

**Experiment title:**

Kinetics of vesicle and nanodisk formation in mixtures of cationic and anionic surfactants as probed by means of stopped-flow experiment.

Experiment**number:**

SC-730

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Report:

The self-assembly of amphiphilic molecules is a ubiquitous phenomenon ranging from biological membranes to commercial systems such as detergent, food, etc. Much is known about the static phase behaviour of such amphiphilic systems the dynamics of morphological transitions in such systems have only much less intensively been studied. In that context the transformation of mixtures of cationic and anionic micelles to vesicles has been studied by time-resolved small-angle x-ray scattering (SAXS). Catanionic mixtures are known to have a strong propensity for the formation of vesicular systems or disk-like aggregates.

For that purpose equimolar amounts of ionic surfactant solutions, the anionic TexaponN₇₀-H and the cationic TTAOH, were mixed by a stopped-flow device and the evolution of the scattering curves was followed with time resolution of 20-50 ms. Fig. 1 shows the scattering curves in the larger q-range of the 2 pure surfactant solutions and the temporal evolution of the mixed solutions. It is evident that within the mixing time (< 10 ms), mixed micelles are formed. Immediately after the mixing process, a transient intensity maximum appears at $q \approx 1.25 \text{ nm}^{-1}$ that vanishes within about 400 – 1000 ms. This broad peak has to be due to micelles that are present directly after the mixing

process. Obviously the globular micelles dissolve within about 400-1000 ms and this is the first time than one has observed directly the disappearance of such mixed micelles in a SAXS experiment.

Fig. 2 displays the corresponding scattering curves at low q as a function of time. Already at very short times of 100 ms, the scattering from locally flat objects can be observed in the lower q -range. However, only after much longer times of 5 s the oscillations typical for the presence of unilamellar vesicles are observed. These oscillations move towards lower q and become more pronounced with time, i. e. these vesicles then grow in size and become more monodisperse with a time constant of 20-30 s. It is interesting to note that the vesicle formation is a purely self-associative process and only starts long after the mixing process is over. This demonstrates that these vesicles are not formed due to any shear forces, which is a very important aspect with respect to the thermodynamic stability of such vesicles. As an intermediate structure disclike micelles have been identified that grow with time and then close to form unilamellar vesicles.

Because of the high time resolution, we are able to observe both the break-up of the initial micelles and the formation of the vesicular structures in a single experiment. These results demonstrate that the stopped-flow method combined with ms time-resolved SAXS measurements is a suitable tool for the investigation of fast complex structural reorganization processes in amphiphilic assemblies as well as many other soft matter systems.

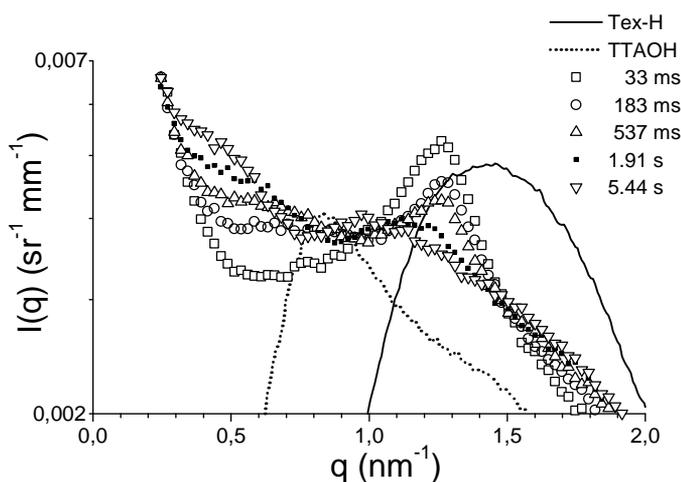


Fig. 1: Time evolution of the SAXS intensity for a system of 50 mM TTA/Texapon- N_{70} at 25 °C following their rapid mixing. In addition curves for 100 mM Texapon N_{70} -H and 100 mM TTAOH are given. [1]

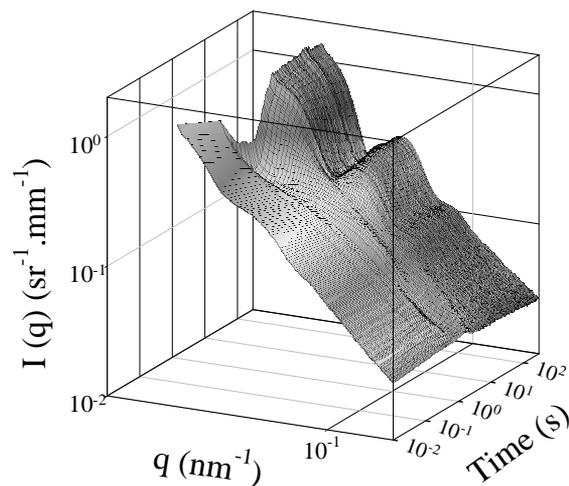


Fig. 2: Evolution of the SAXS intensity in the small q range for a system of 50 mM TTA/Texapon- N_{70} after rapid mixing. The formation of vesicles is marked by the appearance of well-defined oscillations. [1]