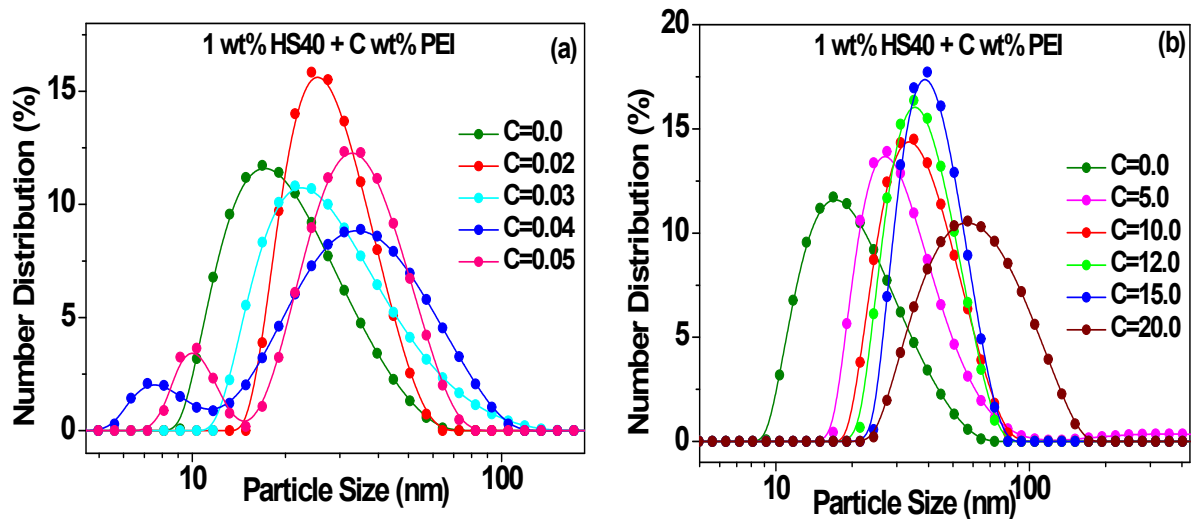
The effective surface charge can be written as:

$$\sigma_e = \sqrt{8N_A \epsilon_r \epsilon_0 k_B T} \sinh\left(\frac{e\zeta}{2k_B T}\right) \quad (1)$$

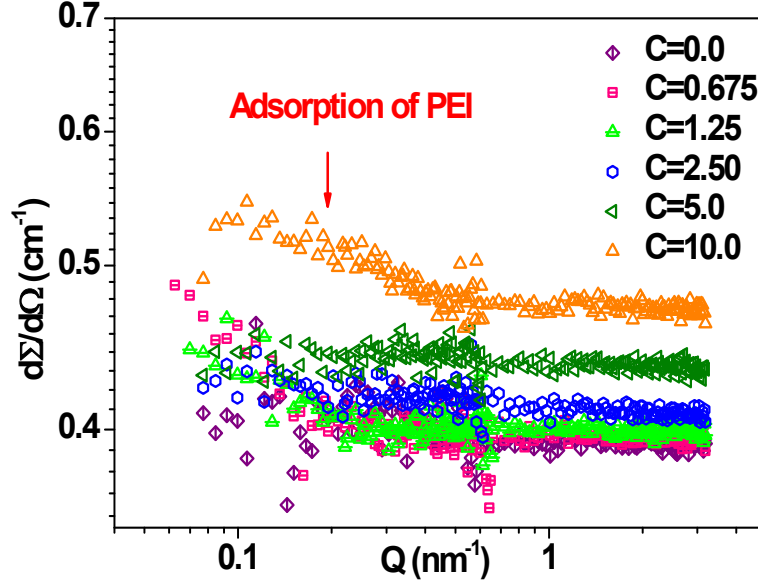
Here,  $N_A(6.022 \times 10^{23} \text{ mol}^{-1})$  is the Avogadro's constant,  $\epsilon_r(78.2)$  is the relative dielectric constant for water at 25 °C,  $\epsilon_0(8.85 \times 10^{-12} \text{ C/Nm}^2)$  is the permittivity of free space,  $k_B(1.38 \times 10^{-23} \text{ J/K})$  is the Boltzmann's constant and  $T$  (Kelvin) is the temperature.



**Figure S2:** Variation in the viscosity of silica-PEI dispersion as function of PEI concentration



**Figure S3:** Nanoparticle Size distribution using Dynamic Light Scattering for 1 wt% HS40 with varying concentration of PEI (a) low concentration regime, (b) high concentration regime.



**Figure S4:** Silica contrast matched SANS profile for 1 wt% HS40 with different concentrations of PEI.

### Dynamic Light Scattering and electrophoretic measurements

In Dynamic Light Scattering (DLS), the characteristic time fluctuations in intensity are measured using monochromatic radiation. The quantitative information for the time scales of the fluctuating intensity of diffusing particles is given by autocorrelation and the autocorrelation function can be defined as <sup>1</sup>:

$$g^2(\tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (2)$$

Here,  $I(t)$  is the scattered intensity at time  $t$ ,  $I(t+\tau)$  is the scattered intensity after the delay time  $\tau$  and  $g^2(\tau)$  is the normalized autocorrelation function.

The normalised intensity auto-correlation function,  $g^2(\tau)$  is related to the normalised field auto-correlation function  $g^1(\tau)$  as:

$$g^1(\tau) = [g^2(\tau) - 1]^{0.5} \quad (3)$$

For a polydisperse population of particles, the normalised field autocorrelation function is given as:

$$g^1(\tau) = \int_0^{\infty} G(\Gamma_d) \exp(-\Gamma_d \tau) d\Gamma_d \quad (4)$$

Here,  $\Gamma_d = DQ^2$ , is the decay constant depending upon the translational diffusion Coefficient,  $D$ .  $G(\Gamma_d)$  represents the weighted distribution of the relative intensity of the scattered intensity.

However, for the narrow distribution of size the mean value of the diffusion coefficient,  $D_c$  with the polydispersity index is yielded by the cumulant analysis, is given as<sup>2</sup>:

$$g^1(\tau) = \exp\left(-D_c Q^2 \tau + \frac{\mu_2 \tau^2}{2}\right) \quad (5)$$

Here  $\mu_2$  is the variance of the distribution  $G(\Gamma_d)$ . The ratio of variance ( $\mu_2$ ) to the square of the mean decay constant ( $\Gamma_m = D_c Q^2$ ) is the polydispersity index. Thus, the hydrodynamic radius ( $R_h$ ) is correlated with the mean diffusion coefficient ( $D_c$ ) by the Stokes-Einstein relation, given as:

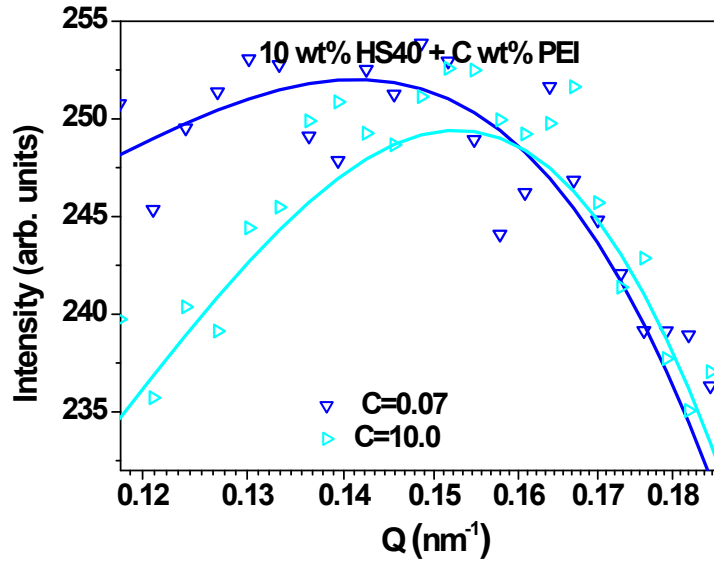
$$R_h = \frac{k_B T}{6\pi\eta D_c} \quad (6)$$

Here,  $k_B$  is the Boltzmann's constant,  $\eta$  is the viscosity, and  $T$  is the absolute temperature of the solvent. Depending upon the hydration and interaction between the particles hydrodynamic radius can be different from the actual size.

However, the electrophoretic mobilities obtained were used to calculate the zeta potential using Henry's equation<sup>3</sup>,

$$\mu = \frac{2\epsilon_r \zeta F(\kappa a)}{3\eta} \quad (7)$$

Here,  $\mu$  is electrophoretic mobility,  $\zeta$  is zeta potential,  $\epsilon_r$  (78.2) is the dielectric constant of water at 25 °C,  $\eta$  is the viscosity and  $F(\kappa a)$  is Henry's function. The value of Henry's constant varies from 1 (Hückel Approximation<sup>4</sup>) for non-polar solvents to 3/2 (Smoluchowski approximation<sup>4</sup>) for polar solvents.



**Figure. S5:** SAXS profile for 10 wt% HS40 with at different PEI concentrations (zoomed view).

**Table S1:** Fitting parameters of SAXS profiles using two-Yukawa model along with the spherical form factor.

Sample	$K_1$ ( $k_B T$ )	$\alpha_1$	$K_2$ ( $k_B T$ )	$\alpha_2$
HS40	102	5	0.01	30
HS40-PEI(0.05)	0.003	50	1	2
HS40-PEI(0.07)	0.002	50	1.5	3
HS40-PEI(3)	0.01	40	1.8	4

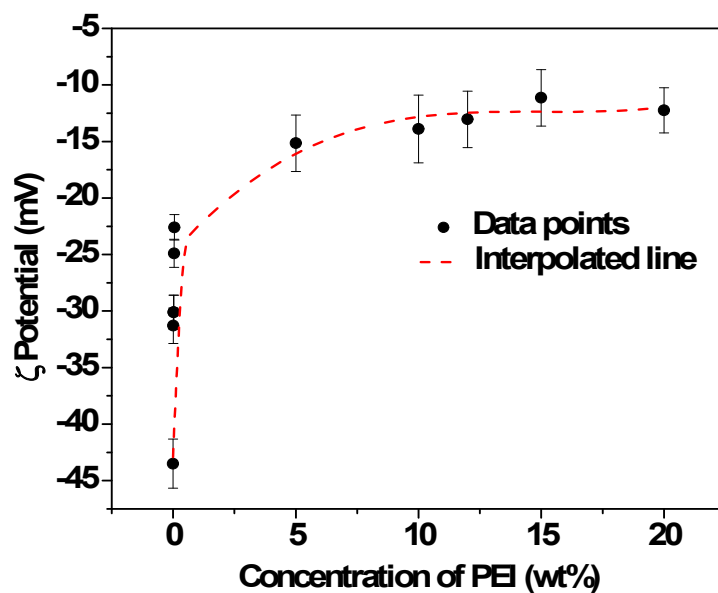
HS40-PEI(5)	0.01	46	0.4	2
HS40-PEI(10)	1.83	1.4	0.01	20

Debye length is given as:

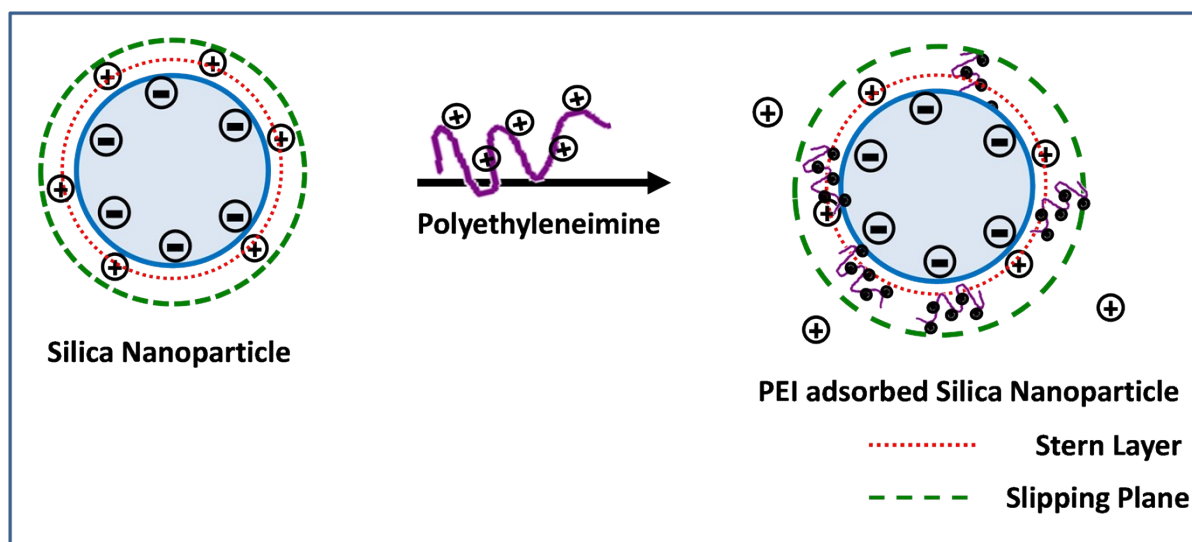
$$\kappa^{-1} = \left( \frac{e^2}{\epsilon_0 \epsilon_r k_B T} \right)^{\frac{1}{2}} \sqrt{Z\rho + 2I_s N_A} \quad (8)$$

Here,  $e$  is the elementary charge,  $\rho$  is the particle number density,  $I_s$  is the ionic strength of the solution,  $N_A$  is the Avogadro's constant.  $\left[ Z = 4\pi \left( \frac{d}{2} \right)^2 \sigma_e \right]$  is the total charge of a particle with surface charge density  $\sigma_e$ .

As the Millipore water is used for the preparation of silica-PEI dispersions, the ionic strength of the Millipore water is very small ( $10^{-4}$ - $10^{-5}$  mol/L), therefore Debye length is estimated to be  $\sim 50$  nm<sup>5</sup>. Also, the addition of a weak cationic polymer will not affect the Debye length significantly (eq. 8), therefore Debye length is kept constant for the silica-PEI dispersion during the modelling of the effective potential.



*Figure S6: Zeta potential for 1 wt% HS40 with the varying concentration of PEI. Dotted lines represent the interpolation of the data set.*



*Schematic S1: Schematic indicating position of slipping plane for the silica nanoparticle and PEI adsorbed silica nanoparticle.*

**References:**

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