Experimental report

13/06/2021

Proposal: EASY-440 **Council:** 4/2019

Title: Bulk structure of nonionic and mixed nonionic-ionic surfactant micelles determined by SANS

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Michael LUDWIG

Experimental team:

Local contacts: Ralf SCHWEINS

Samples: NaC12H25SO4

Instrument	Requested days	Allocated days	From	To
D11	12	12	29/08/2019	30/08/2019

Abstract:

The aim of this work is to improve the understanding of structural forces in mixtures of nonionic-ionic surfactant micelles (nonionic: Tween 20, ionic: SDS). Therefore, the structural forces of these systems are already successfully measured by AFM, indicating that the micellar shape remains spherical after adding up to 30% of ionic species to nonionic dispersions. This doping of uncharged surfactant micelles can be used for a very precise control of the structural forces in those systems. By using SANS we want to determine the bulk structure (i.e. the micellar shape (extracted from P(Q)) and average inter-micellar distance (extracted from S(Q))) of these dispersions to complement this work. In works by other groups it is shown that the average interparticle spacing in bulk matches the wavelength of the structural forces so that the bulk nanostructure determines the structural forces itself. Even though this outcome marked a huge success in the description of the structural forces a quantitative theoretical model to describe the experimental data is still missing. This work is part of the PhD project of M. Ludwig which is supposed to finish spring 2020.

Bulk structure of nonionic and mixed nonionic-ionic surfactant micelles determined by SANS

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(Dated: June 13, 2021)

Date Performed: 29/08/19 - 30/08/19
Proposal number EASY 440
Beamline: D11

EXPERIMENT DESCRIPTION AND OBJECTIVES

Small-angle neutron scattering experiments were carried out on the D11 beamline at the Institut Laue-Langevin (ILL, Grenoble, France). A neutron wavelength of $\lambda = 5.5$ nm with $\Delta\lambda/\lambda = 0.1$ and sample-detector distances of 1.8 and 8 m were used to cover a q-range of 0.006 to 0.395 Å^{-1}. Samples were measured in Hellma quartz cells with a path-length of 2 mm. The temperature was adjusted to 20.0 °C. The sample scattering was normalised with respect to incident intensity, transmission, sample thickness, acquisition time and background. The data were brought to absolute scale using ultrapure water as secondary standard. Data reduction was done using the Lamp software on site of the ILL.

MATERIALS

The nonionic surfactants Tween20 (also known as polysorbate 20) and BrijL23 ($C_{12}E_{23}$, previous brand name: Brij 35 were purchased from Sigma Aldrich (Darmstadt, Germany). The anionic surfactant sodium dodecyl sulfate (SDS, ultrapure) was purchased from PanReac AppliChem (Darmstadt, Germany). Heavy water (D_2O, 99.9 atom% D) was purchased from Sigma Aldrich (Darmstadt, Germany). All chemicals were used without further purification. Before use, all glassware was cleaned by soaking in aqueous Hellmanex III (Hellma Analytics, Müllheim, Germany) solution for at least one hour and rinsing with large amounts of ultrapure water (milliQ-grade, 18.2 MΩ cm resistivity, Merck, Darmstadt, Germany). The surfactant solutions were prepared in D_2O. The mixed surfactant systems were prepared by mixing surfactant stock solutions. All samples were prepared three days before each experiment to allow sufficient dissolution.

DATA ANALYSIS

A monodisperse core-shell ellipsoid model is used to describe the form factors $P(q)$ of single micelles, see SASView 5.0.3 documentation for details). The main parameters in this model are: the equatorial radius of the core (r_c), the axial ratio between the polar and the equatorial radius of the core (x_c), and the thickness of the shell (t_s), which is assumed constant throughout the whole area. The scattering length density of the core (ρ_c), the shell (ρ_s), and the solvent (ρ_{D_2O}) represents the contrast of the micelles.

Two different interaction potentials to fit the structure factor $S(q)$ are used. For micelles with a charged surface, the RMSA (rescaled mean spherical approximation) based on the mean spherical approximation (MSA) from Hayter and Penfold is used. For uncharged particles, a hard-sphere interaction potential with the Percus-Yevick closure relationship is used (HS-PY).

In order to reduce the number of fit parameters, following assumptions are made: the micellar core consists of hydrophobic hydrocarbon chains; the shell contains the surfactant polar headgroups hydrated by water molecules that can penetrate the shell but not the core. The equatorial radius of the micelle core r_c is fixed to 1.67 nm, being the length of a fully extended dodecyl hydrocarbon chain. The core extends in the direction of the polar radius and is fitted by the axial ratio of the core x_c. The core is assumed to only contain hydrocarbon chains, so that the scattering length density (SLD) of the core is fixed to $\rho_c = -0.39 \times 10^{-6}$ Å^{-2}. The solvent SLD is $\rho_{D_2O} = 6.34 \times 10^{-6}$ Å^{-2}. The fitted shell thickness t_s is constant throughout the whole area of the micelle. The strong hydration of the surfactant polar groups was taken into account by fitting the SLD of the shell ρ_s. Self-consistent fitting was checked using material balance equations from known molecular volumes and SLDs. Nonionic surfactants feature low critical micelle concentrations which are neglected in the calculations.

PRELIMINARY RESULTS

Mixed micelles in dilute conditions

Fig. 1 shows the SANS scattering data of mixed solutions of (a) nonionic Tween20 and anionic SDS and (b) nonionic BrijL23 and anionic SDS. The molar mixing ratio $X = [\text{SDS}]/([\text{SDS}]+[\text{nonionic}])$ is kept constant at $X = 0.35$ and $X = 0.32$, for SDS/Tween20 and SDS/BrijL23, respectively. The total surfactant concentration c, [SDS]+[nonionic], is being varied. For comparison, the scattering data of the respective pure nonionic surfactant solutions are added to the graph (grey squares).

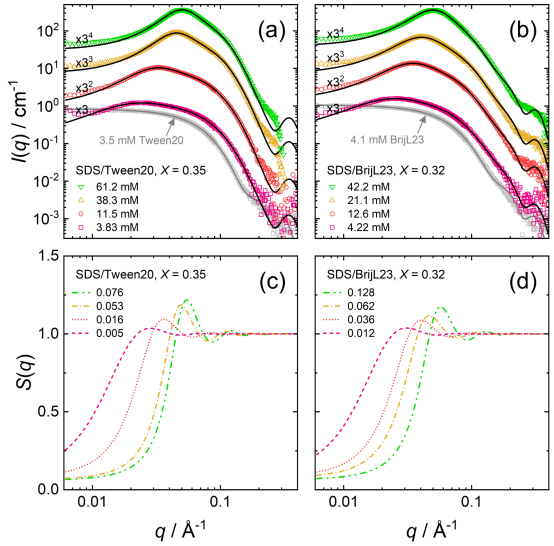

FIG. 1. SANS data for mixed micellar dispersions at various concentrations: (a) SDS/Tween20, (b) SDS/BrijL23. Symbols are experimental scattering data. The black solid lines are model fits to the data. Data sets are scaled by the factors in black for clarity. Extracted structure factors $S(q)$ from the model fits: (c) SDS/Tween20, (d) SDS/BrijL23. Data are given for different volume fractions ϕ.

Table I summarises the parameters extracted from the SANS model fits (core-shell ellipsoid + RMSA structure factor) of SDS/Tween20 and SDS/BrijL23 solutions. Fitted values: volume fraction ϕ, axial ratio of the core x_c, shell thickness t_s, the shell scattering length density ρ_s, and the charge per micelle z. Calculated values: the effective radius r_{eff}, the aggregation number N_{agg}, and the fractional charge β.

TABLE I. Parameters extracted from SANS model fits (core-shell ellipsoid form factor + RMSA structure factor) of mixed nonionic-anionic micelles in D_2O at 20.0 °C

X	c mM	ϕ	x_c	t_s nm	$\rho_s \cdot 10^{-6}$ Å^{-2}	r_{eff} nm	N_{agg}	β
SDS/Tween20								
0.35	3.83	0.005	1.94	1.85	5.35	3.70	94	0.10
	11.5	0.016	1.87	1.82	5.36	3.61	85	0.15
	38.3	0.053	1.88	1.74	5.40	3.63	88	0.18
	61.2	0.076	1.90	1.74	5.36	3.65	99	0.17
SDS/BrijL23								
0.32	4.22	0.012	1.89	2.28	5.78	4.39	77	0.12
	12.7	0.036	1.80	2.20	5.71	4.28	69	0.17
	21.1	0.062	1.82	2.18	5.68	4.26	66	0.18
	42.2	0.128	1.77	2.18	5.64	4.24	63	0.20

Concentrated mixed micelles

Fig. 2 shows SANS data of mixed surfactant solutions at high total surfactant concentrations c and at various mixing ratios X.

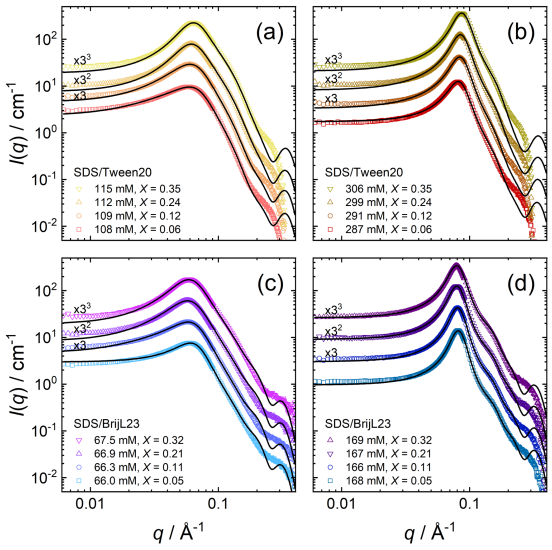

FIG. 2. SANS data for surfactant mixtures at varying mixing ratios $X = [\text{SDS}]/([\text{SDS}]+[\text{nonionic}])$: (a), (b) SDS/Tween20, and (c), (d) SDS/BrijL23. Symbols are experimental scattering data. The black solid lines are model fits to the data. Data sets are scaled by the factors in black for clarity.

Table II summarises the parameters extracted from the SANS model fits (core-shell ellipsoid + RMSA structure factor) of SDS/Tween20 and SDS/BrijL23 solutions, respectively. Fitted values: volume fraction ϕ, axial ratio of the core x_c, shell thickness t_s, shell scattering length density ρ_s, and the charge per micelle z. Calculated values: the effective radius r_{eff}, the aggregation number N_{agg}, and the fractional charge β.

TABLE II. Parameters extracted from SANS model fits (core-shell ellipsoid form factor + RMSA structure factor) of mixed SDS/Tween20 surfactants in D_2O at 20.0 °C. For some solutions fits with the RMSA structure factor did not converge and fitting was carried out using the HS-PY structure factor instead with no fractional charge β extracted.

X	c mM	ϕ	x_c	t_s nm	$\rho_s \cdot 10^{-6}$ Å^{-2}	r_{eff} nm	N_{agg}	β
0.06	108	0.207	2.26	1.83	5.14	4.10	91	0.06
	143	0.257	2.17	1.80	5.14	4.03	92	0.06
	216	0.343	2.09	1.77	5.21	3.96	98	–
	287	0.369	1.85	1.73	5.26	3.82	109	–
0.12	109	0.215	2.21	1.85	5.22	4.10	88	0.11
	146	0.270	2.17	1.82	5.21	4.05	90	0.10
	218	0.340	2.01	1.74	5.20	3.90	96	0.09
	291	0.390	1.85	1.67	5.19	3.76	100	0.08
0.24	112	0.200	2.02	1.78	5.37	3.94	87	0.18
	149	0.278	2.12	1.78	5.33	3.99	86	0.16
	224	0.352	1.99	1.71	5.30	3.86	93	0.13
	299	0.396	1.87	1.63	5.28	3.73	99	0.11
0.35	115	0.202	1.92	1.71	5.44	3.83	81	0.21
	153	0.268	1.96	1.71	5.47	3.85	82	0.20
	230	0.349	1.93	1.65	5.44	3.77	89	0.16
	306	0.395	1.83	1.56	5.37	3.64	94	0.13

Simliar trends are observed for the SDS/BrijL23 fit parameters.