NS-CP429M

EXAM 1
SOFT CONDENSED MATTER
April 20th, 2010

- *This is an open book exam. You can use the book (R. J. Hunter, Foundations of Colloid Science) and the handouts provided by the lecturers.*
- *Constants:* *Boltzmann:* $k = 1.38 \times 10^{-23}$ J/K
  vacuum permittivity: $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2/N$\cdot$m^2
  Avogadro's number: $N_{\mathrm{Av}} = 6.022 \times 10^{23}$ mol^{-1}

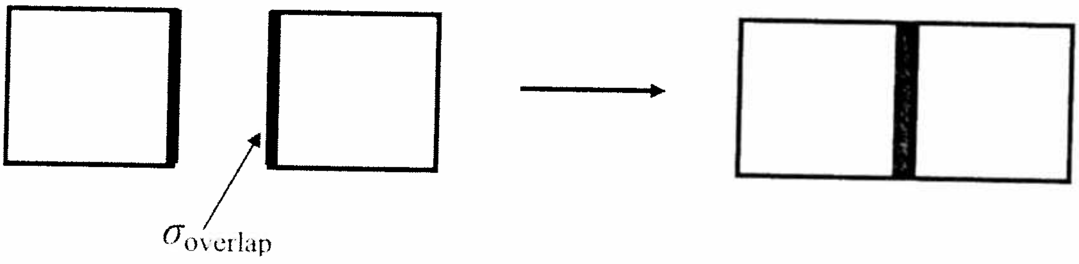
1. Micelles have been observed to form in so-called block-copolymers dissolved in aqueous solvent. Block copolymers are effectively 'super-surfactants', where the polar and apolar moieties are polymers.

   a. Argue, referring to the assumptions that underly the derivation in the handout, that the critical micelle concentration in these systems is given by

   $$x_0 = \exp\left(\frac{(\mu_n^0 - n\mu_1^0)}{(n-1)kT}\right).$$

   (So: no derivation is required, only a discussion whether the underlying assumptions in the handout apply to this case!)

   b. Let's assume the interactions between the super-surfactant molecules are dominated by hydrophobic interactions. Argue that the strength of hydrophobic interactions between two objects is given by $w \approx -2\gamma\sigma_{\mathrm{overlap}}$. Here γ is the interfacial tension between the polymers and the solvent, and $\sigma_{\mathrm{overlap}}$ is the contact area between two block copolymers when they stick. The definition of $\sigma_{\mathrm{overlap}}$ is illustrated below for two rectangles both with a sticky side of 'area' $\sigma_{\mathrm{overlap}}$. What assumption(s) have you made?



   c. Show that the cmc can be expressed (approximately) as

   $$x_0 \approx \exp\left(\frac{-<n_c> \gamma\sigma_{overlap}}{kT}\right),$$

   where $<n_c>$ is the average number of contacts of a surfactant molecule in the micelle.

   d. With the excess entropy $s^\sigma = -(\partial\gamma/\partial T)_{p,\sigma} < 0$, would you expect the cmc to increase, to decrease, or to remain constant with temperature? Prove that.

2. a. Give the dependence of the size of an isolated polymer coil on the (effective) step length and the total length of the polymer in an ideal solvent. How would this change in a good solvent?

   b. Describe the origin of the depletion attraction between 2 spherical colloidal particles in a dilute polymer solution. What determines the range and strength of the attraction?

   c. Argue what would change in the previous answer if the polymer solution is more concentrated (semi-dilute instead of dilute).

3. As mentioned in the lectures as an example, the Stöber synthesis is a general way of producing monodisperse silica particles from e.g. tetraethoxysilane in a mixture of water (e.g. 20 vol%) and ethanol and NH_3 (e.g. 1 M = 1 mol/L). Electrophoresis was used to measure a surface charge of 50 mV in this solvent mixture for silica particles. The particles result from the hydrolysis and subsequent condensation of the reactive monomer. Both these reactions are catalyzed by base and their rates increase in an almost similar, monotonic way as a function of pH.

Table: **Solvent properties**

	density (g/ml)	***relative dielectric constant***	***Hamaker constant*** A_{11} (***pure component***) x 10^{-20} J
Methanol	0.8	33	3.9
Ethanol	0.8	24	4.2
Water	1.0	88	3.7
Silica	1.9	4	6.5

   a. It has been established that addition to the Stöber synthesis of 1 mM LiCl, a salt that dissociates completely, does not affect these reaction rates. However, the particle size is dramatically changed. Explain why this is a strong indication that the Stöber synthesis does not only rely on nucleation and growth in its reaction mechanism. Also indicate if the particle size has increased after the addition of the salt or decreased and explain why.

   b. The concentration of NH_3 is systematically increased from 0.1 M to 3 M, while everything else in the synthesis stays constant and the final silica particle size is measured. The particle size has a clear maximum around 1 M after which it decreases. Explain possible mechanisms that could explain this maximum.

   c. Subsequently, the ethanol is replaced by methanol (see table above for different properties). During the two syntheses (one with 80 vol% ethanol as the solvent and one with 80 vol% methanol) the ionic strength of the solvent is measured as a function of time. There is hardly a difference in the two synthetic runs, and also the surface charge is roughly the same at 50 mV. However there is a significant change in the particle size. Explain through a calculation how this could be explained and predict in which solvent the largest particles were formed.