SUPPORTING INFORMATION

Tuning the Aggregation Behaviour of Single-Chain Bolaamphiphiles in Aqueous Suspension by Changes in Headgroup Asymmetry

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Physicochemical investigations

DMAPPC-C32-POH

Analysis of parameters of micelles and cross section geometry of fibres from SANS data

In general it was assumed that all studied systems are dilute solutions, which means the scattering intensities depend only on the size and shape of the aggregates and the interaction between aggregates is small. In this case the scattering intensities are written as

$$d\Sigma(q)/d\Omega = n\langle |F(q)|^2 \rangle, \qquad (1)$$

The values inside the brackets < > represent an average weighted by the distribution of particle sizes and/or orientations, *n* is the number density (corresponding to the concentration) of the particles in the solution, F(q) is the amplitude of the form factor and is written as

$$F(q) = V \Delta\rho \, f(q,V,sh), \qquad (2)$$

where *V* is the volume of the micelle, $\Delta\rho$ is the contrast of scattering length densities between the particles and the solvent, and the scattering function $f(q,V,sh)$ depends on the volume (size) and the shape (*sh*) of the aggregates. The simplest situation is for spherical objects**,** where the IFT method describes the experimental data perfectly and the shape of *p(r)* is near to symmetrical (homogeneous sphere). The scattering function for an ellipsoid of revolution with semi axis *b*, *b* and *a* ($a = \varepsilon b$) was taken in the fitting procedure [Feigin, L. A.; Svergun, D.I. *Structure Analysis by Small-Angle X-Ray and Neutron Scattering*; Plenum Press: New York, 1987, p. 331]. The fitting of the scattering data by the model of an ellipsoid of revolution with semi axii *a*, *b*, shows the same quality of agreement as in the case of the IFT method. The obtained semi axis values are shown in Table 1S. We did not apply more complicated models, for example two shell aggregates, because it will significantly increase the number of fitting parameters.

SANS data of DMAPPC-C32-POH in acetate buffer at pH 5 (c = 2 mg ml^{-1}) can be fitted quite well with the model of stiff cylinders. The obtained length of cylinders is of order 1000 Å. This does not mean that the rod-like objects have a persistence length of order 1000 Å The measured interval of scattering vectors corresponds to the persistence length of > 200 Å. That is why our results indicate that the stiffness of studied objects is higher than 200 Å and total length is in order of 1000 Å or longer

Table 1S: Elliptical cross section of fibres with semi axii *a* and *b*, estimation of length *L*; semi axii of ellipsoid of revolution of micelles *a*=*b*, *c*; mass fraction of bolas in aggregates $f_m = M_L/(\pi abc\rho)$ for fibres or $f_m = M_L/(4\pi/3abc\rho)$ for micelles, here $\rho = 1$ g ml^{-1}.

	T [°C]	*aggregate shape*	a, Å	b, Å	L or c, Å	*Mass fraction of bolas in aggregates, f_m*
DMAPPC-C32-POH in acetate buffer (pH 5)	25	stiff cylinders	21.0±1.0	28.0±1.0	~1000	0.740
	55	stiff cylinders	21.0±1.0	24.0±1.0.	~1000	0.745
	70	micelles	23.0±1.0	23.0±1.0	38.0±1.0	0.705
Me_2PE-C32-Me_2PE in acetate buffer (pH 5)	20	flexible fibres	18.0±1.0	28.5±1.0	~750	0.860
	50	fibres	17.0±1.0	28.0±1.0	~750	0.880
	75	micelles	25.5±1.0	25.5±1.0	50.0±1.0	0.756

Rheology:

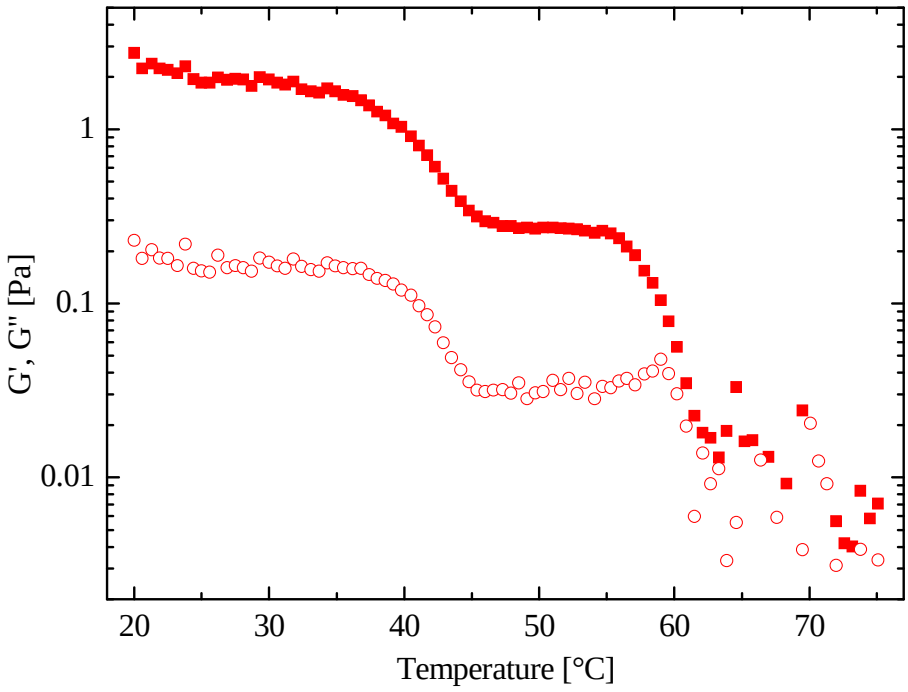

Figure S1: Rheological data of a DMAPPC-C32-POH suspension in acetate buffer at pH 5 (c = 1 mg ml^{-1}) with ω = 1 rad s^{-1} and γ = 1 % inside the linear viscoelastic region. The heating rate was 60 °C h^{-1}. G': filled squares, G'': open circles.

DMAPPC-C32-OH

FT-IR:

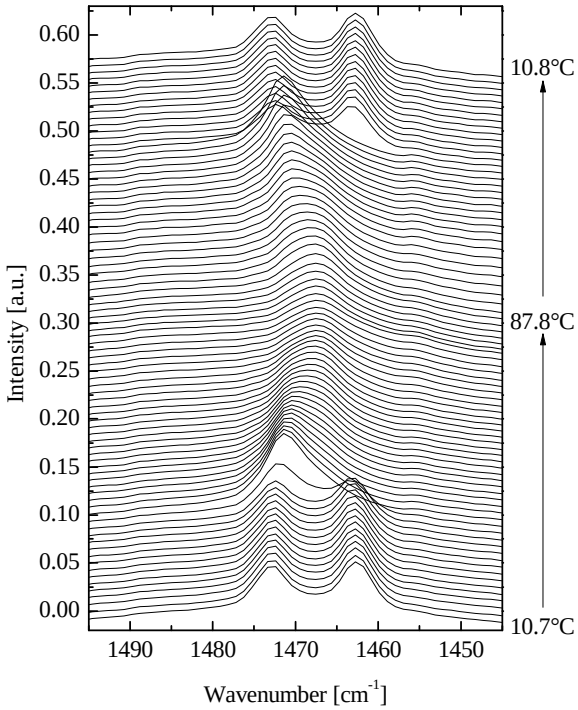

Figure S2: FT-IR spectroscopic data of DMAPPC-C32-OH suspensions (c = 50 mg ml^{-1}) in carbonate buffer at pH 10: methylene scissoring vibrational bands between 1450 and 1490 cm^{-1} at different temperatures from 10.7 to 87.8 °C and back (2 K steps). The curves are vertically shifted for clarity.

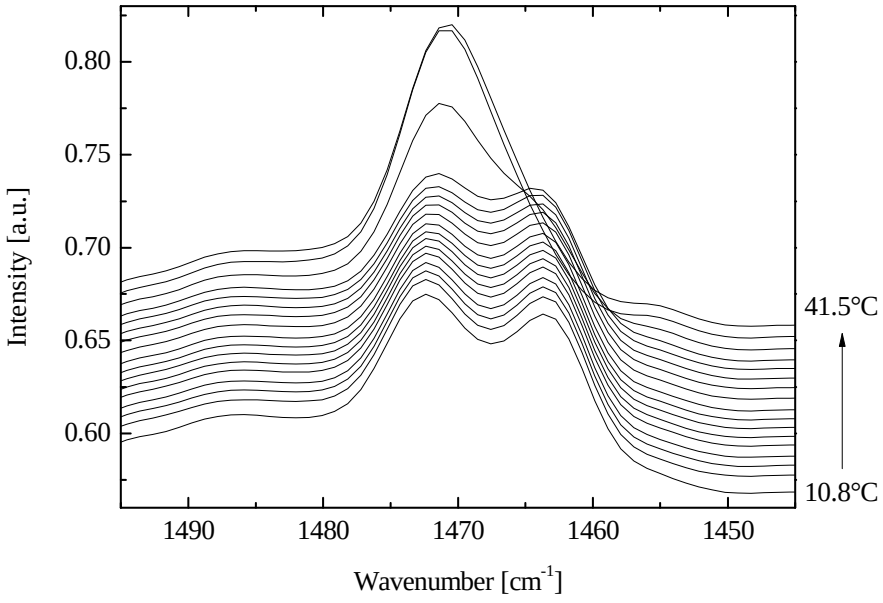

Figure S3: FT-IR spectroscopic data of DMAPPC-C32-OH suspensions (c = 50 mg ml^{-1}) in acetate buffer at pH 5; methylene scissoring vibrational bands between 1450 and 1490 cm^{-1} at different temperatures (10.8–41.5 °C, 2 K steps). The curves are vertically shifted for clarity.

