Structural control of polyelectrolyte/microemulsion droplet complexes (PEMECs) with different polyacrylates

Miriam Simon^a, Patrick Krause^a, Leonardo Chiappisi^{ab}, Laurence Noirez^c and Michael Gradzielski^a

Supporting Information

Analysis of SANS Data:

The smearing of the SANS Data due to resolution effects was taken into account during data analysis by integrating with a resolution function according to.⁴¹ The wavelength spread, finite collimation and detector resolution are all approximated by Gaussian functions which are then convoluted into a total resolution function. The resulting total resolution function is also a Gaussian function with the width squared given by the sum of the widths squared of all three contributions. The wavelength spread (FWHM) was 10% and the detector pixels 5x5 mm.

Fits were performed in absolute units using eqn S1:

$$I(q) = {}^{1}N \cdot V^{2} \cdot \Delta SLD^{2} \cdot P(q) \cdot S(q)$$
(S1)

where ¹N is the number density of scattering particles, V is the volume of the particles, ΔSLD is the contrast (Table S1), P(q) is the form factor and S(q) is the structure factor.

It was assumed that all of the surfactant, cosurfactant, and oil are contained in the aggregates. Due to the very weak polyelectrolyte contrast and its very dilute state in the sample, the polyelectrolyte was not considered explicitly for modelling of the data.

The form factor P(q) describes the shape of the scattering particles. In this case here, a simple polydisperse homogeneous sphere model with a log-normal size distribution was assumed for the radius of the microemulsion droplets.

$$P(q) = \left(3 \cdot \frac{\sin(qR) - qR \cdot \cos(qR)}{(qR)^3}\right)^2 \tag{S2}$$

$$L_N = \frac{1}{R\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{(\ln R - \ln \mu)^2}{2\sigma^2}\right)$$
(S3)

The structure factor describes the inter-particle interactions at small q, which can be repulsive or attractive. In general, the structure factor S(q) is related to the direct correlation function C(q) as follows:

$$S(q) = \frac{1}{1 - {}^{1}N \cdot C(q)}$$
(S4)

In the random phase approximation (RPA) the correlation function C(q) is approximated by the Fourier transform of the corresponding pair interaction potential U(r). In the case of charged microemulsion droplets that are linked together by a polyelectrolyte chain, the structure factor is not trivial. A repulsive term for the charged droplet interaction is needed as well as an attractive term accounting for the

attractive bridging interaction introduced by the polyelectrolyte chain, which, in addition to screening the droplet charges induces the droplets to move closer together. A possibility for taking into account the electrostatic interactions is a model based on the perturbation theory that can be solved with the random phase approximation (RPA) that was applied by Grimson *et al.*⁴⁴ For this model, the electrostatic interaction between the colloidal particles is treated as a decoupled perturbation to a given reference system. When the RPA is applied, the direct correlation function can be written as the sum of the different, independent contributions to the interaction potential.

$$C(q) = C_0(q) - \frac{1}{k_B T} U_{eff}(q)$$
(S5)

 $C_0(q)$ is the correlation function of the reference system without electrostatic interaction. Here we used the sticky hard sphere model by Baxter for the Percus-Yevick approximation, which is describing hard sphere particles with an excluded volume but also including an adhesive force.⁴²

$$C_{0}(q) = \frac{2\eta\lambda}{\kappa}\sin(\kappa) - \frac{2\eta^{2}\lambda^{2}}{\kappa^{2}}(1 - \cos(\kappa))$$

-[\alpha\kappa^{3}(\sin(\kappa) - \kappa\cos(\kappa)) + \beta\kappa^{2}(2\kappa\sin(\kappa) - (\kappa^{2} - 2)\cos(\kappa) - 2)) (S6)
+ \frac{\eta\alpha}{2}((4\kappa^{3} - 24\kappa)\sin(\kappa) - (\kappa^{4} - 12\kappa^{2} + 24)\cos(\kappa) + 24)]

with:
$$\kappa = q \cdot \sigma$$
, $\eta = \Phi_{HS} \left(\frac{\sigma + \Delta}{\sigma}\right)^3$, $\epsilon = \tau + \frac{\eta}{1 - \eta}$, $\delta = \Phi_{HS} \frac{1 + \eta/2}{3(1 - \eta)^2}$, $\lambda = \frac{6}{\eta} \left(\epsilon - \sqrt{\epsilon^2 - \delta}\right)$,
 $\mu = \lambda \eta (1 - \eta), \ \beta = -\frac{3\eta (2 + \eta)^2 - 2\mu (1 + 7\eta + \eta^2) + \mu^2 (2 + \eta)}{2(1 - \eta)^4}, \ \alpha = \frac{(1 + 2\eta - \mu)^2}{(1 - \eta)^4}, \ \Delta = \text{ width of potential.}$
When applied the limit $\Lambda \to 0$ is taken, so that $\eta = \Phi$

When applied the limit $\Delta \rightarrow 0$ is taken, so that $\eta = \Phi_{HS}$.

 $U_{\rm eff}(q)$ is the Fourier transformed perturbation potential, in this case the classical DLVO potential⁴³:

$$\frac{1}{k_B T} {}^{1}N \cdot U_{eff}(q) = 24\phi_{HS} \cdot \gamma \cdot \exp(-s) \frac{\kappa \cos(\kappa) + s \sin(\kappa)}{\kappa(\kappa^2 + s^2)}$$
(S7)

with:

s =

 k_D

$$D_{eff}/k_D, \qquad \gamma = \frac{1}{k_B T} \pi \varepsilon D_{eff} \psi_{0,eff}^2 \cdot \exp(s), \qquad \psi_{0,eff} = \frac{Z \cdot e_0}{\pi \varepsilon D_{eff}(2 + D_{eff}/k_D)} \qquad \text{and}$$
$$= \left(\frac{\varepsilon \cdot k_B T}{2N_A \cdot e_0^2 \cdot I}\right)^{1/2}.$$

For the Baxter model, the effective hard sphere radius $R_{\rm HS}$ is needed, which is a bit larger than the radius obtained from the form factor fit (due to the hydration shell, which is effectively seen in the hard sphere repulsion we took $R_{\rm HS} = R + 2.5$ Å). The hard sphere volume fraction ϕ_{HS} is coupled to $R_{\rm HS}$ by the number density, which only leaves the stickiness parameter τ free for fitting. For the DLVO potential in RPA (shown before to be a good approximation for describing scattering curves³⁶⁻³⁷), the same $R_{\rm HS}$ and ϕ_{HS} as for the Baxter model were used and the ionic strength *I* was calculated from the sample composition (taking into account all free Br⁻ and Na⁺ Ions, i. e. assuming a complete dissociation). This leaves the number of charges per particle *Z* the only free parameter for this fit.

The scattering curves arising from samples with higher Mw polyacrylates, cannot be described with a model of interacting microemulsions droplets anymore. The experimentally observed extended q^{-1} power law indicates the presence of 1-dimensional elongated clusters. Therefore the scattering patterns were described with a cylindrical arrangement of the microemulsion droplets, whose form factor was

previously developed in our group.⁴⁵ The model describes the presence of clusters formed by N aligned particles of radius R and separated by a border-to-border distance D. To properly take into account the polydispersity of size and separation distance, the scattering pattern has to be computed by numerically solving the Debye equation. For the calculations, a log-normal distribution of the ME droplet radii, a normal distribution for the border-to-border separation distance and a Poisson distribution for the number of object forming each cluster, were used. To obtain the scattering curves given in Fig. 5 and 7, 1000 objects described by distinct values of R, D and N generated by random number generators according to the distributions defined by the parameters given in Table S3, were computed and averaged.

The forward scattering intensity I(0) was obtained from all SANS curves by employing the Guinier approximation eqn S8 to the first (~ 20) data points.

$$I(q) = I(0) \cdot \exp\left(-\frac{R_g^2 \cdot q^2}{3}\right)$$
(S8)

For non-interacting particles, this forward scattering intensity is directly proportional to the molecular weight and consequently the aggregation number. In this case, the forward scattering intensity I(0) was divided by the theoretical forward scattering intensity of one single non-interacting droplet P(0) to obtain the aggregation numbers (= number of ME droplets aggregated in one complex). This procedure results in aggregation numbers < 1 for droplets with repulsive interactions, as they are present in the microemulsion excess regime of the phase diagrams. Those numbers were manually set to 1.

To perform a reliable Guinierfit, the SANS data has to reach a plateau at low q as it was the case for most of the data shown here. Some of the data sets (for very long NaPAs) don't show this plateau, so here the I(0) value can only be estimated. The resulting aggregation number is therefore a minimum value and marked with empty symbols.

Table S1: Scattering length densities (SLDs) of all individual components.

		ρ	SLD
	Formula	g∙cm ⁻³	10 ⁻⁴ nm ⁻²
deuterium oxide	D_2O	1.1	6.335
decane	$C_{10}H_{22}$	0.73	-0.489
hexanol	C ₆ H ₁₃ OH	0.82	-0.323
TDMAO	$C_{14}H_{29}N(CH_3)_2O$	0.897	-0.197
TTAB	$C_{14}H_{29}N(CH_3)_3Br$	1.026	-0.476

Table S2: Fit parameters of structure factor fit for the ME00-PAA05 series. R_{HS} was fitted for the pure microemulsion and kept constant for all fits, volume fraction ϕ and ionic strength *I* were calculated from the sample composition.

z	R_{HS} / nm	ϕ	τ	Ζ	I/mM	
0	3.37	0.0372	1	9.7	5.03	
0.01		0.0380	1	10	5.21	
0.04		0.0378	1	9.5	5.36	
0.05		0.0379	1	9.5	5.44	
0.10		0.0376	0.95	9	5.72	
0.20		0.0368	0.8	8	6.33	
0.29		0.0379	0.4	6	7.44	
0.41		0.0372	0.2	4	8.74	
0.52		0.0375	0.12	1.5	10.46	
0.62		0.0373	0.098	1	13.06	
0.64		0.0375	0.095	1.3	14.18	
0.70		0.0376	0.092	3.8	16.75	
0.80		0.0375	0.092	8.5	24.86	
0.90		0.0381	0.098	18	50.33	

Table S3: Parameters for the cylindrical arrangement of droplets - model. ϕ was calculated from the sample composition. *R* and the standard variation $\sigma(R)$ were fitted for the pure microemulsion and then kept constant, *D* is the mean distance between particles with a Gauß distribution of width $\sigma(D)$ and N_P the mean number of particles per complex with a poisson distribution.

	ϕ	<i>R</i> / nm	$\sigma(R)$	D / nm	$\sigma(D) / nm$	N_P	fit quality
ME00-NaPA05-0.70	0.0273	3.0	0.13	3.9	1	1.5	good
ME00-NaPA15-0.71	0.0271	3.0	0.13	3.9	2	3	good
ME00-NaPA60-0.69	0.0273	3.0	0.13	5.2	3	11	good
ME00-NaPA315-0.69	0.0275	3.0	0.13	5.2	3	17	poor
ME50-NaPA05-0.70	0.0421	4.1	0.14	6.9	3	3.4	good
ME50-NaPA15-0.70	0.0410	4.1	0.14	7	3	5	good
ME50-NaPA60-0.70	0.0416	4.1	0.14	10	3	30	very poor
ME50-NaPA315-0.70	0.0428	4.1	0.14	10	3	35	very poor
ME75-NaPA05-0.70	0.0625	6.3	0.15	8	3	5	poor



Fig. S1: Degree of deprotonation of NaPA with Mw = 15 kDa. All samples were prepared between pH 7 and 8 where the NaPA should be more than 85% deprotonated, the area is shaded in red.



Fig. S2: SANS spectra (V4 at HZB) of two samples with the same composition but prepared in different ways. Sample 1 (black circles) was prepared by first preparing microemulsion and polyacrylate stock solutions seperately, which were then mixed in the desired ratio, sample 2 (red squares) was prepared by mixing all 'dry' compounds (TDMAO, TTAB, hexanol, decane, NaPA) first and adding the water afterwards. The almost perfect overlap of the curves shows, that the formed complexes are in their thermodynamic stable state.



Fig. S3: Samples prepared from ME50 (c = 100 mM) mixed with NaPA60 at different charge ratios *z*. Photo was taken 5 min after preparation. Precipitating samples have already turned turbid in this photo, at larger charge ratios the blueish tinge of the samples is visible.



Fig. S4: Mw and R_h obtained from static and dynamic light scattering show the presence of differently sized aggregates of ME and PE in dependence of the charge ratio z and the Mw of the NaPA. Metastable regions are shaded in red.



Fig. S5: SANS spectra (PAXY at LLB) obtained for samples of small droplets (R = 3.1 nm) with NaPA of 5.1 kDa in different mixing ratios *z*. Black lines are best fits according to the RPA structure factor model by Grimson.



Fig. S6: SANS spectra (ME00 and ME50 from PAXY at LLB, ME75 from D11 at ILL) obtained for samples with NaPA of 5.1 kDa and differently sized droplets at different charge ratios in the polyelectrolyte excess.



Fig. S7: Forward scattering intensity I(0) as obtained from SANS measurements for differently sized droplets at z = 0.7 in dependence of the Mw(NaPA).

(ME00-NaPA05 and 15 and ME50-NaPA05, 15 and 60 from PAXY at LLB; ME00-NaPA60 and 315 and ME50-NaPA315 from V4 at HZB)



Fig. S8: I(0) values obtained by Guinier analysis from SANS Data for different microemulsion droplet sizes and molecular weights of the polyacrylate over the charge ratio *z*. Dotted lines are the theoretical forward scattering of the pure droplets without interactions.

(ME00-NaPA05 and 15 and ME50-NaPA05, 15 and 60 from PAXY at LLB; ME00-NaPA60 and 315 and ME50-NaPA315 from V4 at HZB and ME75-NaPA05 from D11 at ILL)



Fig. S9: Comparison of the homogeneous cylinder model and a cylindrical arrangement of droplets to describe the SANS data (PAXY at LLB). The cylindrical arrangement of droplets shows a much better agreement with the measured data, indicating that the microemulsion droplets are linked by the polyelectrolyte, while retaining their droplet shape. The droplets do not 'melt' together into a cylindrical object. Residuals are calculated as [I(q) - Fit] / I(q).



Fig. S10: Scattering curves (PAXY at LLB) for different concentrations of ME00-NaPA15 samples, charge ratios are z = 0.10 in the microemulsion excess and z = 0.70 in the polyelectrolyte excess of the phase diagram. Both samples were prepared at 600 mM surfactant concentration and then diluted stepwise down to 10 mM.



Fig. S11: Scattering curves (PAXY at LLB) for ME00-NaPA15 samples with different charge ratios: z = 0.10 in the microemulsion excess and z = 0.70 in the polyelectrolyte excess of the phase diagram. Different amounts of NaCl were added to the sample.