Electronic Supplementary Material

Molecular diffusion in ternary poly(vinyl alcohol) solutions

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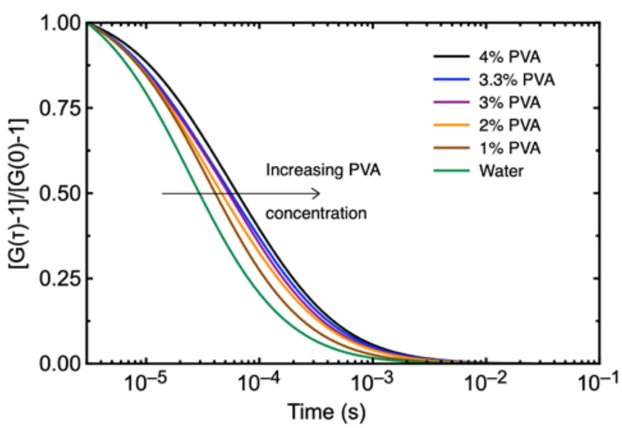

Figure S1. FCS autocorrelation functions of PVA solutions of various concentrations (samples 2-6). The percentage of polymer in the graph is given in (w/v)%.

Table S1. Average diffusion coefficient of Rhodamine B in samples of various compositions (T≈28°C).

Sample		PVA concentration (wt%)	Glycerol concentration (wt%	Average D ($\mu m^2/s$)
Addition of water	2	1.0	0.0	359.8 ± 13.7
	3	2.0	0.0	274.9 ± 9.3
	4	3.0	0.0	247.9 ± 6.5
	5	3.3	0.0	220.5 ± 5.1
	6	4.0	0.0	188.4 ± 3.8
Addition of glycerol solution	1a	0.0	4.0	416.6 ± 19.4
	2a	1.0	3.0	295.0 ± 13.1
	3a	2.0	2.0	259.5 ± 6.5
	4a	3.0	1.0	218.7 ± 7.0
	5a	3.3	0.7	208.5 ± 6.0

The DLS autocorrelation function can be described using Equation S1:[1]

$$g(\tau) = A \cdot e^{-Dq^2\tau} + B \tag{S1}$$

where A is the amplitude of the correlation function, B is the baseline, D is the translational diffusion coefficient of the particles, and q is the magnitude of the scattering vector described by Equation S2:

$$q = \frac{4\pi n \cdot sin(\frac{\theta}{2})}{\lambda} \tag{S2}$$

where λ is the laser wavelength and n is the refractive index of the medium. Radius of the particle can be obtained from Stokes-Einstein Equation S3:

$$D = \frac{kT}{6\pi\eta r_h} \tag{S3}$$

where r_h is the hydrodynamic radius, η is the solvent viscosity, and T is the absolute temperature. In case of polymers, the particle is not expected to be spherical, therefore r_h is the apparent hydrodynamic radius or equivalent sphere radius in this case.

Denoted equations were used to make a conclusion about the changes in diffusion coefficient of the analysed species and, accordingly, changes in their size with composition variations. For normalised autocorrelation functions, the diffusion coefficient can be obtained from fitting the curve to a single exponential decay (Equation S1). Presented autocorrelation functions are very similar in the first part of the curve – this region can be connected with the exponential decay of diffusion coefficient for particles of the highest intensities (diameter 1 nm-15 nm). The value of this diffusion coefficient is approximately constant for all investigated PVA/glycerol compositions (Figure S2), therefore, the weighted average radius of the particles shows a nearly linear dependence on the viscosity of the solution, increasing with decreasing viscosity. Autocorrelation functions together with decreasing viscosity of the solution with increasing glycerol concentration result in larger particle size for solutions with higher glycerol content.

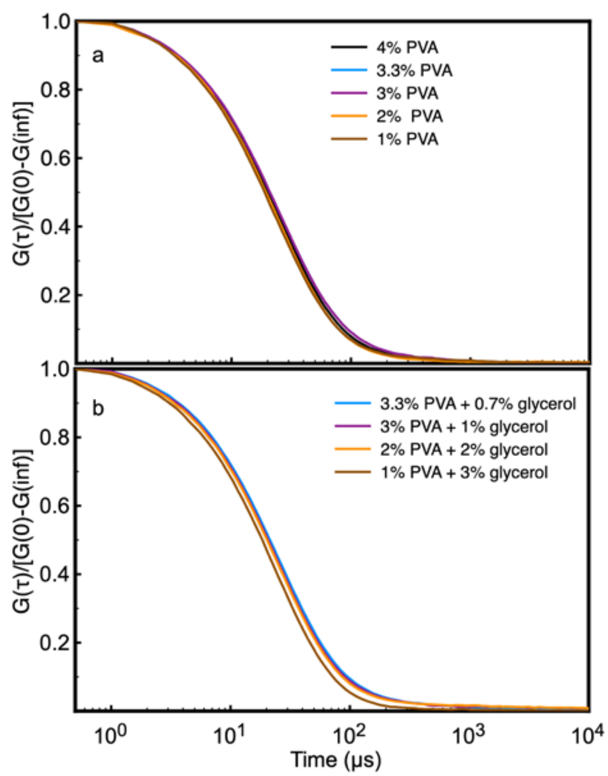

Figure S2. DLS autocorrelation functions of **a)** PVA solutions of various concentrations (samples 2-6) and **b)** PVA/glycerol solutions (samples 2a-5a) of various ratio of components. The percentage of polymer in the graph is given in (w/v)%.

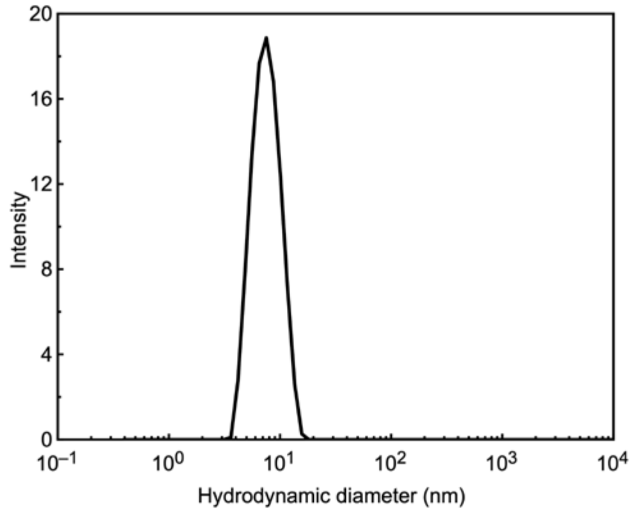

Figure S3. Average size distribution for $C_{12}E_{10}$ stock solution investigated by DLS.

REFERENCES

1. Hassan, P. A.; Rana, S.; Verma, G. Making Sense of Brownian Motion: Colloid Characterization by Dynamic Light Scattering. *Langmuir* **2015**, *31* (1), 3–12.