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SANS contrast variation for the localization of anionic dyes in DTAB-micelles

Aqueous solutions of dye and surfactant are of major significance in industrial 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 induced 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 the first question. 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 the second question, contrast variation in small-angle neutron scattering (SANS) needs to be employed.
We studied the interaction of two commercial, anionic azo dyes (**Blue** and **Red**) with the cationic surfactant dodecyltrimethylammoniumbromide (**DTAB**) in an aqueous, alkaline buffer solution. These azo dyes self-assemble in the absence of surfactant. Whereas **Blue** forms dimers, **Red** self-assembles to higher aggregation numbers in the employed buffer. At a given dye concentration, addition of **DTAB** leads to a change in the absorption spectrum of the dye, indicating a redistribution of intermolecular interactions. Using SANS, we were not only able to determine shape and size of dye-surfactant aggregates, but also to locate the dye within the dye-surfactant micelle employing contrast variation by isotopic substitution of h34-**DTAB** with a mixture of d25-**DTAB**/d34-**DTAB**. We will present SANS-data that reveal the formation of oblate ellipsoids, cylinders or flexible cylinders from **Blue** and **DTAB**, dependent on **Blue**/**DTAB**-ratio, and data showing the formation of prolate ellipsoids or cylindrical structures from **Red** and **DTAB**. In all cases, the dye was found to be located on the outside of the surfactant micelle.

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1 A. R. Tehrani-Bagha, K. Holmberg, Materials, 6 (2013), 580–608.
[2] A. Kutz, G. Mariani, F. Gröhn, Colloid Polym. Sci, 294 (2016), 591–606.

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