SANS Study on Self-Assembled Structures of Pluronic F127 Triblock Copolymer Induced by Additives and Temperature

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- SANS Model

A polymer micelle consisting of block copolymers with amphiphilicity can be described with the water insoluble core region and water soluble corona region surrounding the core. The scattering intensity for a polymer micelle contains four different terms: the self-correlation term of the core and the corona, and the cross-term between the core and the corona and between different chains, which can be written as following,

$$I(q) = N_{agg}\beta_{core}^2 P_{core}(q) + N_{agg}\beta_{corona}^2 P_{corona}(q) + 2N_{agg}^2\beta_{core}\beta_{corona}S_{corona-core}(q) + N_{agg}(N_{agg}-1)\beta_{corona}^2 S_{corona-corona}(q)$$

where N_{agg} is the aggregation number of F127 polymer forming the micelle and $\beta_{core} = V_{core}(\rho_{core} - \rho_{solvent})$ and $\beta_{corona} = V_{corona}(\rho_{corona} - \rho_{solvent})$, which are the excess scattering length of a block in the core and corona, respectively. V_{core} and V_{corona} are the total volume of a block in the core and the corona, respectively. ρ_{core}, ρ_{corona} and $\rho_{solvent}$ are the scattering length density of core, corona and solvent, respectively. $P_{core}(q)$, $P_{corona}(q)$, $S_{corona\text{-}core}(q)$ and $S_{corona\text{-}corona}(q)$ depend on the structure of micelle and can be described as following.

For the spherical shape,

$$P_{core}(q) = A^2(qR_{core}) \qquad A(qR) = 3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}$$

$$P_{corona}(q, R_g) = 2\frac{1 - \exp(-x) - 1 + x}{x^2} \qquad x = R_g^2 q^2$$

$$S_{coron-core}(q, R_{core}, R_g) = A(qR_{core})\,\phi(qR_g)\frac{\sin(q(R_{core}+R_g))}{q(R_{core}+R_g)}$$

$$\phi(qR_g) = \frac{1 - \exp(-qR_g)}{qR_g}$$

$$S_{coron-corona}(q, R_{core}, R_g) = \phi^2(qR_g)\left[\frac{\sin(q(R_{core}+R_g))}{q(R_{core}+R_g)}\right]^2$$

where R_{core} is the radius of the micelle core, R_g is the radius of gyration of polymer in the corona region. $P_{core}(q)$ was averaged over a Shultz-Zimm distribution of core radius.

For the cylindrical shape,

$$P_{core}\left(q, R_{core}, H\right) = \int_0^{\pi/2} \varphi^2(q, R_{core}, H, \alpha)\sin\alpha\, d\alpha$$

$$\varphi\left(q, R_{core}, H, \alpha\right) = \frac{2J_1(qR_{core}\sin\alpha)}{qR_{core}\sin\alpha}\frac{\sin\left(\frac{qH}{2}\cos\alpha\right)}{\frac{qH}{2}\cos\alpha}$$

$$P_{corona}\left(q, R_g\right) = 2\frac{1-\exp\left(-x\right)-1+x}{x^2} \qquad x = R_g^2 q^2$$

$$S_{coron-core}\left(q, R_{core}, H, R_g\right) = \phi\left(qR_g\right)\int_0^{\pi/2} \varphi(q, R_{core}, H, \alpha)\psi(q, R_{core}+R_g, H+2R_g, \alpha)\sin\alpha\, d\alpha$$

$$\psi\left(q, R_{core}+R_g, H+2R_g, \alpha\right) = \frac{R_{core}}{R_{core}+H}\frac{2J_1(qR_{core}\sin\alpha)}{qR_{core}\sin\alpha}\cos\left(\frac{qH}{2}\cos\alpha\right) + \frac{H}{R_{core}+H}J_0(qR_{core}\sin\alpha)\frac{\sin\left(\frac{qH}{2}\cos\alpha\right)}{\frac{qH}{2}\cos\alpha}$$

$$S_{coron-corona}\left(q, R_{core}, H, R_g\right) = \phi^2\left(qR_g\right)\int_0^{\pi/2} \psi^2(q, R_{core}+R_g, H+2R_g, \alpha)\sin\alpha\, d\alpha$$

where H is the length of the cylindrical micelle. $J_0(x)$ and $J_1(x)$ is the zeroth order and the first order Bessel function, respectively. α is the angle between the cylinder axis and the scattering vector, *q*. $P_{core}(q, R_{core}, H)$ was averaged over a Shultz-Zimm distribution of core radius.

- SANS Intensities of F127-5mS mixture at 308 K and 318 K

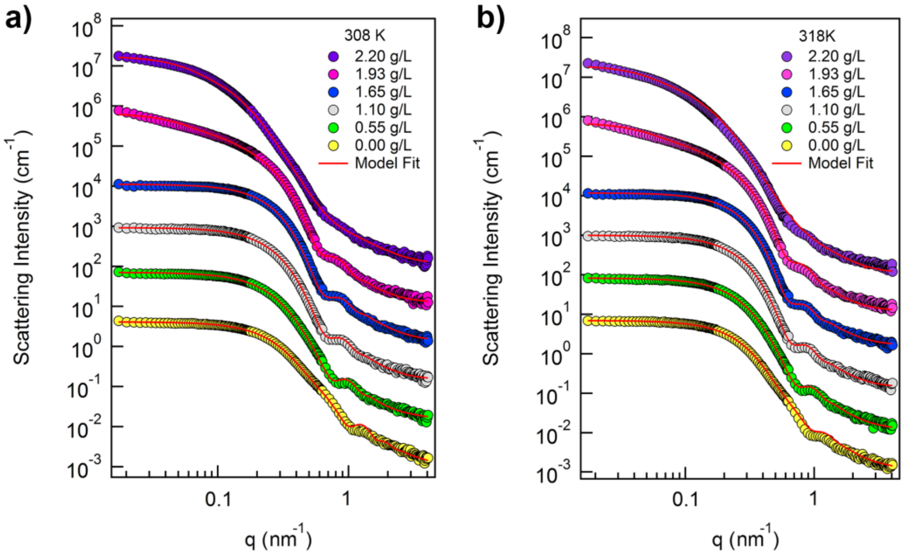

Figure S1. SANS intensities of F127-5mS mixture in D_2O with increasing 5mS concentrations at a) 308 K and b) 318 K. SANS intensities were vertically shifted for visual clarity.