

Time-Resolved SAXS on the Aggregation of Azo Dyestuffs

R. Michels and K. Huber

Department Chemie, Universität Paderborn, Warburger Straße 100, 33098 Paderborn, Germany

By this experimental report, we tend to give a brief overview on representative results and general aspects that may be deduced from the scattering data collected at ID02 between the 3rd and 5th September 2010. Data evaluation is not yet entirely completed and will still keep us busy for while.

The aggregation process of anionic azo dyestuffs in the presence of strontium and barium cations has been followed by time-resolved small-angle x-ray scattering (SAXS). Aggregation was initiated by combining aqueous solutions of dyestuff and the chlorides of the earth alkaline metals. To achieve a well defined start and the feasibility to record the scattering during the first second of the aggregation process, mixing of components was performed by means of a stopped-flow device. SAXS measurements were performed on samples with different dyestuff-to-metal ratios at detector distances of 10 m, 5 m and 1 m.

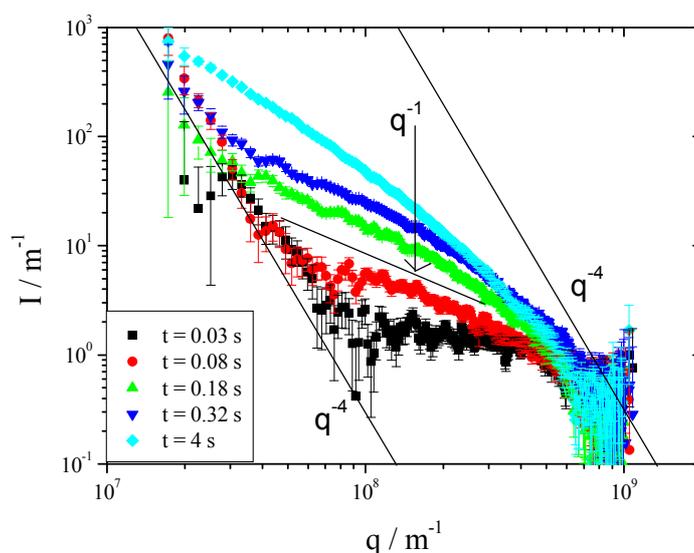


Figure 1: Representative set of scattering curves recorded at 10 m detector distance.

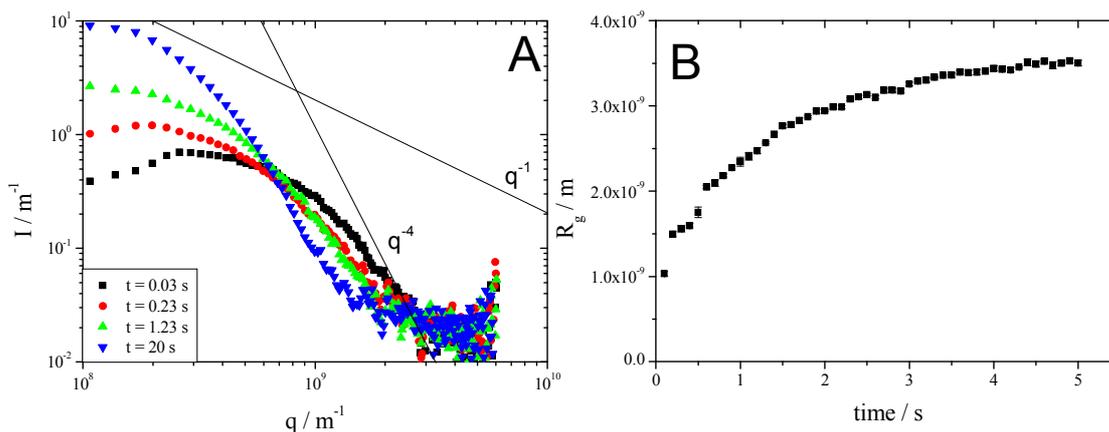


Figure 2: Representative scattering patterns recorded at 1 m detector distance (A) and the evolution of the extracted size parameter R_g (B).

A representative set of scattering curves measured at 10 m detector distance is shown in figure 1. In the underlying experiment, the dyestuff was 0.33 g/l and the barium concentration was 1.6 mM. The first curve recorded just ~ 30 ms after mixing the components already exhibits a q^{-4} decrease at 0.1 nm^{-1} , which probably denotes the existence of large micells the Guinier regime of which is not captured by the present q -regime. In the middle q range, scattering intensity increases strongly within the first half second, and the representative curves recorded at 80, 180 and 320 ms exhibit a distinct q^{-1} decrease. This indicates the growth of local rod-like structures by a very fast aggregation process. At high q , even a Porod regime becomes apparent for curves recorded after 320 ms. However, the corresponding q -regime is captured superiorly at 1 m detector distance. For measurements at 1 m detector distance, a representative set of scattering curves is shown in figure 2 (A). Here, the dyestuff was 0.33 g/l and the barium concentration was 0.8 mM. The curves illustrate how the Porod regime is shifted to smaller q over the time. This aspect may be interpreted by a growing cross-section of cylindrical structures. The “Guinier regime” of the cross-section of cylindrical structures is situated at slightly lower q than the Porod regime which represents the curved surface. It generally superposes with the typical q^{-1} decrease of the rod-like structure. Thus a more quantitative analysis of the trend illustrated in figure 2 (A) can be performed by means of a plot $\ln(q \cdot I(q))$ versus q^2 . In this plot mode, the curves indeed exhibit a pronounced “Guinier regime”. The corresponding size parameter may be interpreted as the radius of gyration (R_g) of a cylinder cross-section. Its evolution is illustrated in figure 2 (B) and denotes a decreasing growth from 1 to around 3.5 nanometers.