Exercise 02 - Solutions

Energy and Entropy Competition in Micelle Formation

a) The change in entropy is given by

$$\Delta S = k_b lnW_f - k_b lnW_i = k_b \ln(\frac{W_f}{W_i})$$

Where W_f and W_i are the multiplicities for the system in the final and initial states respectively. If we schematise water in solution as described in the problem, with the oxygen at the center of a tetrahedron and the hydrogens pointing towards any two of the vertices, then there are six possible configurations for a water molecule to hydrogenbond with its neighbors. We remember from combinatorics that

$$W = \frac{n!}{k!\,(n! - k!)}$$

where n = 4 vertices to choose from and k = 2 hydrogens to arrange and thus a total 6 combinations or degrees of freedom. However, when a watermolecule is next to a apolar molecule, it cannot form a hydrogen bond in the direction of the vertex near this hydrophobic molecule. Therefore, $n_f = n_i - 1$ and the degrees of freedom reduce to 3.

$$\Delta S = k_b \ln\left(\frac{W_f}{W_i}\right) = -k_b \ln(2)$$

The change in the free energy per water molecule will then be

$$\Delta G = -k_b T \ln(0.5) = k_b T \ln(2)$$

Note that this change in energy is positive because it is unfavorable to immerse a hydrophobic molecule in water and thereby reduce the entropy of one or more water molecules.

b) For a molecule (ethane or methane) which we are approximating as a sphere of radius r, the surface area will be given by $SA_{\text{molec}} = 4\pi r^2$. To calculate the number of water molecules surrounding this sphere we caculate the surface area of one of the faces of the tetrahedra. We then divide SA_{molec} by this facial surface area per water molecule.

Note: there are other ways to do this, such as starting with the density of water and therefrom calculating the average spacing of water molecules. Then, using this distance as the radius of a circle of area that each water molecule takes up.

To get the length of each edge of the tetrahedra, we need to know the distance between each oxygen and the hydrogen it is hydrogen-bonded to. The length of a H-bond is about 1.8 Å, while a covalent O-H bond is about 1 A. So each tetrahedral edge a is given by $a = R * \frac{4}{\sqrt{6}} = 4.57$ Å , where R is the distance from one oxygen to any vertex of the tetrahedron and thus $R = 2.8$Å . Since each tetrahedral face is an equilateral triangle, the total surface area of each face is $a^2 * \frac{\sqrt{3}}{4} = 9.16$ Å^2 . The number of water molecules surrounding a sphere of radius r is then $\frac{4\pi r^2}{9.16\text{Å}^2}$ and the total interfacial energy is

$$\frac{4\pi r^2}{9.16\text{Å}^2} * \ln(2) k_b T = 0.95\ r^2 k_b T$$

The interfacial energy γ is then given by $\gamma = \frac{ln(2)k_bT}{9.16\ \text{Å}^2} = \frac{0.69}{9.16\ \text{Å}^2} = \frac{0.075k_bT}{\text{Å}^2}$. We will round γ = 0.1 $k_bT/\text{Å}^2$.

Now considering Methane, and CH-bonds = 1.1 Å as well as a van der Waals radius for Hydrogen of 1 Å, we will call it a sphere of radius 2 Å and surface area 50 Å^2. Using above equations and $\frac{50\text{Å}^2}{9.2\text{Å}^2} = 5$, we know that around 5 water molecules will be surrounding a methane. The total interfacial eneregy will be about 5 k_bT. Using 1 k_bT = 4.1*10^{-21} J and 1 Joule = 0.239 calories this amounts to 2 *10^{-20} Joule.
In the case of ethane, it is almost 2 methanes stuck together and we estimate the total surface area as 100 Å^2. Total number of watermolecules surrounding are then ca. 11 and the energy cost to dissolve methane in water amounts to about 10 k_bT.

c) If we approximate lipids as cylinders of hydrophobic surface, the total surface area will be $2\pi rL + \pi r^2$. Note that one end will have a polar headgroup and will not contribute to the total hydrophobic surface area. For long tails (i.e. large L), the contribution of the apolar end will also be negligible, so from now on we will only consider the tails area $2\pi rL$. As for methane, we can take the radius = 2 Å. To calculate the length L as a function of numbers of carbon we take C-C bond length = 154 pm and we know the bond angle to be 110°. Together, we thus add 1.54 sin(110°) = 1.45 $2\pi rL$ per Carbon. We can then use $\Delta G_{lipid} = 2\pi rL\gamma$.
To account degrees of saturation, we use 13 3pm or 1.32πrL for C=C double bonds which have a bond angle of 180°. To consider multiple tails, we can then multiply the radius by a factor of 1.5, as the tails are usually in close proximity and exclude water between them. On the other hand, they could also be treated as separate cylinders, if we want to consider the total dissolution energy of a particular lipid.

d)

$$-2\pi RL\gamma = k_B T ln\left(c\lambda_{th}^3 h^3\right)$$

$$=> c = \left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3 e^{-2.8\pi RN\gamma/k_B T}$$

To get the mass m in terms of the number of carbons in the tail: each carbon (assuming single C-C bonds only and ignoring the terminal carbon) contributes 13g/mol for its weight plus 2g/mol for two hydrogens. Next we need to add the weight of the headgroup (note that we excluded this in the calculation of the hydrophobic surface are but m enters into the term corresponding to the entropy of arranging pipids in solution which is independent of how they interact with water and therefore the headgroup needs to be included. Using phosphatidylcholine as our model we can say that each headgroup is 8 oxygens + 1 nitrogen + 1 phophorus + 10 carbons + 19 hydrogens = 312 g/mol = 51.2 * 10^{-23}g. So we can write the mass m1 of a single tailed as (51.2 + 2.33N) * 10^{-26}kg and m2 of a double tailed lipid as (51.2 + 4.66N) * 10^{-26}g. A plot of the critical micelle concentration as a function of tail length is shown in the next figure. The units of λ_{th}^3 are 1/m^3 = 1/L. To plot the critical micelle concentration in molar units, we need to divide our equation by Avogadro'2 number, to get mol/L.

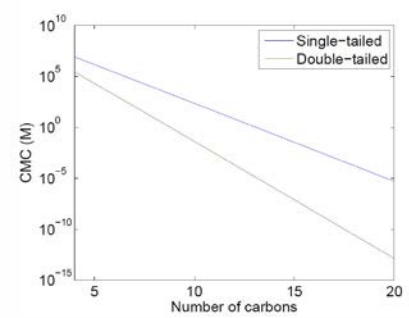

Figure 2: Critical micelle concentration in moles/liter as function of the number of carbons in a single- or double-tailed lipid.