Supporting Information for: On the Mechanism of Shear Thinning in Viscous Oppositely Charged Polyelectrolyte Surfactant Complexes (PESCs)

Giuseppe Rosario Del Sorbo,[†,‡] Sylvain Prévost,[‡] Emanuel Schneck,[†,¶] Michael Gradzielski,[*,§] and Ingo Hoffmann[*,‡]

†*Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany*

‡*Institut Max von Laue-Paul Langevin (ILL), 71 avenue des Martyrs, CS 20156, F-38042 Grenoble Cedex 9, France*

¶*Soft Matter Biophysics, Department of Physics, TU Darmstadt, Hochschulstraße 8, D-64289 Darmstadt, Germany*

§*Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, Sekr. TC 7, D-10623 Berlin, Germany*

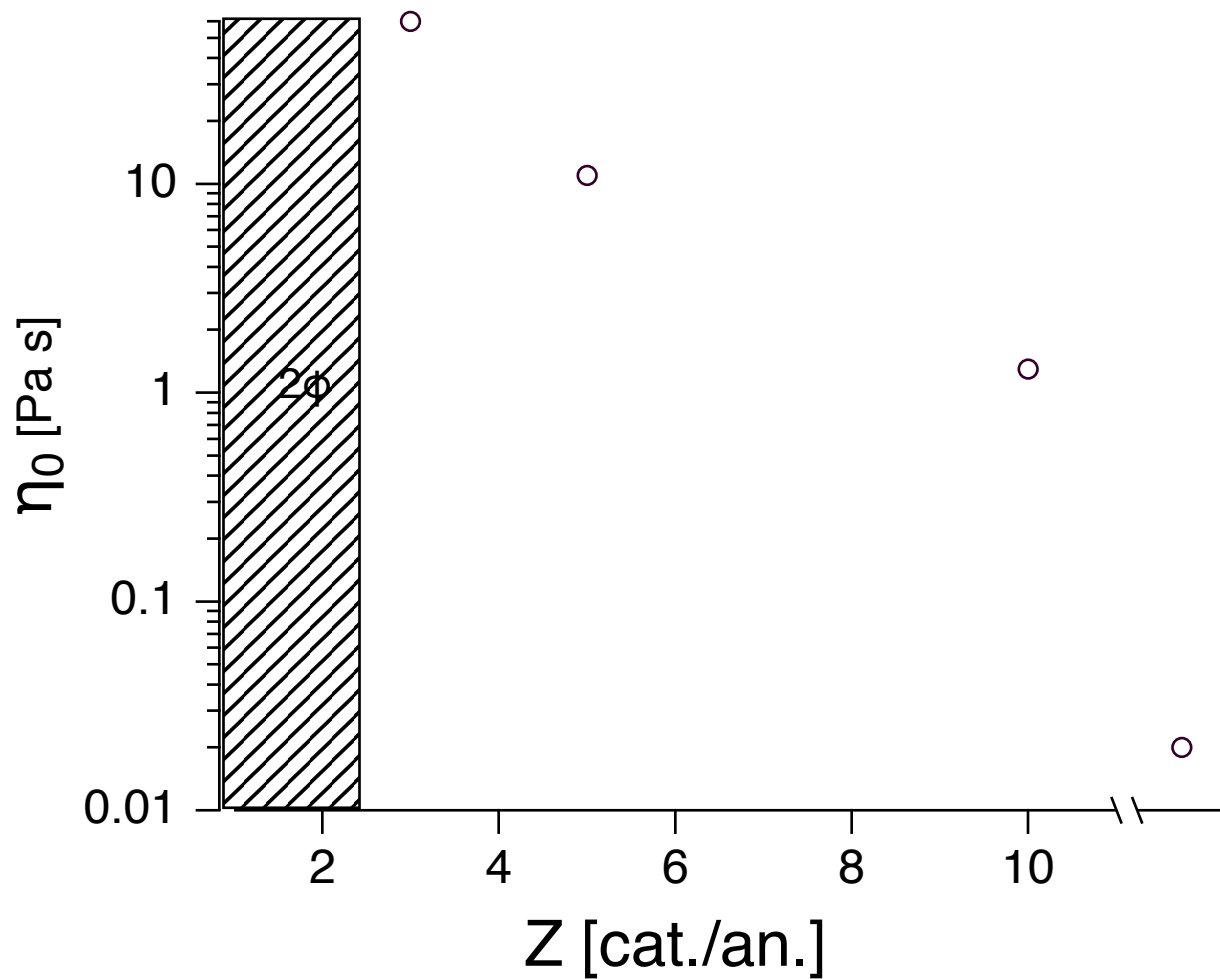E-mail: michael.gradzielski@tu-berlin.de; hoffmann@ill.fr

Figure S1: Zero shear viscosity η_0 as a function of charge ratio Z for samples with 1 wt% JR 400 (10 mM of charges), the value after the axis split is the value for a pure JR 400 solution, the shaded area at low values of Z indicates the onset of the 2-phase region.
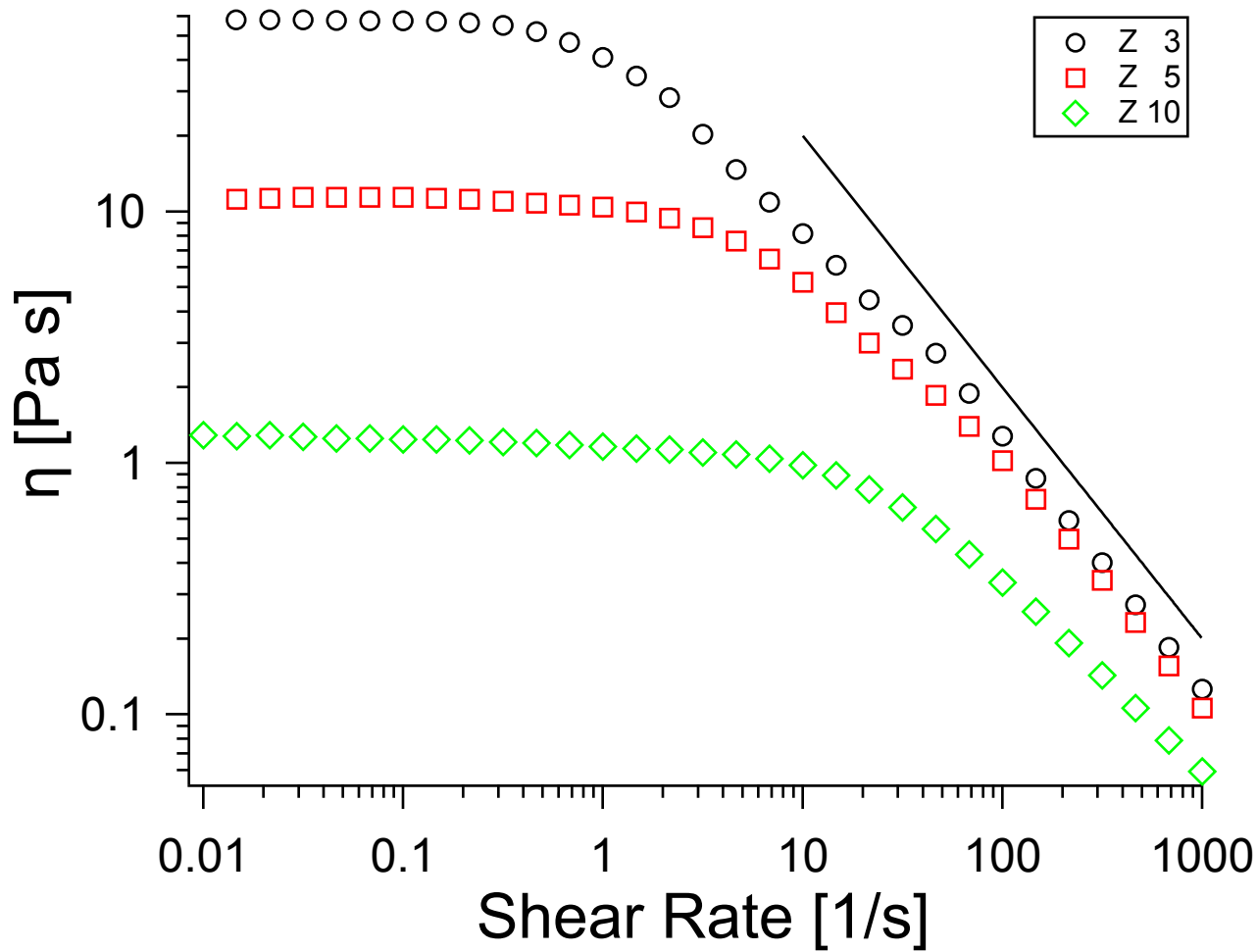
Figure S2: Viscosity as a function of shear rate for samples with 1 wt% JR 400 and charge ratio Z indicated in the graph. The samples are shear thinning with a critical shear rate $\dot{\gamma}$ which decreases with increasing surfactant concentration. Black line is $\eta \sim \dot{\gamma}^{-1}$, fitting the high shear rate part with a power law yields exponents of -1.01 ($Z = 3$),-0.96 ($Z = 5$) and -0.75 ($Z = 10$).
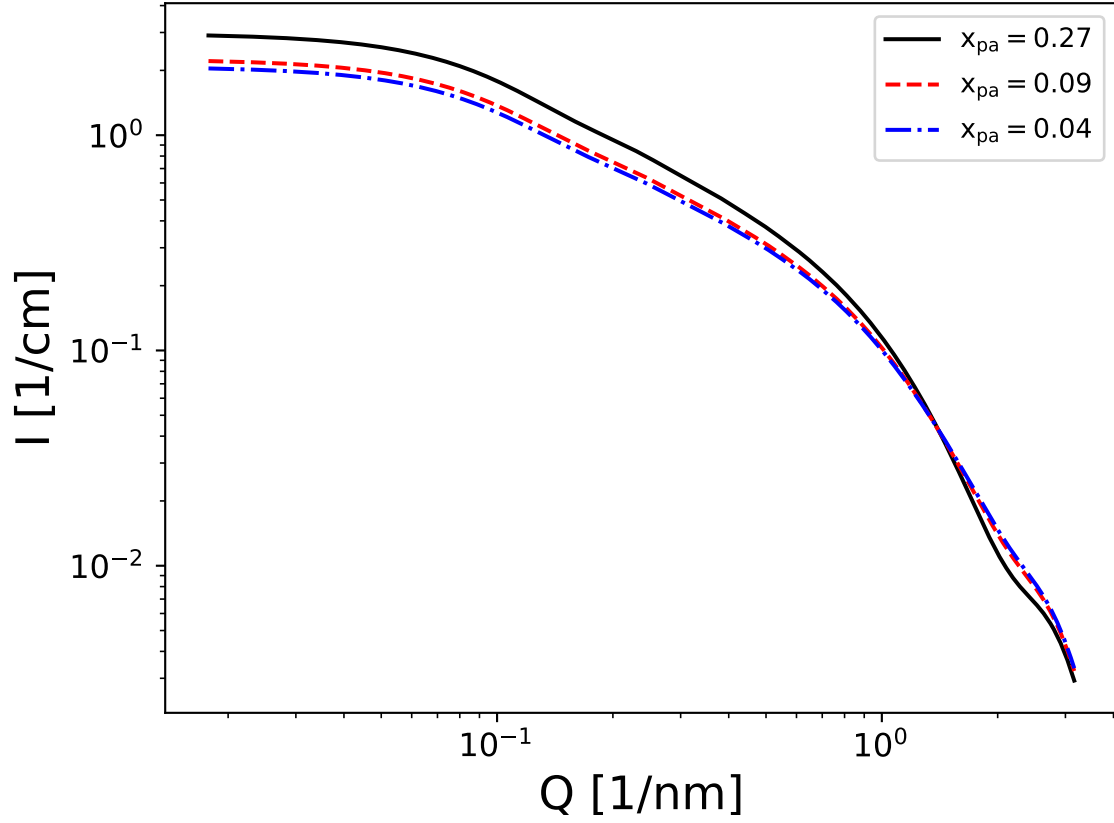
Figure S3: Theoretical curves calculated from eq. (S1) using parameters obtained for SDS/JR 400 $Z = 3$ from Hoffmann et al.[1] and macroscopic volume fractions ($R_{agg} = 1.8$ nm, $R_{PE} = 0.8$ 1/nm, $\phi_{surf} = 0.001$, $\phi_{PE} = 0.007$ and $x_{pa} = 0.27$) together with two lower values of x_{pa} corresponding to roughly 3, 2 and 1 PE chains per aggregate. A reduction of x_{pa} would result in a noticeable change in intensity
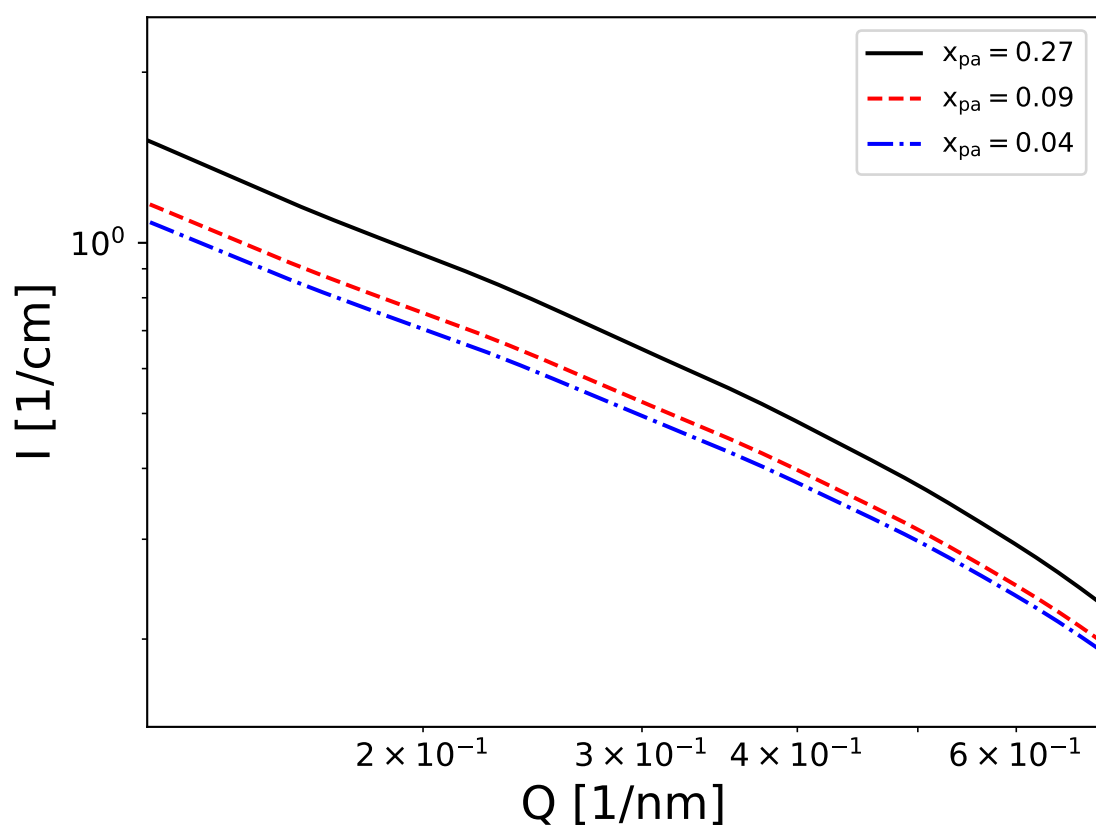
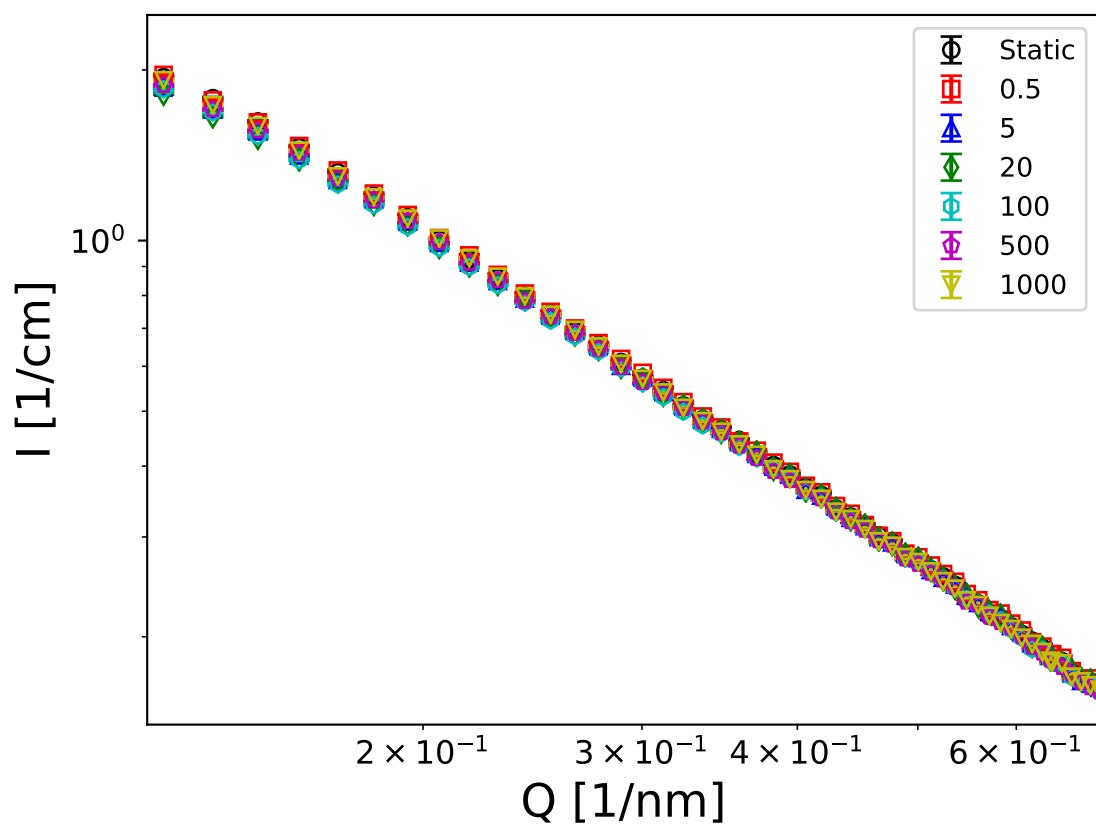Figure S4: Same data as fig. S3 but in the mid Q range from 0.12 to 0.7 1/nm.

Figure S5: Magnification of the data in fig. 1 in the Q range from 0.12 to 0.7 1/nm. No change in intensity with shear rate is observed.

Figure S6: 45° sector averages parallel (0°) and perpendicular (90°) to the direction of shear in the Q range from 0.12 to 0.7 1/nm of the sample with 1 wt% JR 400 and $Z = 3$ at rest. No difference can be seen and the scattering is isotropic.
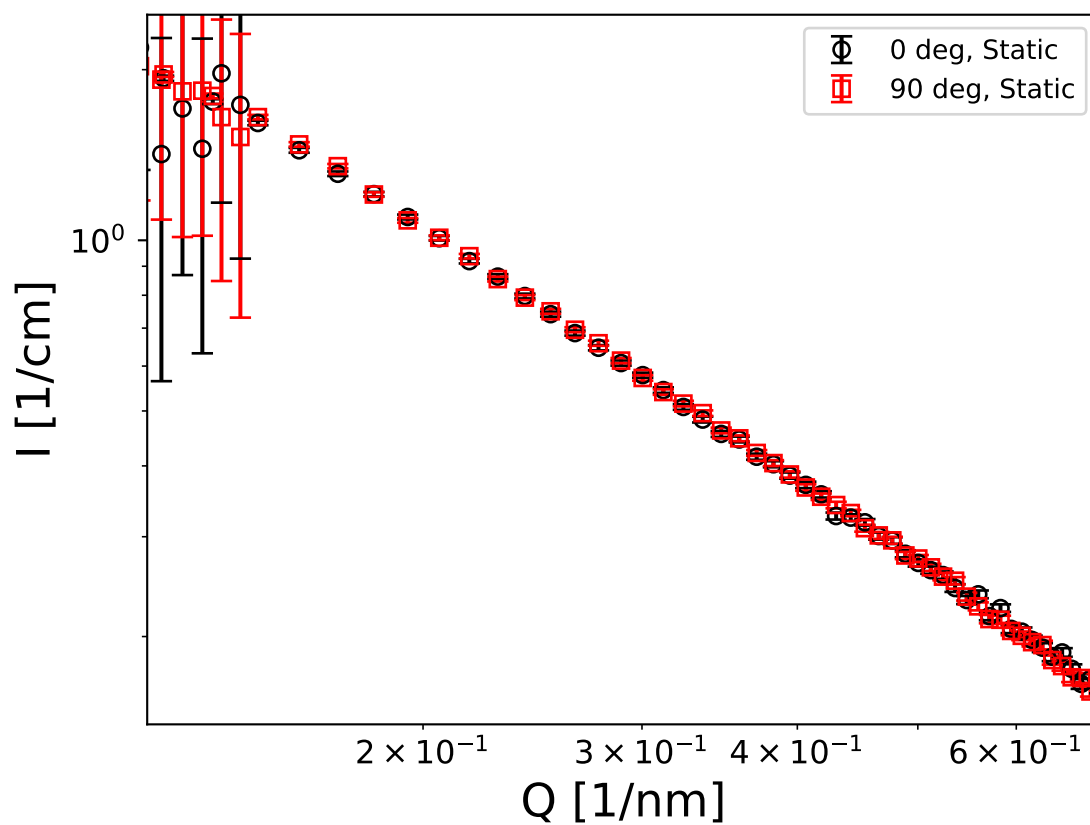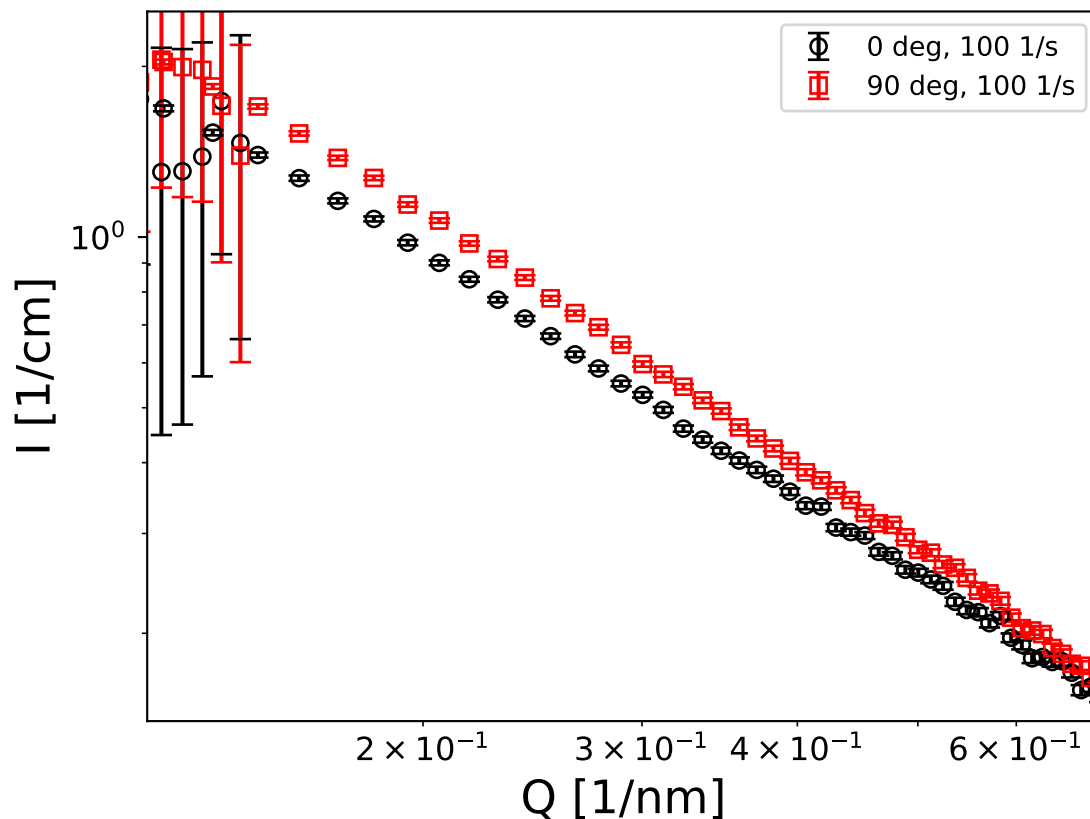
Figure S7: 45° sector averages parallel (0°) and perpendicular (90°) to the direction of shear in the Q range from 0.12 to 0.7 1/nm of the sample with 1 wt% JR 400 and $Z = 3$ at $\dot{\gamma} = 100$ 1/s. The sector perpendicular to the direction of shear shows a somewhat higher intensity, meaning that the rodlike aggregates are aligned in the direction of shear.
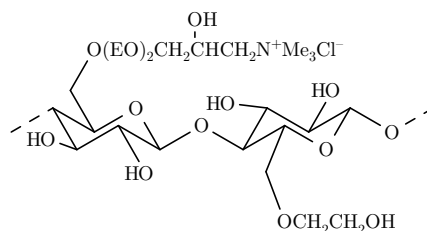

Figure S8: Chemical structure of JR 400, about 27% of the monomeric units are cationically modified

Modelling the SANS Data

The radially averaged intensity of rodlike particles can be modelled as a linear combination of the intensity from the aggregates and the intensity from free PE chains. The aggregates consist of all of the surfactant in the sample and a fraction of the PE x_{pa}, so that their volume fraction $\phi_{agg} = \phi_{surf} + \phi_{PE} x_{pa}$ and the intensity reads

$$I(Q) = \frac{\phi_{agg}}{V_{agg}} P_{agg}(Q) + \frac{\phi_{PE}(1 - x_{pa})}{V_{PE}} P_{PE}(Q), \tag{S1}$$

where ϕ_{surf} and ϕ_{PE} are the volume fraction of surfactant and PE, respectively, V_{agg} and V_{PE} are the volume of an aggregate and a PE segment and P_{agg} and P_{PE} are the form factors of aggregate and PE. In our previous publications, we have modelled both the PE and the aggregates as cylinders, the form factor of which is given by

$$P(Q) = \int_0^1 |F(Q, x)|^2 \, dx, \tag{S2}$$

with

$$F(Q, x) = \pi R^2 L \, \Delta SLD \frac{4 J_1(Q, R\sqrt{1 - x^2}) \sin(QLx/2)}{Q^2 R\sqrt{1 - x^2} Lx}, \tag{S3}$$

where R and L are radius and length of the cylinder and ΔSLD is the difference in scattering length density between the cylinder and the solvent. For the aggregates, ΔSLD_{agg} depends on the amount of PE which they contain:

$$\Delta SLD_{agg} = \frac{\phi_{surf}}{\phi_{agg}} SLD_{surf} + \frac{\phi_{PE} x_{pa}}{\phi_{agg}} SLD_{PE} - SLD_{solv}, \tag{S4}$$

where SLD denotes the scattering length density of a component and the subscripts $surf$, PE and $solv$ represent surfactant, PE and solvent. As we are using all hydrogenated components in a deuterated solvent, resulting in a high contrast between aggregates and solvent and a low internal contrast it is sufficient to model the aggregates as homogeneous cylinders.

Assuming a homogeneous structure of the aggregates along their long axis, we can calculate the average number of PE chains per aggregate N_c by relating the volume fractions of surfactant and PE in the aggregates to the radii of the whole aggregate and individual PE chains:

$$N_c = \frac{x_{pa}\phi_{PE}}{x_{pa}\phi_{PE} + \phi_{surf}}\frac{R_{agg}^2}{R_{PE}^2},\tag{S5}$$

where R_{agg} is the radius of the mixed aggregates and R_{PE} is the radius of an individual PE chain. Previously, we had seen that at values of $N_c < 2$ no pronounced increase in viscosity can be observed as the aggregates do not act as efficient cross links anymore.

References

(1) Hoffmann, I.; Farago, B.; Schweins, R.; Falus, P.; Sharp, M.; Prévost, S.; Gradzielski, M. On the mesoscopic origins of high viscosities in some polyelectrolyte-surfactant mixtures. *J. Chem. Phys.* **2015**, *143*, 074902.