Experimental report

12/01/2021

Proposal:	**9-12-580**	**Council:**	4/2019
Title:	Understanding like-charge attraction in protein-surfactant-polyelectrolyte mixtures for improved laundrydetergents		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: H2O
D2O
NaC12H25SO4
C3H4O2
NaC12D25SO4

Instrument	Requested days	Allocated days	From	To
D11	0	2	08/02/2020	10/02/2020
D33	3	0		

Abstract:

We have recently reported that addition of anionic polyelectrolyte sodium polyacrylate (NaPA) to solutions of anionic surfactants (SLES) enhances their detergency if divalent ions are present. This boost in washing performance was found to be even larger in the presence of a protease enzyme, which is a common ingredient in laundry detergents. While a NaPA solution shows little detergency, its addition to either a surfactant solution or a surfactant-enzyme mixture in the presence of divalent ions was able to boost their performance by a factor of 2. It was proposed that the mechanism involves the formation of surface-active calcium bridged NaPA-SLES aggregates. This proposal seeks to understand the molecular origin underpinning this effect by use of selectively contrast matched surfactants, polymers and proteins. We aim to obtain an experimental validation of the polymer-surfactant aggregates observed in molecular dynamics simulations and extend the measurements to a more complex system including an enzyme, which is relevant to real laundry detergents.

Experimental report: Understanding like-charge attraction between surfactants and proteins

Jan 2021

Background: In an earlier experimental report, it was observed that addition of anionic polyelectrolytes to anionic detergents lead to an increase in detergency power of the solutions if divalent ions were present. This led us to postulate that divalent ions promote attractive interactions between like-charged anionic surfactants and polymers in aqueous solution. The proposal aimed at gaining a molecular understanding of this mechanism. To this end, several mixtures of surfactant, proteins and polymers were measured under different contrast conditions. The results are then compared with molecular dynamic simulations.

Summary: The solution of pure protein was found to contain aggregates, as evidenced by an upturn in the Guinier region, which presumably occurred due to the temperature rising above 4 °C during the transportation of the samples to the ILL, we therefore do not discuss those results further. Below we outline the measurements for the single component surfactant systems and for the single polyelectrolyte system. A paper for the single polyelectrolyte system has been written up and will be submitted to *Macromolecules* in the coming weeks. A second manuscript on the single surfactant systems is in preparation.

Polyelectrolytes with divalent ions

Figure 1a shows the scattering profiles of MgPSS in salt-free D2O for different concentrations. Panel b plots the concentration dependence of the scattering peak for MgPSS (measured in this work) and literature results for NaPSS (blue symbols) and CaPSS (black symbols) from literature results. In the low concentration region, PSS with either monovalent or divalent counterions displays a power-law of $q^* \approx c^{1/2}$ as predicted by the scaling model of Dobrynin et al for polyelectrolytes with monovalent counterions. The values of q* for MgPSS are found to be ≈ 1.5 times lower than those of NaPSS, indicating a correspondingly larger correlation length. In principle the scaling theory relates the correlation length to the effective monomer size b' as

$$\xi = (b'c)^{-1/2}$$

b' = b/B, where b is the chemical monomer length and B is a stretching parameter. Larger values for x at the same molar concentration therefore

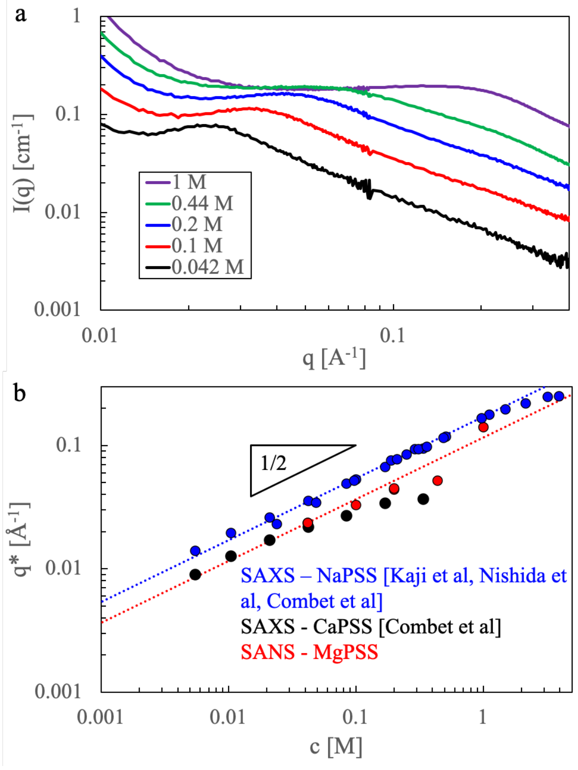


FIG. 1. a: Scattering profiles of MgPSS in salt-free D_2O for various polymer concentrations, indicated on the legend. b: Position of scattering peak as a function of polymer concentration. Red points are for MgPSS (this study), black points are for CaPSS, measured using SAXS by Combet et al[63,64] and blue points are for NaPSS, data by Kaji et al[70] Nishida et al[71] and Combet et al[63,64] using SAXS. Lines are power-laws: $q^* = 0.12c^{1/2}$ Åand $q^* = 0.17c^{1/2}$.

correspond to higher values of *B* indicating more locally collapsed chains. Fitting the high-q region of the SANS spectra to a worm-like chain form factor is expected to show this difference in the mass per unit length of NaPSS and MgPSS. This is however not observed in our experiments.

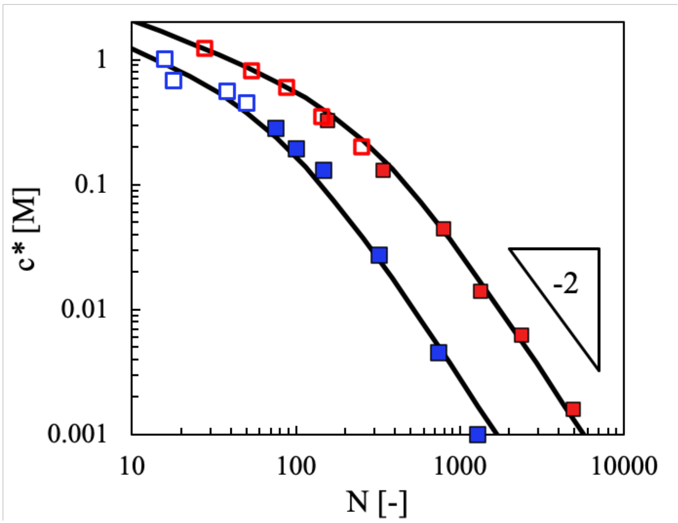


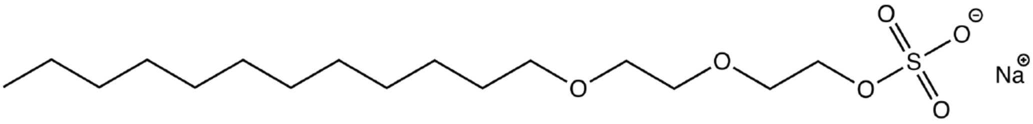
FIG. 4. Overlap concentration of MgPSS (red symbols) and NaPSS (blue symbols) in DI water as a function of degree of polymerisation. Full symbols are estimates obtained from a viscosity-concentration plots and hollow symbols are obtained from viscosity-molar mass plots. In both cases c^* is determined using the Colby criterion ($\eta_{sp}(c^*) = 1$). Lines are empirical fits to Eq. 4 with $g_T = 205$ (MgPSS) and $g_T = 65$ NaPSS.

Given this discrepancy, we compare the viscosimetric size of chains for NaPSS and MgPSS as a function of degree of polymerisation in Figure 2 (colour scheme is the same as in Figure 1). The overlap concentration ($c^* \approx N/R^3$, where R is the chain size) scales as the N^{-2} for both polyelectrolytes, which is consistent with a solvent quality exponent of $\nu = 1$ and with the $\xi \approx c^{-1/2}$ observed by SANS. The larger values of c* for MgPSS compared to NaPSS are also consistent with the correlation length data discussed above. Still, the question remains as to the lengthscale on which MgPSS is more collapsed than NaPSS. As we are not able at present to reach a satisfactory conclusion on this point, we will be investigate the issue in future work.

SLES and MES in water with and without divalent ions

The two surfactant systems studied, sodium lauryl ether sulfate (SLES) and methyl ether sulfonate (MES) were measured as a function of surfactant concentration in aqueous D_2O solution at an ionic strength of 0.011 M. For the SLES system, the content of Ca2+ ions in the aqueous media was varied. The MES surfactant was found to precipitate upon addition of calcium and hence was not measured.

Figure 2 shows the structure of the SLES surfactant and the scattering curves for the highest and lowest measured concentrations of SLES in D_2O without calcium ions. The data are fitted to a tri-axial ellipsoid form factor and the interparticle structure factor is calculated using the Hayter-Penfold mean spherical approximation. For the highest concentration, where we obtain the best agreement between model and experiment, we find R1 ≈ R2 ≈ 22Å and R3 ≈ 42 Å, revealing rather anisotropic micelles. These results differ from simulation results using either fully atomistic or coarse grained surfactant molecules, both of which show R1 ≈ R2 ≈ R3 within about 10% accuracy. The reason for the discrepancy is not clear to us at present and we are working to resolve it.



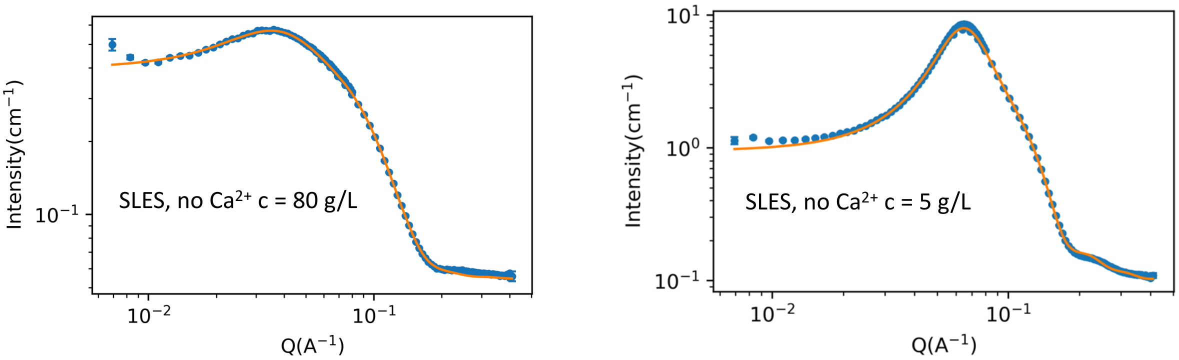


Figure 2: Top panel: structure of SLES. Modelling of SLES surfactants using an ellipsoidal form factor combined with the mean spherical approximation.