Supplementary information

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Scattering contrast: What do we "see"?

Form factors $P(q)$ are directly determined for solutions composed of particles with shape and size independent of concentration. In dilute regimes, these solutions are composed of non-interacting particles, resulting in structure factor $S(q) \approx 1$, thus $P(q)$ is measured independently of $S(q)$. Measuring a series of increasing concentration, $S(q)$ is then obtained, once $P(q)$ is known. For micellar aggregates, this method is not applicable, as micellar structure depends on surfactant concentration and formulation. Additionally, micellar aggregates disassemble at concentrations lower than CMC_1, thus measurements of $P(q)$ independent on $S(q)$ are not feasible. Dilution means zero intermicellar interactions for SAS and ionic micelles are considered "concentrated" even at the CMC_1, as counterion dissociation leads to repulsive forces.[1–3]

Scattering length densities related to different parts of a micelle form profiles, as sketched on the left of Fig. S1. Basically, the contrast between micellar core and solvent, $\Delta\rho_{core}$, and between polar shell and solvent, $\Delta\rho_{shell}$, define a model to be assumed as form factor $P(q)$. The example in Fig. S1(a) exhibits $\Delta\rho_{core}$ and $\Delta\rho_{shell}$ with opposite signs, taking the solvent scattering length density as reference.[1] Specifically in this case, the form factor $P(q)$ forms a peak with lower magnitudes towards $P(0)$.[4] This is typical of core-shell form factors, leading to a double peak in scattering cross section $d\sigma/d\Omega(q)$.

A second case is illustrated in Fig. S1(b), in which the contrast between $\Delta\rho_{core}$ or $\Delta\rho_{shell}$

and solvent have same signs. Now, the core of the particle is seen as a whole and a dense core form factor is assumed. Instead of a peak, the form factor contribution decays with increasing q. The contribution of structure factor $S(q)$ is independent on $P(q)$, for both cases shown in Fig. S1. A correlation peak results from the multiplication of $P(q)$ and $S(q)$. Later we discuss that in some cases, this correlation peak is masked by an intense form factor peak, similar to the example in Fig. S1(a).
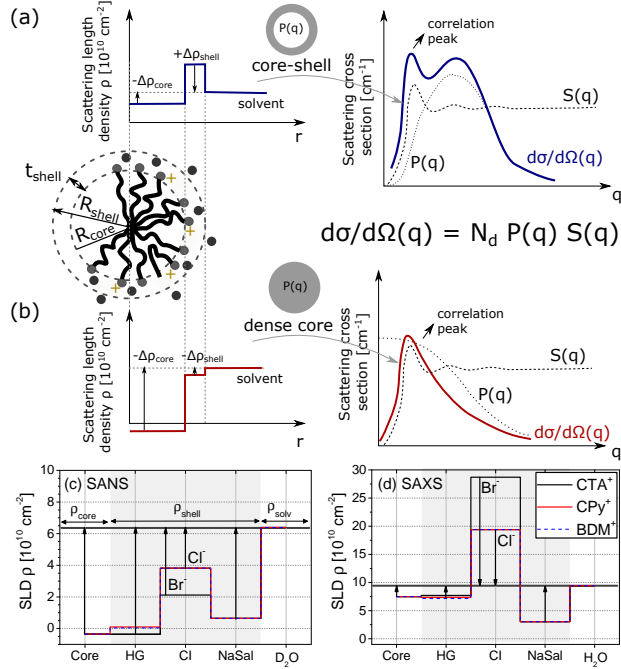

Figure S1: Micelles with different scattering length density profiles. (a) The form factor $P(q)$ exhibits a peak only when the core contrast $\Delta\rho_{core}$ and polar shell contrast $\Delta\rho_{shell}$ have opposite signs, characteristic of core-shell form factors. (b) If $\Delta\rho_{core}$ and $\Delta\rho_{shell}$ have the same sign, so the form factor decreases with scattering vector q (no peak is formed). This is characteristic of dense core form factors. The scattering length density profiles SLD ρ are calculated for SANS (c) and SAXS (d). The final contrast ρ_{mean}, based on ρ_{core} and ρ_{shell} (headgroup HG, counterions CI and sodium salicylate NaSal), is calculated taking the solvent as reference ρ_{solv}.

Scattering length density profiles differ for SANS and SAXS. For SANS, the contrast between hydrocarbonic micellar core and solvent D_2O is the strongest signal, as neutrons interact mostly with hydrogen nuclei and deuterium isotopes. For SANS, micellar polar shell and solvent have comparable contrasts. Therefore, scattering of counterion and salt in the

polar shell is negligible, as we "see" mostly the micellar core, according to a dense core form factor, shown in Fig. S1(b).

A different particle is "seen" by X-rays, as the contrast between micellar core, polar-shell and solvent vary accordingly to the electron density of involved atoms. For SAXS, both cases shown in Fig. S1 are possible. If salt molecules are added to a pure surfactant solution, apart from the interactions in the polar shell, salts further dissociate in solution, changing the solvent contrast itself. In some cases, a core-shell form factor leads to a peak, as shown in Fig. S1(a), even without any interference effects.[5] SAXS interpretation of ionic micellar systems are more complex than SANS, as their scattering varies with high electron densities of counterions and dissociated salt ions within a polar shell, instead of the hydrocarbonic core and solvent for SANS. Although if combined, both techniques can be complementary as a contrast method. Our aim is to understand the contribution of organic salt addition to anisotropic micellar growth of cationic surfactants by identifying the contributions to the scattering cross section.

To fit the form and structure factors, apart from the scattering cross section in absolute scale, the contrast factor $\Delta\rho$ has to be known to restrict the set of fitting parameters. For that, the scattering length density ρ was calculated for the core ρ_{core} and polar shell ρ_{shell} of micellar aggregates considering neutrons and X-rays radiations as indicated in Fig. S1(c) and (d). ρ_{core} considers the specific density of the hydrophobic portion of a surfactant molecule, while ρ_{shell} considers only the surfactant headgroup. When the molar ratio R increases, the scattering length density associated to the salt molecule will contribute to ρ_{core}, if its hydrophobic (organic portion) penetrates the micellar core. If the salt's hydrophilic portion stays at the polar shell (for partial core penetration), then ρ_{shell} varies. The mean micellar scattering length density ρ_{mean} is calculated as the sum of scattering length densities from all components divided by their effective volume, based on molecular density.[6] The scattering length density of the solvent ρ_{solv} (water or D_2O) is considered as a reference, thus the final contrast is obtained from the difference $\Delta\rho = \rho_{mean} - \rho_{solv}$.

Correlation peak: intermicellar interactions

For SANS, the contrast between micellar core and solvent is similar for all surfactant solutions, practically independent of headgroup structure, counterion or salt content. This reduces the number of fitting parameters, so a Hayter-Penfold structure factor[1] can be applied, while simultaneously fitting a dense core form factor for SANS and a core-shell form factor for SAXS, both dependent on micellar shape. The mean intermicellar distance d_{im} is promptly accessed from the correlation peak between $S(q)$ and $P(q)$. Figure S2(a) compares SANS and SAXS scattering curves of solutions with 100 mM of CTAC and 10 mM of NaSal (molar ratio $R = 0.1$). The same curves are shown in linear scale in Fig. S2(b) and (c) to compare peak shapes. Both measurements have a common structure factor, which increases from its osmotic compressibility limit at $S(0)$, the structure factor at zero scattering angle, in the low q region.[5] $S(q)$ forms a peak at intermediary q before reaching a plateau $S(q) = 1$, in which no long-range micellar interactions are present. Both SAS curves display similar form factors, although decaying from plateaus with different magnitudes at $P(0)$. The correlation peak is labeled as q_{corr} in Fig. S2(a) at approximately 0.57 nm^{-1} for both SANS and SAXS measurements. Similar values were previously reported by Aswal et al.[7] for pure CTAC solutions.

Ionic micellar solutions show considerable long-range intermicellar repulsive interactions when surfactant headgroups are not fully screened by salts.[3,8] q_{corr} identifies the contribution of structure factor in SANS and SAXS independently of form factor, thus it is independent of radiation type. If a strong correlation peak is observed by SANS, it is also measured by SAXS, although the high contrast of the polar shell complicates the determination of the SAXS form factor. We see that q_{corr} is the same for SAXS and SANS in Fig. S2. For example, d_{im} is about 11 nm for the solution depicted in Fig. S2.
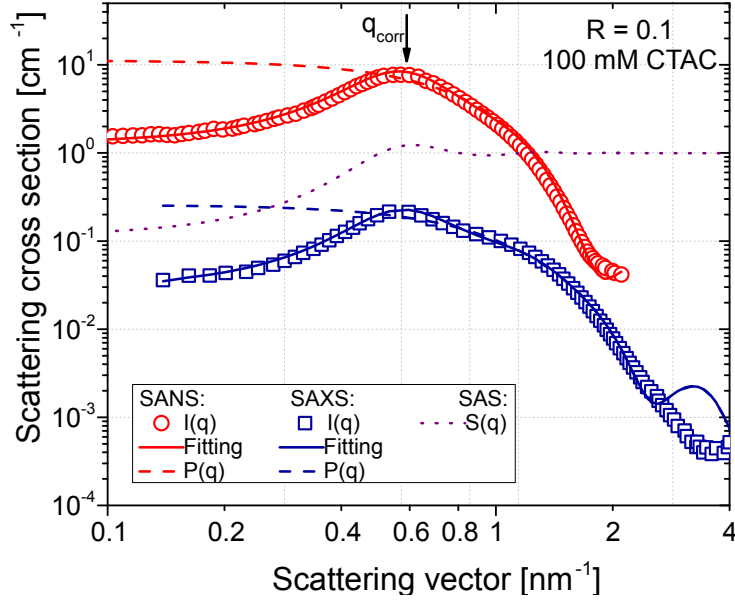
Figure S2: (a) Comparison between SANS and SAXS differential scattering cross section $d\sigma/d\Omega$ as a function of scattering vector q for 100 mM CTAC and 10 mM of NaSal ($R = 0.1$). A common structure factor $S(q)$ is determined from SANS with an ellipsoidal dense core form factor. $S(q)$ is combined with a ellipsoidal core-shell form factor $P(q)$ to fit the SAXS signal. Correlation peaks q_{corr} are generated by the product between structure and form factors. The deviation of the fitting at high q for SAXS is probably related to the polydispersity of the micelles, which has not been considered here.

Table 1: Parameters used for the fittings shown in Fig. 6 of the main manuscript.

Parameters	Ellipsoidal core-shell (SAXS)		Ellipsoidal dense shell (SANS)	
	CPyCl	CPyBr	CPyCl	CPyBr
semi-axis a (nm)	3.14	3.49	3.53	4.47
semi-axis b (nm)	1.49	1.59	2.14	2.46
shell thickness (nm)	0.28	0.42	0	0
SLD ρ_{core} (cm^{-2})	7.49E+10	7.49E+10	-3.51E+09	-3.51E+09
SLD ρ_{shell} (cm^{-2})	1.15E+11	1.36E+00	-3.51E+09	-3.51E+09
SLD ρ_{solv} (cm^{-2})	9.45E+10	9.45E+10	6.39E+10	6.39E+10
Parameters	Structure factor (SAXS and SANS)			
RHS (nm)	2.62	4.23		
Z (charge)	22.63	17.86		
Volume fraction	0.04	0.04		
T (K)	293.00	293.00		
Salt (M)	0.01	0.01		
Dielectric constant H$_2$O	71.08	71.08		
Dielectric constant D$_2$O	77.94	77.94		

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