Fusion and fission of catanionic bilayers

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Supplementary Information

Tetradecyltrimethylammonium octylsulfonate ($TA_{14}So_8$)-water system

Preliminary data on the tetradecyltrimethylammonium octylsulfonate ($TA_{14}So_8$)-water system also supports the view that these fusion and fission phenomena may be extensive to other salt-free catanionics with asymmetric chain lengths. Fig. B1a shows the temperature-composition map with the observed structures at rest. At room temperature polydisperse vesicles exist, as suggested by SANS data (q^{-2} decay) combined with light microscopy (which shows vesicles in Brownian motion). At high temperatures the solutions are clear and viscous, suggesting the existence of elongated micelles, in analogy to $TA_{16}So_8$. At intermediate temperatures the samples also become extremely turbid (Fig. B1b). SANS data (Fig. B2) further suggests that the turbid region consists of a two-phase region of lamellae coexisting with micelles.

In this system, we followed the cooling process only by microscopy and turbidity. The microscopy data suggest again that the planar lamellae first form when the micellar phase is cooled down. As can be seen in Fig. B 3, a rough texture appears initially on cooling the samples (in the case of $TA_{16}So_8$ attributed to the coexistence between lamellae and micelles), followed by vesicles in Brownian motion on further cooling.

Considering that the hexadecylpyridinium octylsulfonate ($P_{16}So_8$) – water system also displays similar properties (though not yet studied in detail[1]) we suggest that this type of bilayer fusion and fission phenomena is a general feature for salt-free asymmetric catanionic surfactants.

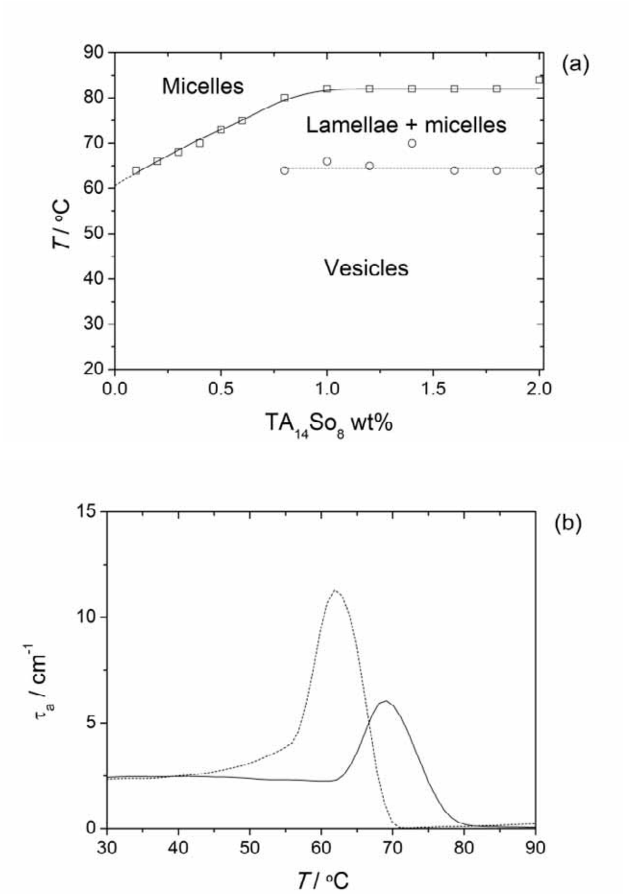

Fig. B1. (a) Temperature-composition map for the $TA_{14}So_8$-water system with the intermediate regions (i)-(iv) signaled as suggested by turbidity, optical microscopy and SANS. In analogy with the $TA_{16}So_8$ system the micelles are inferred by the fact that at high temperatures the samples are isotropic and viscous. (b) Turbidity scans for a 0.8 wt% sample, with the turbid region well evident between the vesicle and micelle regions. The straight line corresponds to heating and the dashed line to cooling.

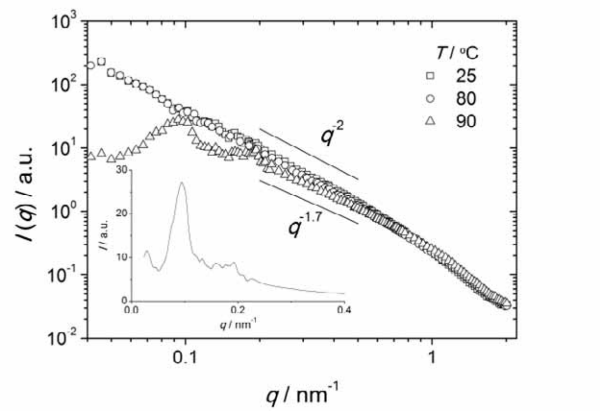

Fig. B2. SANS data for a 1 wt% $TA_{14}So_8$ in D_2O sample. At 25 and 80 ºC the SANS pattern displays a q^{-2} decay, consistent with polydisperse vesicles. At 90ºC two Bragg peaks develop, which are consistent with a lamellar arrangement. The decay also shifts to $q^{-1.7}$, which suggests that the lamellar phase may be coexisting with elongated micelles (which in the $TA_{16}So_8$ case displayed a $q^{-1.3}$ decay). The insert highlights the Bragg peaks in linear scale.

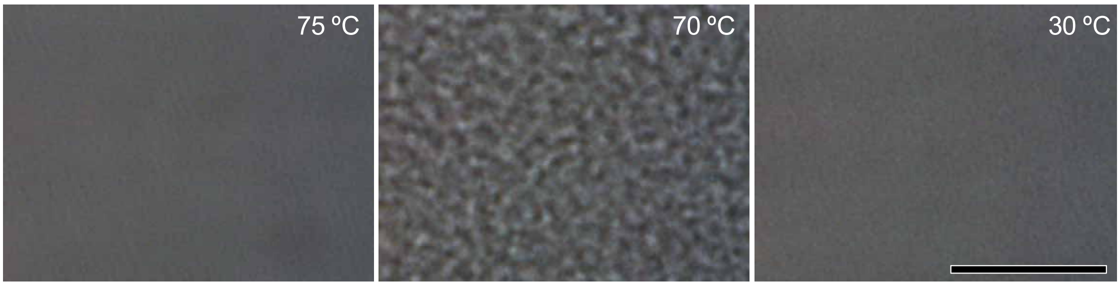

Figure B3. Cooling of a 0.8 wt% $TA_{14}So_8$ in water sample. The isotropic texture at 75 ºC transforms into a static and rough texture at ca. 70ºC (also observable on heating), before giving turn to polydisperse vesicles. At 30ºC the fraction with larger radius is visible with light microscopy in strong Brownian motion. The scale bar (common to all pictures) is 50 µm

1. B. F. B. Silva, E. F. Marques, U. Olsson and R. Pons, *Langmuir*, 2010, **26**, 3058-3066.