

Supporting Information:

Effect of hydrostatic pressure on the supramolecular assembly of surfactant-cyclodextrin inclusion complexes:

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Contents

S1 Additional information on materials and methods used

S1.1 Materials

The surfactant, an oligo ethylene oxide alkylether carboxylic acid, was obtained from Kao Chemicals and is available under the trade name AKYPO[®] RLM 45 CA. The surfactants are of technical grade, and were used without purification. They were previously characterized by ¹H-NMR spectroscopy.[?] The alkyl chain is 2:1 mixtures of C₁₂ and C₁₄ chains. The degree of ethoxylation is 4.6 for and the degree of carboxymethylation is ca. 0.9. The surfactant was fully ionized using Sodium Hydroxide from Sigma-Aldrich.

S1.2 Methods

Small-angle neutron scattering Small-angle neutron scattering (SANS) experiments were performed at 25 ° on the D33 diffractometer[?] at Laue-Langevin Institute (ILL) in Grenoble. Experiments were performed with a monochromatic beam, wavelength $\lambda = 6 \text{ \AA}$ and $\Delta\lambda/\lambda = 10\%$. The detector consists of a central panel set at 10.3 m and 4 side panels set at 1.7 m. The collimation length was set to 10.3 m. Scattering data were corrected for the empty cell contribution, normalized by transmission, and azimuthally averaged using the GRASP software package.[?] Data analysis was performed in absolute units using the scattering length density values and molecular volumes given in Table ??.

Table S1: Density (ρ), scattering length density (SLD), and molecular volume (v) used for the description of the neutron scattering results. The exchange of labile protons of the cyclodextrin with the deuterated solvent has been taken into account.

Compound	$\rho / \text{g cm}^{-3}$	SLD / 10^{-4} nm^{-2}	v / nm^3
D ₂ O	1.10	6.33	0.30
C ₁₂ /C ₁₄	0.75	-0.31	0.340
(OCH ₂ CH ₂) _{4,6} OCH ₂ COONa	1.21	1.00	0.345
α -CD (C ₆ H ₇ D ₃ O ₆) ₆	1.50	3.40	1.08

Densitometry The densities of aqueous solution of surfactant/cyclodextrin inclusion complexes, at mixing ratio 1:2 were measured as a function of inclusion complex concentration using an Anton-Paar DMA 4500 M apparatus. The apparent partial molar volume of the inclusion complex is obtained as:

$$\bar{V} = \frac{Mw}{d} - \frac{d - d_0}{mdd_0} \quad (\text{S1})$$

with Mw being the molar mass of the 2:1 inclusion complex, m concentration expressed in moles of inclusion complex per kilogram of solvent, and d and d_0 are the densities of the inclusion complex solution and of the solvent, respectively.

S2 Model for the analysis of SANS data

The data presented in the main text were analysed with a model of stacked bilayers, approximated using a form factor of extended bilayers ($P(q)$) and their stacking using the modified Caillé theory^{??} ($S_{MCT}(q)$) as:

$$I(q) = {}^1N \cdot P(q) \cdot S_{MCT}(q) \quad (\text{S2})$$

whereby 1N is the number density of the scattering objects.

Form Factor To describe the scattering of the extended bilayers, the form factor is decomposed as:

$$P(q) = P'_D(q) \cdot P_{cs}(q) \quad (\text{S3})$$

with $P'_D(q)$ being the shape form factor of an infinitesimally thin disk with radius $R_D = 1 \mu\text{m}$:

$$P'_D(q) = \frac{2\pi^2 R_D^4}{(qR_D)^2} \left(1 - \frac{J_1(2qR_D)}{qR_D} \right) \quad (\text{S4})$$

and $P_{cs}(q)$ being the cross-section form factor describing the core-shell system with thicknesses d_{shell} , and d_{core} , total thickness $d = d_{core} + 2d_{shell}$, and corresponding scattering length densities η_{core} , η_{shell} :

$$P_{cs}(q) = \left[(\eta_{core} - \eta_{shell}) \frac{d_{core} \sin(qd_{core}/2)}{qd_{core}/2} + (\eta_{shell} - \eta_{soln}) \frac{d_{shell} \sin(qd_{shell}/2)}{qd_{shell}/2} \right]^2 \quad (\text{S5})$$

The scattering length densities values of the inner and outer part of the bilayer were calculated assuming that:

- the inner part is anhydrous, and includes cyclodextrins and surfactant alkyl tails only in a 1:1 ratio. The SLD is obtained as the volume weighted average of the SLD of the surfactant tail and of the cyclodextrin.

- the outer part of the bilayer includes cyclodextrins, surfactant head groups and solvent, and the SLD of the layer is obtained as the volume weighted average of the SLDs of the three components. The volume fraction of surfactant in the outer part ϕ_s^o is constrained to take into account the molar volumes of the alkyl tail and head group as well as the thicknesses of the inner and outer part as:

$$\phi_s^o = \frac{\phi_s^i d_{core}}{\nu_{alk}} \cdot \frac{\nu_{head}}{d_{shell}} \quad (S6)$$

with ϕ_s^i being the volume fraction of the surfactant in the inner part of the layer, and ν_{alk} and ν_{head} the molecular volumes of the hydrophobic and hydrophilic parts of the surfactant, respectively, as provided in Table ??.

All data were fitted assuming constant values of $d_{core} = 1.2$ nm, $\phi_s^i = \nu_{alk}/(\nu_{alk} + \nu_{CD}) = 0.25$, $d_{shell} = 1.1$ nm, and $\phi_{CD}^o = \phi_s^o \nu_{CD}/(\nu_{head}) = 0.6$, which well describe the decay of the scattering intensity at $q \sim 1.5$ nm⁻¹.

Structure Factor The structure factor, described within the modified Caillé theory,^{??} is given by:

$$S_{MCT}(q) = \sum_{N_k=N-2\sigma}^{N+2\sigma} x_k S_{k,MC} \quad (S7)$$

N is the average number of layers in the stacks described by a Gaussian distribution, x_k is the weighting factor of a stack with N_k layers:

$$x_k = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(N_k-N)^2}{2\sigma^2}} \quad (S8)$$

$\sigma = \sqrt{N}$ the standard deviation of the distribution of stacks and $S_{k,MC}$ is the structure factor of a stack of N_k layers

$$S_{k,MC} = N_k + 2 \sum_{m=1}^{N_k-1} (N_k - m) \cos(mqd) e^{-\left(\frac{dq}{2\pi}\right)^2 \eta_c \gamma} (\pi m)^{-\left(\frac{dq}{2\pi}\right)^2 \eta_c} \quad (S9)$$

with γ being the Euler constant, and η_c the Caillé parameter. The standard deviation σ of the size distribution shall not be confused with an uncertainty on the mean number of layers.

S6 Additional densitometric data

Through accurate densitometric experiments of a dilution series of CD surfactant inclusion complexes, with a constant mixing ratio of 2:1, the concentration-dependent partial molar volume of the inclusion complex was determined and is reported in Figure ???. For completeness, the same figure also indicates the critical aggregation concentration above which the inclusion complexes assemble into supramolecular structures, as determined previously.[?] No notable change can be observed below or above this critical value. Accordingly, we conclude that the supramolecular assembly of the inclusion complexes into ordered structures is not associated with any significant volume change.

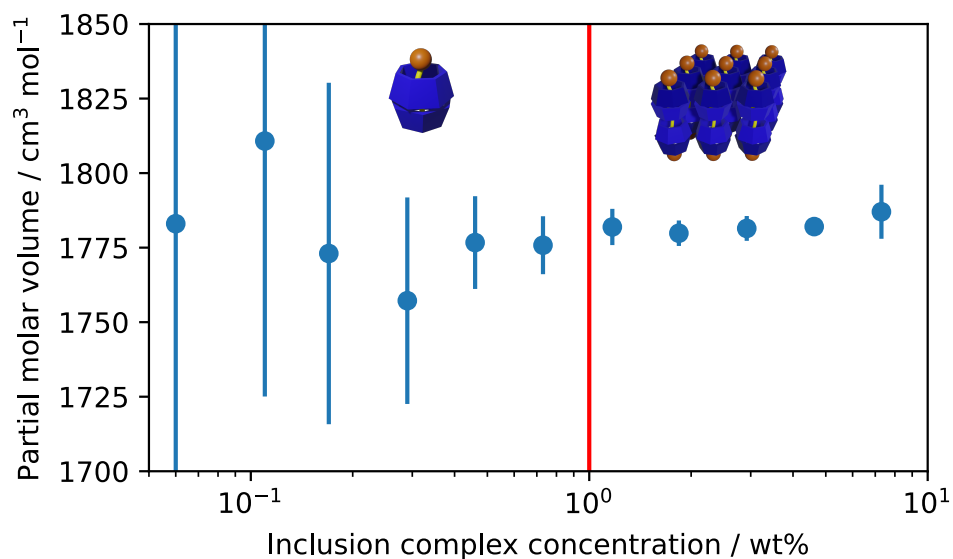


Figure S1: Partial molar volume of the α CD- $C_{12}E_5CH_2COONa$ complexes as a function of inclusion complex concentration determined through accurate densitometric experiments. Red vertical line indicates approximate critical aggregation concentration above which the inclusion complexes are shown to assemble into aggregates with local planar structure.