TMT4320 Nanomaterials, fall 2015
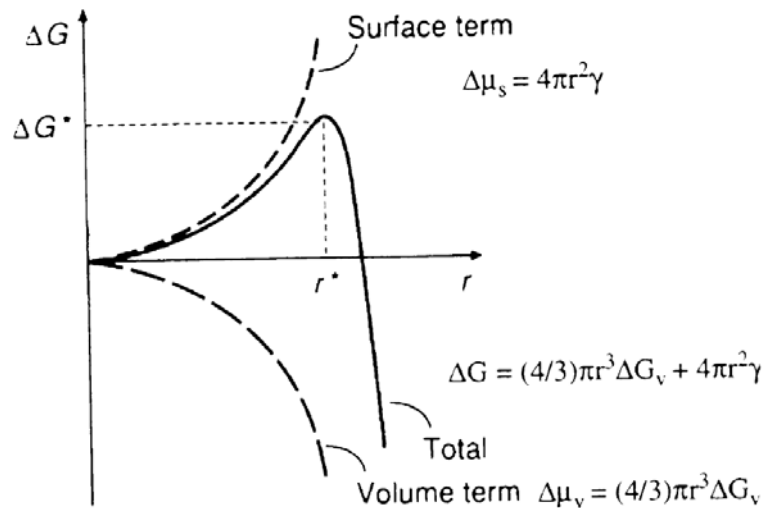
EXERCISE 4 - SOLUTION

PROBLEM 1

Given:

$$\Delta G = \Delta \mu_V + \Delta \mu_S = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

The surface term will give a positive contribution and the volume term a negative contribution to the total energy:

A formed nucleus will be stable if the size of the nucleus is above a certain critical size (r^*), at which the volume term will start to dominate over the surface term. From the graph we can see that at this point the derivative of the function will be zero:

$$\frac{d\Delta G}{dr} = 0$$

$$\frac{d\Delta G}{dr} = \frac{d}{dr}\left(\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma\right) = \frac{4}{3}\pi 3 r^2 \Delta G_V + 4\pi 2 r\gamma = 0$$

$$r^* = r = -2\frac{\gamma}{\Delta G_V}$$

The expression for the critical energy (energy barrier for nucleation, ΔG^*) is then obtained by inserting the expression for the critical size into the expression for ΔG:

$$\Delta G^* = \Delta G(r^*) = \frac{4}{3}\pi\left(-\frac{2\gamma}{\Delta G_V}\right)^3 \Delta G_V + 4\pi\left(-\frac{2\gamma}{\Delta G_V}\right)^2 \gamma = \frac{16\pi\gamma^3}{3(\Delta G_V)^2}$$

PROBLEM 2

a) See the figure below. Starting at time zero, when the concentration of the solute increases as a function of time, no nucleation would occur even above the equilibrium solubility (C_S). The nucleation occurs only when the supersaturation reaches a certain value above the solubility, which corresponds to the energy barrier for the formation of a stable nucleus (at C^{nu}_{min}). At C^{nu}_{min} the nucleation rate is very low, but the nucleation rate increases with increasing concentration above C^{nu}_{min}. After the initial nucleation, the concentration or supersaturation of the growth species decreases and the change of the Gibbs free energy reduces. When the concentration decreases below this specific concentration (C^{nu}_{min}), which corresponds to the critical energy, no more nuclei will form, whereas the growth will proceed until the concentration of growth species has attained the equilibrium concentration of solubility.
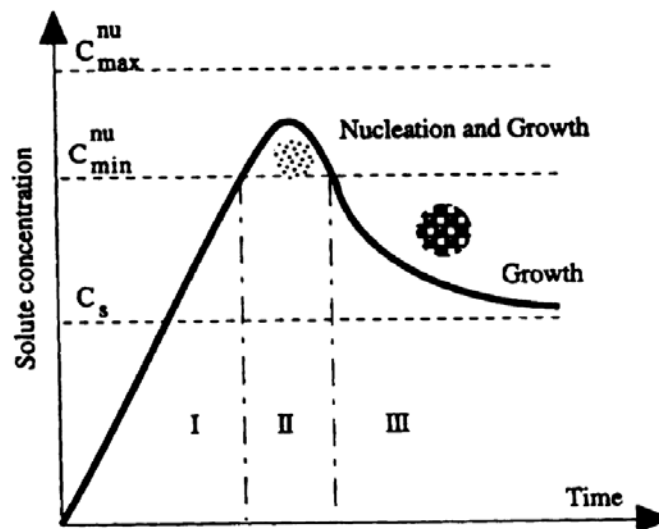
C_S = concentration of the solute at equilibrium solubility
C^{nu}_{min} = concentration of the solute at which the supersaturation corresponds to the energy barrier for nucleation (ΔG^* in problem 1)
C^{nu}_{max} = concentration of the solute at which the nucleation rate is extremely fast

I – No nucleation
II – Nucleation and growth
III – Growth

b) In spinodal decomposition there is no energy barrier for the transformation from one phase into two phases.

c) A-B represents nucleation and growth.
   C-D represents spinodal decomposition.

d) Yes, nucleation can happen if the system is not at the critical point (the point where the spinodal line and the binodal line meet). To reach the spinodal region of the phase diagram, a transition must take the material through the binodal region or the critical point. Often phase separation will occur via nucleation during this transition, and spinodal decomposition will not be observed. To observe spinodal decomposition, a very fast transition, often called a quench, is required to move from the stable to the spinodally unstable region of the phase diagram.

In the region between the binodal line and the spinodal line, if the energy barrier of nucleation is not overcome, the system is in a metastable one-phase state. Then, if the system is moved into the spinodal region, for instance by lowering the temperature, spontaneous formation of two phases will occur, called spinodal decomposition, as there is no energy barrier for phase separation in the spinodal region.

PROBLEM 3
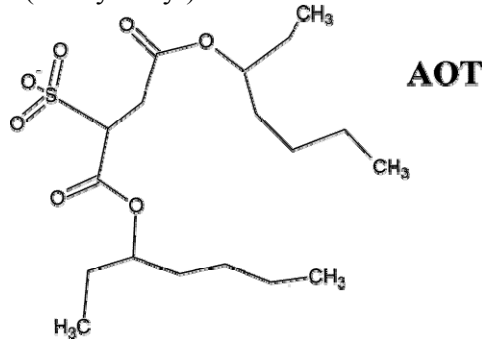
a) <u>Cationic surfactants:</u>
   CTAC – cetyltrimethylammonium chloride
   CTAB – cetyltrimethylammonium bromide
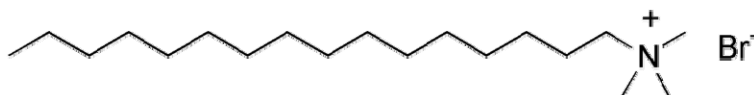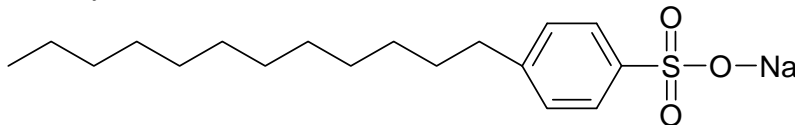

<u>Anionic surfactants:</u>
   NaAOT – sodium bis(2-ethylhexyl)-sulfosuccinate

   Sodium dodecylsulfate
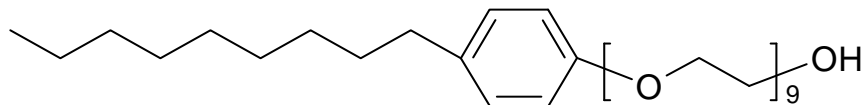
$$CH_3 - (CH_2)_{11} - O - SO_3^- \ Na^+$$
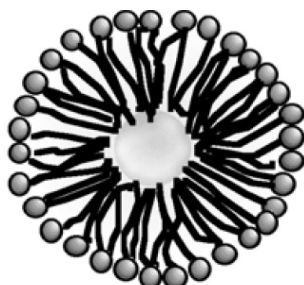
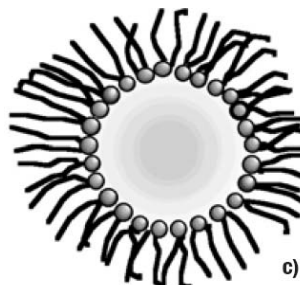   Sodium dodecylbenzenesulfate

Non-ionic surfactants:
    Polyoxyethylene nonylphenyl ether

b) In a micelle the surfactants have the polar head pointing outwards and the non-polar carbon chain pointing inwards. In a reverse micelle the surfactants have the polar head pointing inwards and the non-polar carbon chain pointing outwards.
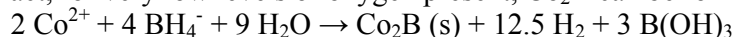

Micelle   Reverse micelle

c) The two reagents are mixed with hexane, water and surfactant in two separate containers to obtain one dispersion of reverse micelles containing aqueous $CoCl_2$ and one dispersion of reverse micelles containing aqueous $NaBH_4$. The two dispersions are then mixed, and because of Brownian motion some of them will collide and form a short-lived larger reverse micelle. The aqueous cores are thus mixed and a chemical reaction can occur.
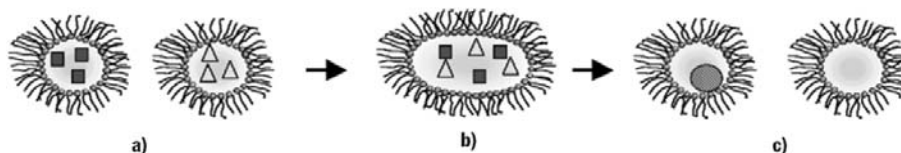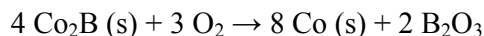

The reaction that occurs is the reduction of Co^{2+} to Co by the reducing agent $NaBH_4$. The exact reaction mechanism can be complex and depends on the amount of oxygen present.

(In fact, for very low levels of oxygen present, Co_2B can be formed:
    $2\ Co^{2+} + 4\ BH_4^- + 9\ H_2O \rightarrow Co_2B\ (s) + 12.5\ H_2 + 3\ B(OH)_3$
In the presence of a relatively low amount of oxygen, Co_2B is reduced and cobalt metal is formed as follows:
    $4\ Co_2B\ (s) + 3\ O_2 \rightarrow 8\ Co\ (s) + 2\ B_2O_3$
An excess of oxygen oxidizes cobalt metal to its oxide derivative.)

d) The size of nanoparticles synthesized in reverse micelles can be controlled by the water content because the size of the reverse micelles increases with increasing water content. The size of the resulting nanoparticles will reflect the size of the reverse micelle, at least for smaller reverse micelles (< ~6 nm in diameter).