Solutions to Soft Matter Exercise - Chapter 3: Micelles

1. Mixing

a. The thermal energy is $E_{therm} = k_B T$. Therefore, $E_{mix}/k_B t \approx 10$.

b. The energy required to place one molecule of pentane from pure pentane into water is much larger than the thermal energy, so this process is unlikely to happen spontaneously. As a result, the system will phase separate.

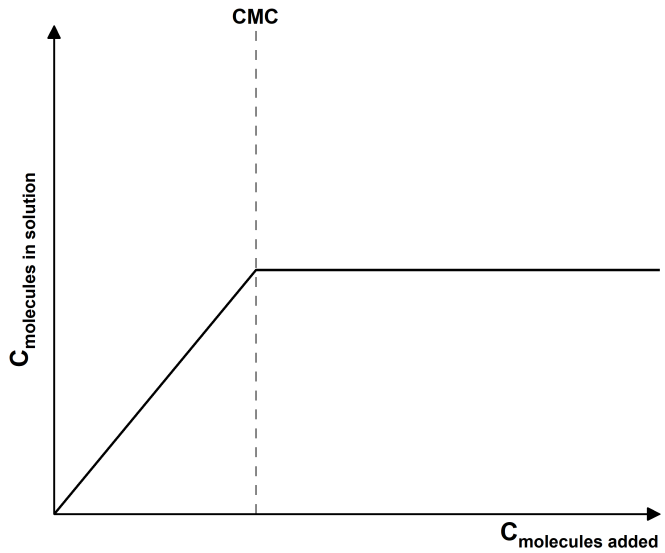
The exchange energy is so high because pentane cannot form hydrogen bonds with water molecules, so the enthalpy of the system does not increase upon the addition of a pentane molecule. However, the entropy decreases because the water molecules surrounding the pentane molecules become structured, thereby reducing their entropy. Therefore, the total Gibbs free energy increases such that pentane does not dissolve in water.

c. The foreign molecule can structure the water because the water molecules surrounding the foreign molecule will arrange themselves to minimize interaction with the foreign molecule and maximize the hydrogen bonds formed with other water molecules.

2. Critical Micelle Concentration

a. The critical micelle concentration (CMC) is the concentration of solutes above which micelles start to form.

b. The CMC is the concentration in solution above which this parameter remains constant, even if more molecules are added to the solution. These additional molecules form additional micelles.



3. Amphiphiles

a. Detergents form micelles that have a hydrophobic core. Hydrophobic dirt can be loaded into the core of the micelle and can thereby be solubilized and removed.

b. Detergents efficiently remove dirt if they form micelles. Micelles form if their concentration is above the CMC. If the CMC is reduced, fewer molecules are free in solution so the concentration of detergent molecules can be reduced without compromising the cleaning efficiency.

c. The CMC can be described as $CMC \approx \exp(-\frac{2\pi lry}{k_B T})$. Therefore, to decrease the CMC, r, l, or y should be increased. This can be achieved, for example, by elongating the hydrophobic chain (adding CH_2 groups to it), increasing l, thus decreasing the CMC. Alternatively, hydrocarbon chains with bulkier side groups or amphiphiles with two hydrophobic side chains can be used to increase r.

4. Micelles

a. The CMC is defined as CMC $\approx \exp(-\frac{\Delta E}{k_B T})$ where ΔE is the excess free energy. Therefore:

$$\begin{aligned}\Delta E = -\ln(CMC) \times k_B T = -\ln(5 \times 10^{-8}) \times 1.38 \times 10^{-23} \frac{J}{K} \times 298\ K \\ = 6.9 \times 10^{-20}\ J = 16.8\ k_B T\end{aligned}$$

b. The concentration of amphiphiles in solution is 50 mM, a concentration that exceeds the CMC ($CMC \approx 2.06 \times 10^{-8}\ M$). Thus, the vast majority of amphiphiles are assembled as micelles. A small fraction ($2 \times 10^{-8}\ M$) of amphiphiles is either dissolved as monomers or forming disordered aggregates. The concentration of aggregates containing N molecules can be calculated using: $X_N \approx N^{\alpha N}$
For spheres:

$$X_N = N[X_1 e^{\alpha}]^N e^{-\alpha N^{\frac{2}{3}}}$$

where

$$X_1 e^{\alpha} \approx 1$$

and from the text: $\alpha = 20$ and $N = 2$. Thus,

$$X_N = 2e^{-20 \times 2^{\frac{2}{3}}} = 3.25 \times 10^{-14} \text{ of } 2 \times 10^{-8} \text{ M}$$

Therefore, 3.25×10^{-12} % of aggregates contain two molecules. We find that a negligible fraction of amphiphiles form aggregates with $N = 2$ and even fewer molecules form larger aggregates. Therefore, the vast majority of molecules that are not contained in micelles are free molecules.
(**Attention!** α in this equation is the ratio of the excess free energy to the thermal energy $\alpha = \frac{\Delta E}{k_B T}$. It is different from the α that determines the shape of the aggregates: $\alpha = v/a_0 I_c$)

5. Surface Tension

a. At $c \geq CMC$, the interfacial tension remains constant. By looking at the table, we find that this is the case for concentrations at or above 8 mmol/L. Therefore, CMC $\approx$ 8 mmol/L.

b. The average area occupied by a single molecule is, by definition, the inverse of the packing density:

$$\alpha_0 = 1/(\text{packing density}) = 0.625 \text{ nm}^2$$

c. The shape is determined by the packing parameter $\alpha = v/a_0 I_c$. SDS has 12 C atoms and therefore 11 CH_2 groups and $n = 11$. As a result, we find that

$$l = (0.154 + 0.1265 \times 10)\ nm = 1.419\ nm$$

and

$$v = (27.4 + 11 \times 26.9) \times 10^{-3}\ nm^3 = 0.323\ nm^3$$

thus

$$\alpha = \frac{v}{a_0 l_c} = \frac{0.323\ nm^3}{0.625\ nm^2 \times 1.419\ nm} = 0.36$$

Therefore, the aggregate would be slightly elliptical.