Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Diffusion of Nanoparticles within a Semidilute Polyelectrolyte Solution

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SI1: Concentration calculations for PAA samples

Density of PAA =1.150 g/ml at 25^0C[1]

Calculated concentrations

Weight fraction (w/w)	C (kg/m³)	Volume fraction (v/v)
0.00042	0.42	0.00037
0.00083	0.83	0.00072
0.00125	1.25	0.00109
0.0017	1.72	0.00148

SI2: Fitting of autocorrelation function in Fig. 1

$$G(\tau) = \frac{G(0)}{1+(\frac{8D\tau}{\omega_0^2})\sqrt{1+(\frac{8D\tau}{z_0^2})}}$$

D: Diffusion coefficient

ω_o: Half-width of laser focus

z_o: Half-height of laser focus

SI3: Experimental Diffusion coefficient

Experimental diffusion coefficients D of AuNPs (in μm²/s) as measured by fluorescence correlation spectroscopy

	d=5 nm		d=20 nm		d=40 nm	
Φ (x10⁻³)	D	δD	D	δD	D	δD
0	102	5	23	1	11	1
0.37	51	1	14	1	7	1
0.72	40	3	11	1	4	1
1.09	30	2	9	0.4	5	0.3
1.48	23	1	7	1	3	0.2

SI4: Fitting parameters β and υ using Phillies equation: D=Do exp(-βϕ^{v})

d (nm)	υ	β
5	0.53	4.00
20	0.64	4.10
40	0.68	4.41

SI5: Debye screening length (*l*) Calculations

$$\frac{1}{l} = \sqrt{\frac{\sum Z_i^{\,2} e^2 \alpha n_i(0)}{\varepsilon_r \varepsilon_0 k_B T}}$$

$$\frac{1}{l} = \sqrt{\frac{\sum Z_i^{\,2} e^2 \alpha C_i N}{\varepsilon_r \varepsilon_0 k_B T}}$$

where,

i= species of ions

$n_i(0)$= density of ions at $\vec{r} = 0$

z_i= valance of charge (=1)

C_i=H^+ concentration

ε_r= relative permittivity (=80)

ε_0= permittivity in vacuum ($8.85*10^{-12}$ F/m)

N= Avogadro's number (=$6.022*10^{23}$ mol^{-1})

e= charge of the electron (=$1.609 *10^{-19}$ C)

k_B= Boltzmann constant (=$1.38 * 10^{-23}$ J/K)

T= absolute temperature (=295 K)

α = Ionization factor[2]

Assumptions:

one monomer emits one H^+ ion

$pH =- log[H^+]$

$[H^+] =- antilog(pH)$

$$l = \frac{1.36 * 10^{-8}}{\sqrt{\alpha[H^+]}}$$

Calculated Debye screening length

Volume fraction Φ (x10^{-3})	pH	Ionization factor (α){Choi, 2005 #19}	$[H^+]$ (mol/m^3)	Debye screening length (l) (nm)
0.37	4.20	0.073	0.063	55
0.72	4.10	0.067	0.080	49
1.09	3.61	0.060	0.25	28
1.48	3.43	0.051	0.37	23

SI6: Dynamic light Scattering Results

Average hydrodynamic radius of PAA : R_h=137 nm

For PAA [3],

$$\frac{R_g}{R_h} = 1.45$$

Radius of Gyration of PAA (R_g)

$$R_g = 1.45 * 137\ nm$$

$$R_g = 198\ nm$$

Overlap Concentration (c^*)

$$c^* = \frac{M_w}{\frac{4}{3}\pi N_{av} {R_g}^3}$$

$$c^* = \frac{1000000 * 10^{-3}\ kgmol^{-1}}{\frac{4}{3} * \pi * 6.02 * 10^{23}\ mol^{-1} * (198.10^{-9})^3\ m^3}$$

$$c^* = 0.05\ \frac{kg}{m^3}$$

Overlap volume fraction, **ϕ*=4.4x10^{-5}**

SI7: Correlation length (ξ) calculation

Correlation length (ξ) [4]

$$\frac{\xi}{R_g} = \left(\frac{c}{c^*}\right)^{-\frac{1}{2}}$$

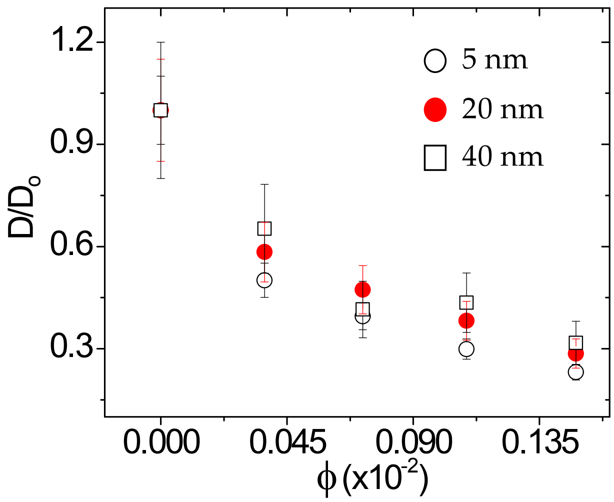
$$\xi = \frac{R_g * \sqrt{4.4 \times 10^{-5}}}{\sqrt{c}}$$

Calculated correlation length for each concentration

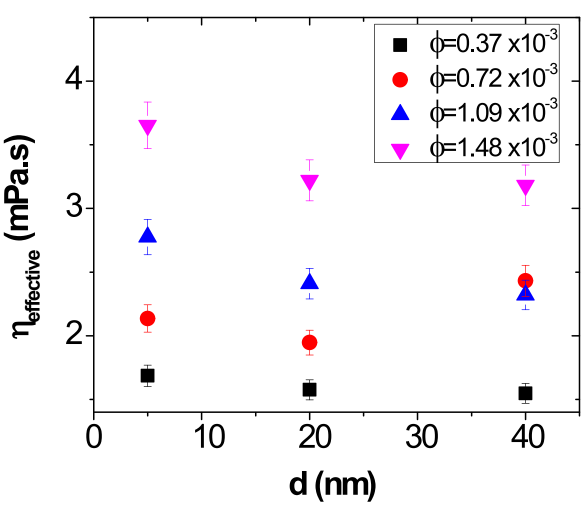
Volume fraction (v/v)	ξ (nm)
0.00037	69
0.00072	49
0.00109	40
0.00148	34

The size-ratio d/ ξ for each particle size in different concentration

Volume fraction (v/v)	ξ (nm)	d/ ξ		
		d=5 nm	d=20 nm	d=40 nm
0.00037	69	0.07	0.29	0.58
0.00072	49	0.10	0.41	0.81
0.00109	40	0.13	0.50	1.00
0.00148	34	0.15	0.59	1.17



SI8: Normalized diffusion coefficient vs. PAA volume fraction



SI9: The effective viscosity as a function of NP size at a constant volume fraction of PAA

Reference

1. Lin, T. H.; Phillies, G. D. *J. Phys. Chem.* **1982,** 86, (20), 4073-4077.

2. Choi, J.; Rubner, M. F. *Macromolecules* **2005,** 38, (1), 116-124.

3. Reith, D.; Müller, B.; Müller-Plathe, F.; Wiegand, S. *J. Chem. Phys.* **2002,** 116, (20), 9100-9106.

4. Dobrynin, A.; Rubinstein, M., *Theory of polyelectrolytes in solutions and at surfaces*. 2005; Vol. 30, p 1049-1118.