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NS-CT 429M

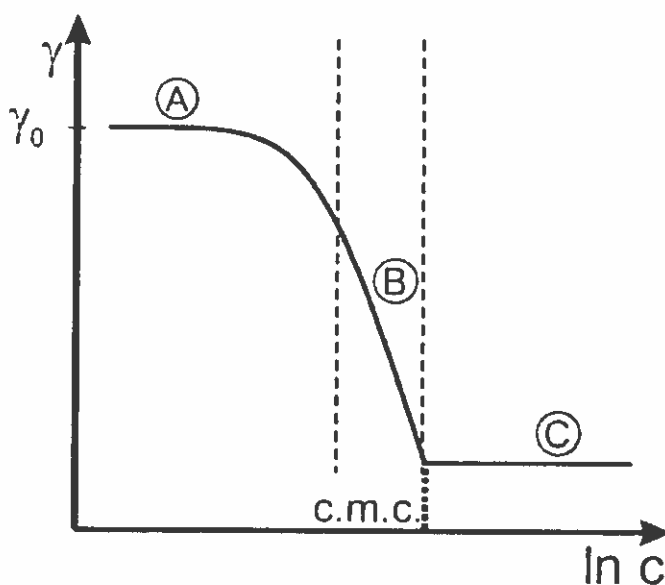
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RETAKE  
SOFT CONDENSED MATTER  
August 27th, 2008

Note: Problems 1 through 3 are compulsory. Then, you can choose to work either problem 4 or 5. Problem 4 is chemistry oriented, while problem 5 is more physics oriented.

1. In the figure below, the interfacial tension between a surfactant solution and air is plotted as a function of the surfactant concentration.



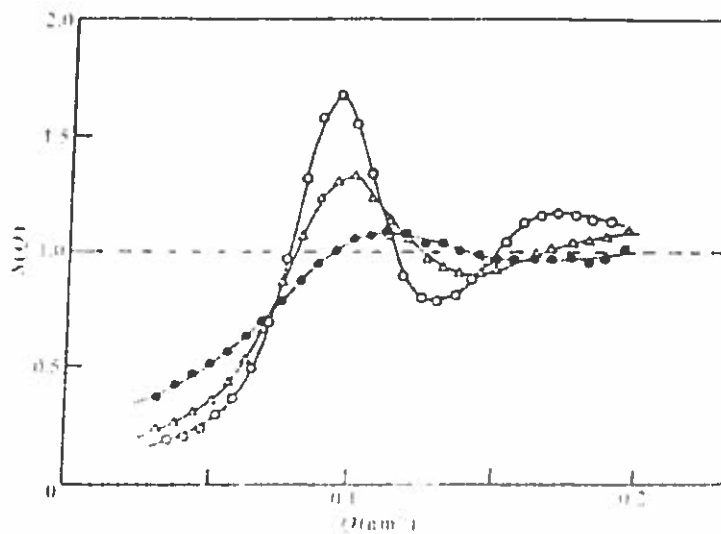
- Estimate, using dimensional arguments, the order of magnitude of  $\gamma_0$ , i.e., the value of the liquid-air interfacial tension without surfactants being present.
- Why does interfacial tension decrease in region A and B of the curve?
- What does the constant slope in region B mean in terms of the adsorption density of the surfactant?
- In region C, where the surfactant concentration is beyond the critical micelle concentration (indicated by 'c.m.c.'), micelles will form. Explain why interfacial tension is approximately constant above the cmc.

2. The Flory-Huggins expression for a polymer blend is given by

$$f_m(\phi) = \frac{1}{N_A} \phi \ln \phi + \frac{1}{N_B} (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi).$$

- Explain the significance of all variables and symbols in this expression.
- Indicate which terms in the expression are of entropic and which are of energetic origin and argue whether a blend will mix easily or not.
- Derive expressions for the volume fraction  $\phi_{cr}$  and parameter  $\chi_{cr}$  at the critical point. What do these tell you about the miscibility of 2 different polymers?

3. The graph below shows structure factors of suspensions of polystyrene spheres with a radius of 15.7 nm in water. The data were measured with neutron scattering at a wavelength of 1.2 nm. The volume fraction was the same in all three cases, but sample A was de-ionized, sample B contained 1 mM sodium chloride, and sample C contained 5 mM sodium chloride.



- Match the samples to each of the three sets of data and motivate your choice.
- Estimate the volume fraction of the polystyrene particles.
- What range of scattering angles was used to measure these data?

Note: You can choose to work either problem 4 or 5.

4. Researchers decide to chemically coat the surface of a dispersion of silica ( $\text{SiO}_2$ ) particles with a diameter of 500 nm with the silane coupling agent aminopropyl-triethoxysilane:  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ . Before the coating step they measured by electrophoresis in well deionized water (concentration of stray ions:  $10^{-5}$  M) a surface potential of  $-60$  mV. After the coating the surface potential was only  $-20$  mV. Silica has a Hamaker constant (in vacuum with itself) of  $7 \times 10^{-20}$  J; the Hamaker constant for pure water (in vacuum) is:  $4 \times 10^{-20}$  J. The relative permittivity of water is 80 and  $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$ .

- (a) Explain chemically by showing the relevant equilibria what gives the particles their surface charge before and after the coating.

It is found that the coated particle dispersion does not remain stable for long if the dispersion is not kept under a nitrogen atmosphere. It is also found that an old dispersion, which was not well closed, after aggregation has an increased conductivity. The conductivity corresponds to an ion concentration of 1 mM (assuming the impurity ions to be monovalent) and a surface charge of + 5 mV. To check for the mechanism, somebody blows air (i.e. exhales) through a straw (exhaled air contains carbon dioxide) into the dispersion in water, which immediately aggregates. The same experiment is done with an uncoated dispersion in water, but this time the dispersion does not aggregate, while the ionic strength increase is similar.

- (b) Calculate the DLVO interaction free energy (i.e. double layer overlap *and* van der Waals interactions) between two silica particles of an 'old' dispersion (i.e., after the change in conductivity and surface potential) at distances: 'in contact', 1 nm, 5 nm and 50 nm. Indicate the approximations made for the calculations.
- (c) Explain what causes the aggregation of the coated silica particles and why this does not happen with an uncoated dispersion.

After several weeks of contact with ion exchange resin an uncoated silica dispersion of the particles with a radius of 500 nm is found to have an ionic strength of  $10^{-6}$  M ionic impurities (assumed to be monovalent). The sedimented dispersion has formed a layer of colloidal crystals which have beautiful interference colors.

- (d) Give a rough estimate (by performing a DLVO potential calculation) of the interparticle spacing in the colloidal crystal. Explain the assumptions made in the calculation.

## 5. Langmuir-Blodgett film

Amphiphilic molecules can adsorb onto air-water interfaces in such a way that the polar head groups are immersed in water and the hydrophobic hydrocarbon tails are pointing towards the air. In this way the molecules form a two-dimensional monolayer (or Langmuir film) at the interface, but such that the molecules can move in the plane of the interface. This implies that the system can be seen as a two-dimensional fluid.

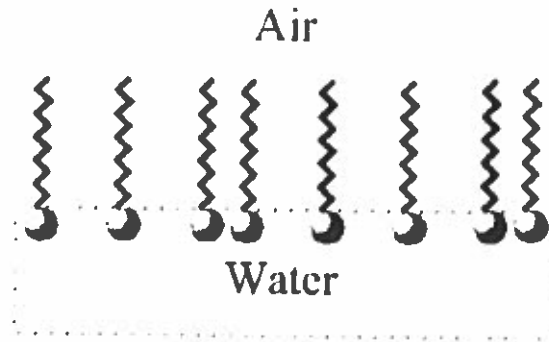


Figure 1: Schematic representation of amphiphilic molecules adsorbed on an air-water interface.

We now consider  $N$  amphiphilic molecules on a surface area  $A$ . At large enough  $A$  the monolayer can be regarded as a dilute two-dimensional non-interacting ideal gas, while the molecules start to feel each other when the available surface area is reduced. The surface pressure  $\Pi$ , i.e. the two-dimensional analogue of the pressure in three dimensions, can be approximated by the Dieterici equation

$$\Pi = \frac{\rho k_B T}{1 - \rho b} \exp[-(a\rho) / (k_B T)],$$

where the surface density is defined by  $\rho = N/A$ , where  $T$  is the temperature, and where  $a$  and  $b$  are phenomenological system parameters. Of course  $k_B$  is the Boltzmann constant.

- Verify that the system reduces to a non-interacting ideal gas for  $\rho \rightarrow 0$ .
- Calculate the second virial coefficient of this system in terms of  $a$ ,  $b$ , and  $T$ .
- At high temperatures the amphiphilic molecules interact as if they are two-dimensional impenetrable hard discs with radius  $R$ . Calculate the second virial coefficient  $B_2$  of these two-dimensional hard discs, and relate  $B_2$  to  $a$ ,  $b$ , and/or  $T$ .
- The film exhibits a gas-liquid transition upon compression, provided  $T > T_c$ , with  $T_c$  the critical temperature. Calculate  $T_c$  and also the critical pressure  $\Pi_c$  and the critical density  $\rho_c$  in terms of  $a$  and  $b$ , assuming that the Dieterici equation of state holds.
- We now introduce reduced variables  $\Pi^* = \Pi / \Pi_c$ ,  $T^* = T / T_c$ , and  $\rho^* = \rho / \rho_c$ . Does the Dieterici equation of state follow the law of corresponding states, i.e., does  $\Pi^*$  still depend on the phenomenological material parameters  $a$  and  $b$ ?