[pex41] Cylindrical micelles and CMC

The energetic argument for the self-assembly of cylindrical micelles differs qualitatively from the that of spherical micelles [pex40]. Cylindrical micelles can grow with no change in curvatures, namely along the axis. The average change in free energy of an amphiphile when it joins a micelle has a much weaker dependence on the size of the micelle. This is reflected in the activation energy,

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{m}, \tag{1}$$

where α is an effective energy of the endcaps in units of the thermal energy. Similar to [pex40] we can write

$$X_m = m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \ldots \tag{2}$$

(a) Infer from expressions (1) and (2) the relation

$$X_m = m \left[X_1 e^\alpha\right]^m e^{-\alpha}, \tag{3}$$

by eliminating the chemical potential μ. Then show that the volume fraction of amphiphiles, $\phi = \sum_m X_m$, is related to the volume fraction of individual amphiphiles in solution, X_1, as follows:

$$\phi = \frac{X_1}{(1 - X_1 e^\alpha)^2}. \tag{4}$$

Solve this relation for X_1 and substitute it into (3) for a closed-form expression of the distribution of micelles, X_m, as a function of the amphiphile volume fraction ϕ and the parameter α that controls the longitudinal growth of cylindrical micelles. Show that for $\phi e^\alpha \gg 1$ that expression simplifies into the asymptotic form

$$X_m^{(as)} = m \left[1 - \frac{1}{\sqrt{\phi e^\alpha}}\right]^m e^{-\alpha}. \tag{5}$$

(b) Below the critical micelle concentration, $\phi < \phi_c$, we expect X_m to be a monotonically decreasing function of m. At $\phi > \phi_c$ we expect X_m to increase with m and reach a maximum for cylindrical micelles of a particular size, $m = m^*$. Infer ϕ_c for given α from the relation $X_1 = X_2$. Infer m^* from the asymptotic expression (5) and show that it approaches the value $\sqrt{\phi e^\alpha}$ for $\phi \gg \phi_c$.

(c) Plot X_m and $X_m^{(as)}$ versus m for $1 < m < 50$, $\phi = 0.05, 0.2, 0.5, 1.0$ (four solid curves and four dashed curves), and fixed $\alpha = 4$. Interpret your findings.

(d) Plot X_m and $X_m^{(as)}$ versus m for $1 < m < 400$, $\phi = 0.05, 0.1, 0.15, 0.2$ (four solid curves and four dashed curves), and fixed $\alpha = 10$. Interpret your findings.

(e) Predict the shape of the function $X_{m^*}^{(as)}$ for large m^* and compare that pediction with the location of the maxima in the curve s X_m versus m from parts (c) and (d).

[adapted from Jones 2002]

Solution: