SOFT MATTER

PRACTICES 3

Thermodynamics of surfactant solution

1 Thermodynamic equilibrium between bulk and surface

We want to relate the surface concentration Γ of surfactant molecules, then the surface tension γ, to the bulk concentration c. We consider only thermodynamic equilibrium of free surfactant molecules (molecules in micelles do not gain much energy to go to the surface, unlike free molecules). Then, c refers to the concentration of free molecules in the bulk.

1.1 Relationship between Γ and c

1. The free molecules in the bulk is treated as a three-dimensional ideal gas. Let μ_{3D} be its chemical potential. Express μ_{3D} as a function of k_BT, c and $\lambda(T)$, the thermal de Broglie length.
2. The molecules adsorbed on the surface will be treated as a two-dimensional gas of hard-spheres with cross-sectional area a_0. Let μ_{2D} be its chemical potential. The gain of energy for a free molecule to adsorb on the surface is $-u_0$. Express μ_{2D} as a function of k_BT, u_0, Γ and $\lambda(T)$.
3. What is the condition that the two chemical potentials must satisfy at equilibrium ? Deduce the relationship between Γ and c.
4. What is the theoretical upper limit for Γ ? What is the maximal possible value for c, the concentration in free molecules ?

1.2 Relationship between γ and Γ

1. Using Gibbs' convention for the surface localization, show that the surface free energy is
$$F_\Sigma(A, \Gamma, T) = A(\gamma + \mu\Gamma), \tag{1}$$
where A is the surface area, and μ the chemical potential of the surfactant molecules.
2. Derive the Gibbs-Duhem relation for the interface, which relates the variation of Γ, μ and T in a transformation.
3. Simplify this expression for an isotherm transformation.
4. Using the expressions of μ and Γ as functions of c, show that the evolution of $\gamma(c)$ is given by:
$$\frac{\mathrm{d}\gamma}{\mathrm{d}c} = -\frac{A}{c+B}, \tag{2}$$
where A and B are two constants that depend on the different parameters of the problem.
5. Finally, express γ as a function of c and/or Γ, and make a plot.