Experimental report

13/09/2022

Proposal: **INTER-557** **Council:** 4/2021

Title: localisation of dye in micelles

Research area:

This proposal is a new proposal

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Experimental team: Wenke MUELLER

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Samples: D_2O
organic Azo dye HCB18 ($C_{13}H_9ClN_4O_3S_2$)
cationic surfactant DTAB ($C_{15}H_{34}BrN$)
d25-DTAB ($C_{15}D_{25}H_9BrN$)
d34-DTAB ($C_{15}D_{34}H_9BrN$)
sodium carbonate buffer ($NaHCO_3/Na_2CO_3$)

Instrument	Requested days	Allocated days	From	To
D11	1	1	13/09/2021	14/09/2021

Abstract:

Abstract: The morphology of co-assemblies from two commercial azo dyes and various surfactants was observed with small-angle neutron scattering (SANS). The experiment was focused on assemblies between the dye Red (Figure *1*) and dodecyltrimethylammoniumbromide (DTAB). Dependent on stoichiometry cylindrical or ellipsoidal micelles are formed. By contrast variation, Red was located on a surface layer of the assemblies. Furthermore, datasets from previous SANS experiments studying the assembly of Blue (Figure *1*) with DTAB were completed and preliminary data for the planning of future experiments recorded.

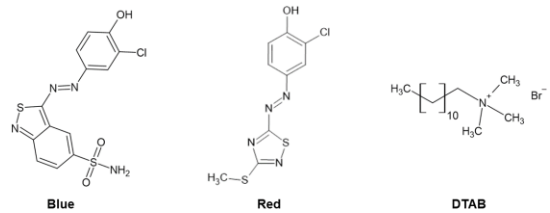

Figure 1: Chemical structure of two dyes and one cationic surfactant

Scientific Background: Aqueous solutions of dye and surfactant are of major significance in practical applications such as textile dyeing, wastewater-treatment and cosmetics. Hence, numerous studies investigating dye-surfactant interaction were performed.[1] Changes in the UV/vis absorption spectrum of the dye upon surfactant-addition gave raise to assumptions about the polarity of the environment of the dye and its location within the surfactant micelle. However, these assumptions have yet to be confirmed with measurements that unambiguously reveal (a) size and shape of the dye-surfactant aggregate and (b) the location of the dye within the aggregate.
Small-angle scattering (SAS) provides answers to task (a). Concerning the investigation of dye-surfactant aggregation with SAS, only one publication describing the aggregation of an anionic dye and cationic surfactants is known to us. Here, worm-like or cylindrical aggregates were described.[2] For an unambiguous localization of the dyestuff within the micelles, as it is addressed in task (b), contrast variation in SANS needs to be employed.

Materials and Methods: All samples were prepared in an alkaline $NaHCO_3/Na_2CO_3$ buffer solution in D_2O with pD = 10.7 and an ionic strength of $I = 0.25$ M. Contrast variation experiments were performed with DTAB. For full contrast measurements, h^{34}-DTAB was used. For measurements, where DTAB was matched to the D_2O-solvent, the scattering length density of DTAB was adjusted to that of the solvent by using a mixture of d^{25}-DTAB and d^{34}-DTAB at matching composition (46 vol%/54 vol%). This composition was determined during previous experiments. All SANS-experiments were performed on the instrument D11 employing a neutron wavelength of 6 Å and three sample-detector distances (38.0 m collimation 40.5 m, 10.5 m collimation 10.5 m, 1.7 m collimation 2.5 m) to cover a q-range of 0.0014 $Å^{-1}$ to 0.5 $Å^{-1}$. A circular neutron beam with a diameter of 14 mm was used.

Results: The experiment was organised into three parts: (1) Continuation of a previous experiment, (2) contrast variation to obtain an information about the location of Red in Red/DTAB-assemblies, and (3) observation of assemblies formed between Blue and other surfactants to record preliminary data for future experiments.

(1) Continuation of previous experiment: Assemblies between Blue and DTAB: Investigations on the assembly between Blue (Figure 1) and DTAB was performed to complete a series of existing investigations. Results are displayed in Figure *2*. Full contrast SANS curves were best described by a form factor consisting of the sum of cylinders and oblate ellipsoids. DTAB-matched curves were fitted with the same form factor model, but assuming a core-shell distribution of scattering lengths densities, leading to the conclusion that Blue is located on the outside of Blue-DTAB assemblies.

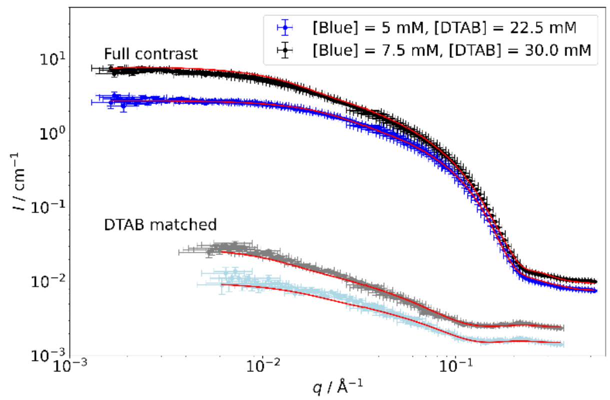

Figure 2: SANS-curves and fits (red) of solutions containing Blue and DTAB at a 1:4.5 ratio (blue) or 1:4 ratio (black/grey). Curves displayed in higher brightness represent DTAB-matched measurements.

(2) Contrast variation for the localization of Red in assemblies between Red and DTAB: A complete series of measurements on the assembly between Red and DTAB was performed. Full-contrast measurements yielded SANS-curves that were best described with cylinder or prolate ellipsoid form factors, dependent on the ratio between Red and DTAB (Figure 3). DTAB-matched curves were fitted with corresponding core-shell models, leading to the conclusion that Red is located on the outside of Red-DTAB assemblies.

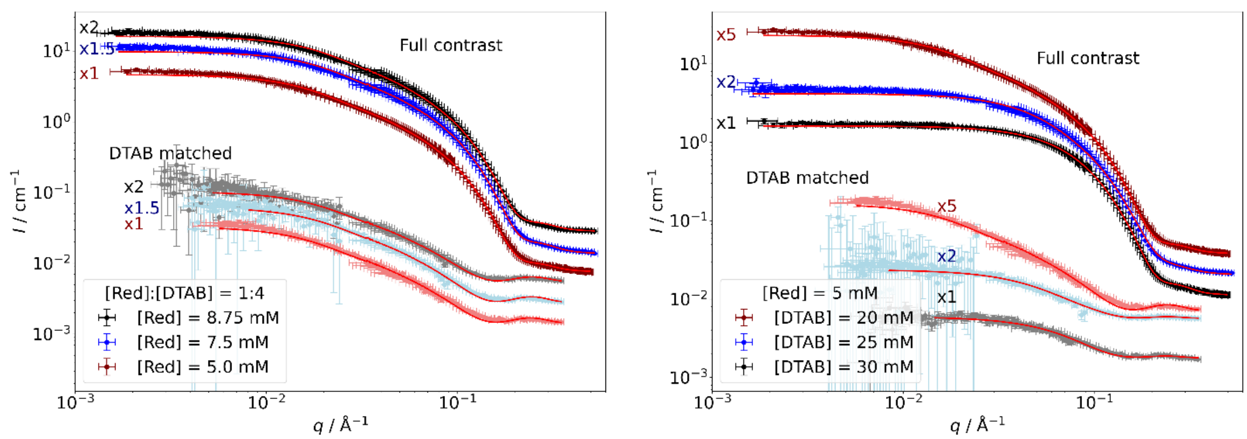

Figure 3: SANS curves and fits containing Red and DTAB at varying ratio. Curves with a lower brightness indicate the full contrast measurement, whereas curves of the same color but with higher brightness indicate the DTAB-matched measurement of the corresponding sample. Form factor fits are displayed in red.

(3) *Assembly of Blue with other surfactants:* The supernatant of a solution containing Blue and the cationic surfactant cetyltrimethylammoniumbromide (CTAB) at equimolar concentration showed the absence of CTAB micelles, whereas in a solution with four-fold CTAB excess oblate ellipsoidal micelles were found (Figure 4, left). Addition of Blue to a solution of sodiumdodecylsulfate (SDS) did not show any effect on the morphology of pure SDS micelles (Figure 4, right).

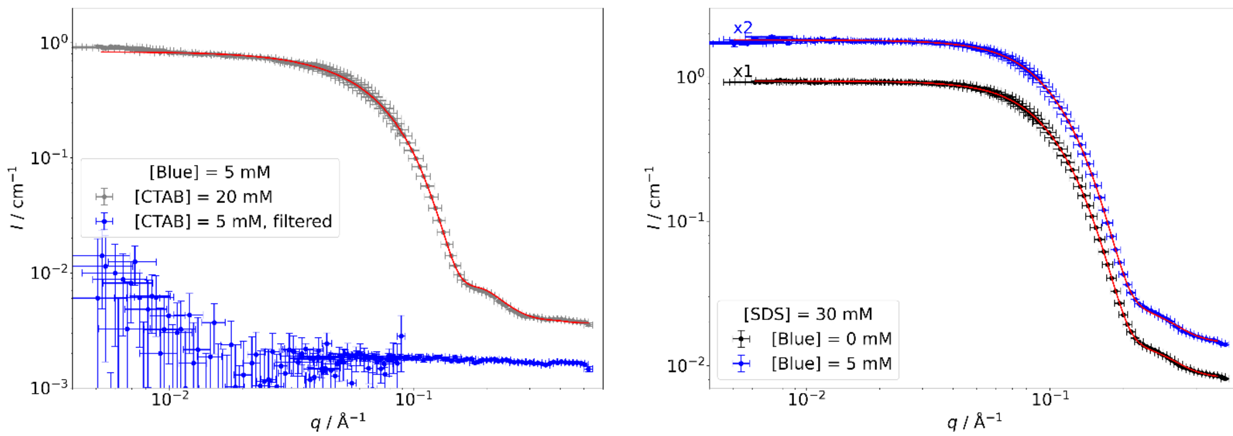

Figure 4: Left: SANS curve of a solution containing Blue and CTAB at a 1:4 ratio (grey) and SANS curve of the supernatant of a sample showing precipitation (blue). Right: SANS curves of solutions containing SDS and no (black) or 5 mM of Blue (blue). Form factor fits are displayed in red.

Sources:

[1] A. R. Tehrani-Bagha, K. Holmberg, *Materials* **2013**, *6*, 580–608.

[2] A. Kutz, G. Mariani, F. Gröhn, *Colloid Polym Sci* **2016**, *294*, 591–606.