Lecture 13

Micelles formation.
Factors affecting the CMC

• Hydrophobic interaction:
  – entropy lowered due to arranging of surfactants into the micelles
  – entropy increased due to removal hydrocarbon chains from water (much higher gain!)
• Head group interaction:
  – hydration repulsion: head group needs to be dehydrated to a approach
  – steric effects: due to reduction of fluctuations (entropy reduction)
  – electrostatic repulsion
Micelle structure considerations

- The structure of a micelle depends on:
  - thermodynamics of self-assembly
  - forces within the aggregate
  - intra-aggregate forces
- Size and shape of the micelles are defined as a distribution (no exact size or shape!)
- The distribution might have several equilibrium values at the same time
Optimal head group area

- We can express the energy factors through the geometrical parameters of the micelle.

Energy gain due to decrease of water-oil surface tension. Thus it can be written as: \( \gamma = 20-50 \text{ mJ/m}^2 \).

Head-head interaction: \( K/a \)
Optimal head group area

\[ \mu_N = \gamma a + K / a \]

- minimizing:

\[ \mu_{N_{\text{min}}} = 2\gamma a_0; \quad a_0 = \sqrt{K/\gamma} \]

optimal head group area, mainly depends on the head (not the tail length)

\[ \mu_N = 2\gamma a_0 + \frac{\gamma}{a} (a - a_0)^2 \]
Optimal headgroup area approach:

• contains essential features of interlipid interaction

• explains an energy minimum about which the energy varies parabolically (equilibrium N!)

• doesn’t include into account
  – specific headgroup interaction, e.g. ionic bridging
  – specific chain-chain interaction
  – effect of surface curvature on the energy
The geometry of aggregate is defined by the following factors:

- optimal headgroup area $a_0$;
- maximum effective length of the chain, “critical chain length” $l_c$;
- volume of the hydrocarbon chain $v$.

$$l_c \leq l_{\text{max}} \approx (0.154 + 0.1265 \cdot n) \text{nm}$$
$$v \approx (27.4 + 26.9 \cdot n) \times 10^{-3} \text{nm}^{-3}$$

packing parameter (shape factor):

$$\frac{v}{a_0 l_c}$$

minimal possible size corresponds to equilibrium (entropy)
Spherical micelles

For a spherical micelle of radius $R$ with aggregation number $M$:

$$M = \frac{4\pi R^2}{a_0} = \frac{4\pi R^3}{3v}$$

$$R = \frac{3v}{a_0}$$

\[
\frac{v}{l_c a_0} < \frac{1}{3}
\]

Example: SDS-micelle
$M=74$; 12 carbon chain; from equation we get:
$v=0.35 \text{ nm}^3$; $l_c=1.67 \text{ nm}$; $a_0=0.57 \text{ nm}^2$; $R=1.84 \text{ nm}$

$v/a_0l_c=0.37$

slightly non-spherical shape
Cylindrical micelles

\[ \frac{1}{3} < \frac{v}{a_0 l_c} < \frac{1}{2} \]

- lipids forming spherical micelles at low salt concentration might switch to cylindrical at higher ionic strength;
- from thermodynamics, the cylindrical micelles are large and polydisperse, mean aggregation number \( \sim C^{\frac{1}{2}} \).
- most energy is associated with ends of the micelle (spherical caps are unfavorable)
Bilayers

\[ \frac{1}{2} < \frac{\nu}{a_0 l_c} \leq 1 \]

- formed when the headgroup is small or chain is bulky, e.g. lipids with two chains
Bilayer: Some estimates

• residence time inside the membrane

\[ \tau_R = \frac{\tau_0}{\exp(-\Delta E / kT)} = 55\tau_0 / \text{CMC} \]

\[ \tau_0 = 10^{-9} - 10^{-7} \text{s} \]

\[ \tau_R(\text{micelles}) \sim 55 \cdot 10^{-9} / 10^{-3} \sim 10^{-4} \text{s}; \]

\[ \tau_R(\text{bilayers}) \sim 55 \cdot 10^{-7} / 10^{-10} \sim 10^{-4} \text{s}; \]
Bilayer: Some estimates

- elastic energy (stretching) of bilayer
  
  \[
  \text{elastic energy} = \frac{1}{2} k_a (a - a_0)^2 / a 
  \]

  \[
  \mu_N^0 = 2\gamma a_0 + \frac{\gamma}{a} (a - a_0)^2 
  \]

  compare:
  \[
  k_a \approx 2\gamma \text{ per monolayer;}
  \]
  \[
  k_a \approx 4\gamma \text{ per bilayer}
  \]
Vesicles

• at some condition it could be energetically favorable to eliminate the edges of a bilayer forming vesicles

• however it requires curvature, so lipids in the outer layer should pack into truncated cones:

\[
\frac{v}{a_0 l_c} \leq 1
\]

• for a vesicle:

\[
R_c \approx \frac{l_c}{1 - \nu/(a_0 l_c)}; N \approx 4\pi \left[ R_c^2 + (R_c - t)^2 \right]/a_0
\]
Lipid bilayers

• biological membrane are formed by lipid bilayers
• prevent diffusion of polar molecules (possess a high resistance for ionic currents)

\[ \frac{e^2}{8\pi\varepsilon_0 R} \left( \frac{1}{\varepsilon_2} - \frac{1}{\varepsilon_1} \right) = 1.37 \cdot 10^{-19} J \approx 33kT \]

0.2nm  4  78

typical resistance \(\sim 10^8\) Ohm/cm\(^2\).
Factors affecting structure changes

- factors affecting headgroup area: ionic strength, pH
- factors affecting chain packing (e.g. chain branching and unsaturation)
- effect of temperature, affects both $a_0$ and $I_c$
- lipid mixtures
Emulsions

- Emulsion – dispersion of two immiscible liquids. **Outer** (continuous) and **inner** phases are distinguished.
- Emulsion are stabilized by addition of surfactants
- Macro- and micro-emulsions can be distinguished:
  - **Macro-emulsions:**
    - concentration of surfactant just above CMC
    - spherical droplets 0.1-10µm, highly polydispersed
    - thermodynamically unstable
  - **Microemulsions:**
    - high concentration of surfactant
    - thermodynamically stable
    - typical sizes 2-50nm
Evolution of macroemulsions

• we expect that from the thermodynamics prospective the emulsions will eventually coalesce

• this is delayed by
  – reducing surface tension (surfactants)
  – repulsive forces
  – kinetics
Emulsion stability

- selection of emulsifier determines which type of emulsion will be formed

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<th>Bancroft rule: the phase the emulsifier is more soluble in will be the continuous phase</th>
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<th>Harkins wedge theory: larger end of the emulsifier lies in the continuous phase</th>
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<th>Winsor theory: based on ratio of cohesive energies</th>
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\[
R = \frac{E_{LO}}{E_{HW}}
\]

- R<1 O/W emulsion is formed
- R>1 W/O emulsion is formed

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<tr>
<th>Griffin’s hydrophile-lipophile balance (HLB) theory:</th>
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<tr>
<td>Surfactants with low HLB (3-6) stabilize water-in-oil emulsions</td>
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<tr>
<td>Surfactants with high HLB(8-18) stabilize oil-in-water emulsion</td>
</tr>
</tbody>
</table>
Evolution of macroemulsions

- Kinetics of demulsification

  separation of drops by gravity

  forming loose clusters without losing identity of drops (secondary minimum)
Evolution of macroemulsions

• Kinetics of demulsification

  – Diffusion limited encounter of droplets (Smoluchowski)

  \[
  \frac{dc}{dt} = -8\pi D R c^2 = \frac{-8\pi k_B T R}{6\pi \eta R} c^2 = -\frac{4k_B T}{3\eta} c^2
  \]

  \[
  \frac{dc}{dt} = -k_f c^2 \quad k_f = \frac{4k_B T}{3\eta}
  \]

  rate of flocculation, depends only on \( T \) and viscosity

  – If a barrier \( E^* \) for coalescence exists:

  \[
  \frac{dc}{dt} = -k_f \exp\left(-\frac{E^*}{k_B T}\right) c^2
  \]

  \[
  \frac{1}{c} = \frac{1}{c_0} + k_f^* t, \quad k_f^* = k_f \exp\left(-\frac{E^*}{k_B T}\right)
  \]
Evolution of macroemulsions

- Stages of droplet coalescence

- Stability of lamella depends on the repulsion forces between the surfactants.
- Formation of bare spots depends on surfactant density.
- Area and curvature of the surfactant film changes.
Microemulsions

- Microemulsions (discovered in 1950s) are
  - thermodynamically stable;
  - formed spontaneously
  - react reversibly on the change in temperature and composition
  - consist of submicron size droplets
Microemulsions

- The radius of the droplet (in case of complete coverage by a surfactant)

\[ V \phi_d = n \frac{4}{3} \pi R^3 \]

- Volume fraction of the dispersed phase:

\[ V \phi_s = n 4\pi R^2 L_s \]

- Surfactant volume fraction:

\[ R = \frac{3L_s \phi_d}{\phi_s} \]

\( R_c \) - core radius – radius of “neutral surface”
Elastic properties of surfactant films

- Laplace pressure is relatively small due to small surface tension
- Gibbs free energy of a curved surface:

\[
G = \int_{\text{surface}} \left[ \frac{1}{2} k \left( C_1 + C_2 - C_0 \right)^2 + \kappa C_1 C_2 \right] dA
\]

Minimum in Gibbs free energy corresponds to “equilibrium” curvature

\[
C_1 = C_2 = k C_0 \left/ \left( 2k + \kappa \right) \right.
\]
Microemulsions

- Emulsion evolution with temperature

Phase diagram of 50:50 water-octane mixture with C_{12}E_{5} surfactant

Decrease in spontaneous curvature

20°C, 22°C, 27°C, 32°C, 36°C, 38°C, 42°C
• delivery of water insoluble vitamins and medicine

**Example**: AquaNova GmbH produces 30nm size micelle system suitable e.g. for delivery of vitamin E and vitamin A. Micelles are thermally, mechanically and pH stable.
Application of surfactants

- Wetting: contact angle is reduced.
- Detergency:
  - detergent: mixture of surfactants with other additives for effective cleansing (builders, brighteners and bleaches, electrolyte filler)
  - cleansing efficiency grows with the concentration up to cmc
- Water repulsion
  - hydrophilic surface can be made hydrophobic
- Emulsification
- Froth flotation in ore treatment:
  - particles with hydrophobic surface stick to bubbles and are carried upwards when foam is formed (lead and copper sulfide ores, oxides, coal etc.)
- Oil recovery
- Membrane disruption
Emulsion polymerization

- monomer is prepared as emulsion in water stabilized by surfactants
- initiator is dissolved in water
- polymerization starts in the aqueous phase

\[ I^* + M \rightarrow M^* \]
\[ M^* + M \rightarrow MM^* \]
\[ ...MM^* + M \rightarrow ...MMM^* \]
\[ ...MM^* + ...MMM^* \rightarrow ...MMM ... \]

initial polymerization in aqueous phase

oligomers solubilized in the micelles

termination
Films and Foams

Structure of a foam layer:

Foam layer has a surface tension, therefore foam film tries to minimize the area:

Laplace equation is applicable as well:

• when a foam thickness decreases due to liquid drainage it forms **black films**: common black film (liquid core) and Newton black film (no liquid core)
Films and Foams

• Foam formation (by bubbling)
Foams

- Wet foam: bubbles are spherical separated by thick liquid films
- Dry foam: mostly gas separated by thin lamellas. Individual cells are polyhedra.
  - three flat sides of polyhedra meet at an angle of 120°.
  - configuration of 4 or more sides connecting at one line is unstable
  - at all corners the 4 edges meet in a tetrahedral arrangement
Films and Foams

- the Plateau border
  - as the curvature radius is smaller at the triple point, the pressure will be lower and the liquid will flow there disrupting the foam
  - foam can be stabilized by repulsive pressure between the adsorbed layers: **disjoining pressure**
Films and Foams

- Permeability to gases

monolayer permeation: \[ J = k_m \Delta c_m \]

diffusion through the solution: \[ J = \frac{DH}{z_b} \Delta c_b \]

\[ J \left( \frac{1}{k_m} + \frac{z_b}{DH} + \frac{1}{k_m} \right) = \Delta c \]

\[ k_i \]
Measuring pressure in foam: Thin Film Balance

- Pressure inside the liquid film:

\[ \Pi = P_g - P_r + \frac{2\gamma}{r_C} - \rho gh \]
Problems

• Below what aggregation number SDS micelles can be spherical?
• Estimate CMC for Hexane in water. Surface tension of Hexane-Water interface is 51.1mN/m
• End-of chapter problems: 12.2, 5, 6