

# Responsive and Evolving Mixtures of a Hydrolyzing Cationic Surfactant and Oppositely Charged Polyelectrolytes

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## Supplementary Information

**Materials.** Sodium poly(acrylate), NaPA, (150 000 g/mol) (Sigma-Aldrich), poly(acrylic acid), PAA, (Aldrich) (450 000 g/mol) sodium poly(styrene sulfonate), NaPSS, (Aldrich) (1 000 000 g/mol), 1-Decanol (Aldrich), gaseous trimethylamine (Fluka), chloroacetyl chloride (Merk), dichloromethane (Merk), sodium hydrogen carbonate (Merck), dodecyltrimethylammonium chloride, DoTAC (TCI Europe) and dialysis membrane with a cut-off of 500 (Spectrum Laboratories, Inc.). All chemicals were used without further purification. All solutions were prepared using water purified with Millipore Milli-Q equipment.

**Synthesis of DeB.** Decyl betainate (DeB) was prepared via a two-step route based on previously described procedures, where decanol was first converted into the corresponding chloroacetate and then further reacted with trimethylamine to yield the final product<sup>1</sup>.

## Sample preparation

**NaPA:DoTAC:DeB.** Each sample was prepared individually. Polymer and surfactant solutions with concentrations double (or triple) the desired final concentration were mixed and left for 20 min under stirring. For the mixtures containing both DoTAC and DeB, the surfactant solutions were mixed first and then the mixed surfactant solution was added to the polymer solution. The final volume of each sample was 3 mL. The samples were stirred for 30 min, and then left to equilibrate.

**NaPSS:DoTAC:DeB and PAA:DoTAC:DeB.** Samples were mixed the same way as for NaPA:DoTAC:DeB. After 24 hours each sample (one-phase or two-phase) was checked again and put into dialysis against 0.5 M of NaOH (pH~14). Final volume of each sample was 3 mL. The samples were dialyzed for 2.5 hours (after this time nothing seemed to change visually).

**Structural characterization.** Small angle X-ray scattering (SAXS) measurements were performed at the I711 line in Max-lab in Lund, Sweden<sup>2</sup>. The experimental setup involved the use of X-rays at the wavelength of 1.1 Å and a sample-to-detector distance around 1250 mm. A cell with mica windows was used and was maintained at the desired temperature (25 or 40°C). Typical acquisition times were 300 and 600 seconds. The volume between the sample and the detector was kept under vacuum during data collection to minimize the background scattering. The analysis of the 2D SAXS scattering data was conducted by the software Fit2D<sup>3</sup>.

The size of the cubic unit cell,  $\alpha_{cub}$ , can be obtained by plotting  $(q/2\pi^2)$ , where  $q$  is the scattering vector, versus the Miller indices  $(h^2+k^2+l^2)$  of the structures according to

$$\alpha_{cub} = \left( \frac{2\pi}{q} \right) (h^2 + k^2 + l^2)^{\frac{1}{2}} \quad (1)$$

It follows from geometry that the center-to-center distance between adjacent rods,  $d$ , of the hexagonal structure can be obtained from the first diffraction peak ( $q_1$ ) using

$$d_{hex} = \left( \frac{2}{3} \right)^{\frac{1}{2}} \left( \frac{2\pi}{q_1} \right) \quad (2)$$

For the lamellar structures the distance between the equivalent planes,  $d_{lam}$ , is given by

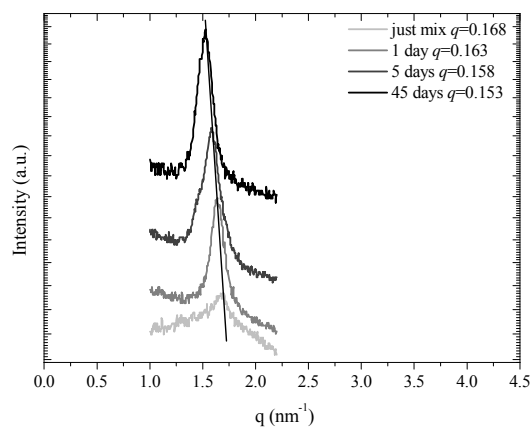
$$d_{lam} = \frac{2\pi}{q_1} \quad (3)$$

The correlation distance between the micelles is given by

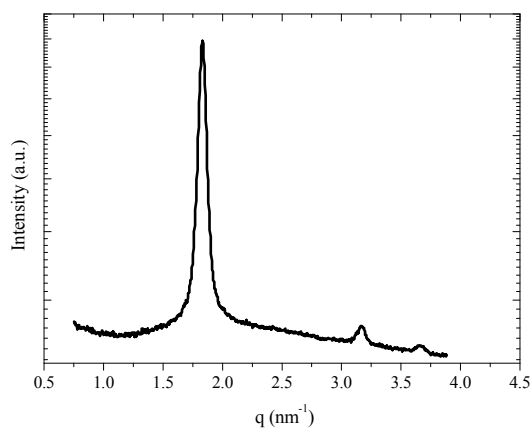
$$d_{mic} = \frac{2\pi}{q} \quad (4)$$

**Cryo-TEM.** Samples for the cryo-TEM experiments were prepared using a controlled environment vitrification system (CEVS)<sup>4</sup>, where the relative humidity was kept close to saturation at around 30°C. A 5 µL drop was placed on a lacey carbon-coated copper grid and the excess fluid was gently blotted away leaving a thin film of aqueous sample covering the grid. The grid was then plunged into liquid ethane at -180°C to allow rapid vitrification of the specimen (avoiding crystallization of water). All prepared grids were stored in liquid nitrogen until being transferred to the electron microscope. Images were digitally recorded using a Philips CM120 Bio TWIN electron microscope, operated at 120 kV, at around -183 °C, equipped with a Gatan MSC791 cooled-CCD camera

system. To minimize beam damage, all samples were imaged under minimal electron dose conditions.



**Figure S1.** SAXS profiles of dispersions of NaPA<sub>10</sub>:DeB<sub>5</sub> mixtures after different times.



**Figure S2.** SAXS profile from the swollen concentrated phase of NaPSS<sub>100</sub>:DoTAC<sub>80</sub>:DeB<sub>20</sub> the system.

## References

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