[pex40] Spherical micelles and CMC

Here we examine the coexistence of individual amphiphiles and spherical micelles containing M amphiphilic molecules in aqueous solution using an energetic argument. Thermodynamic equilibrium dictates that the concentration of micelles of size m have concentrations,

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

where ϵ_m are activation energies of m-molecule aggregates and μ is the chemical potential (common to aggregates of all sizes).

(a) In a scenario that justifies that we only consider free amphiphiles ($m = 1$) and micelles of size $m = M$, infer from (1) the relation

$$X_M = M \left[X_1 \exp\left(\frac{-\Delta\epsilon_M}{k_B T}\right)\right]^M, \quad \Delta\epsilon_M \doteq \epsilon_M - \epsilon_1, \tag{2}$$

which is a special case of expression (3) in [psl14].

(b) Now consider a situation where $e^{-\Delta\epsilon_M/k_B T} = 10$. Plot concentrations X_1 of free amphiphiles and X_M of spherical micelles of size M versus the total volume fraction $\phi = X_1 + X_M$ of amphiphiles for the cases $M = 50, 100, 500, 5000$. Combine one set of four curves representing X_1 and a second set of four curves representing X_M all in the same graph.

(c) Interpret your findings. Identify the critical micelle concentration (CMC), ϕ_c, where the concentration X_1 reaches a plateau and the concentration X_M begins to rise. What is different for small and large values of M? How can these differences be interpreted?

[adapted from Jones 2002]

Solution: