University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2008

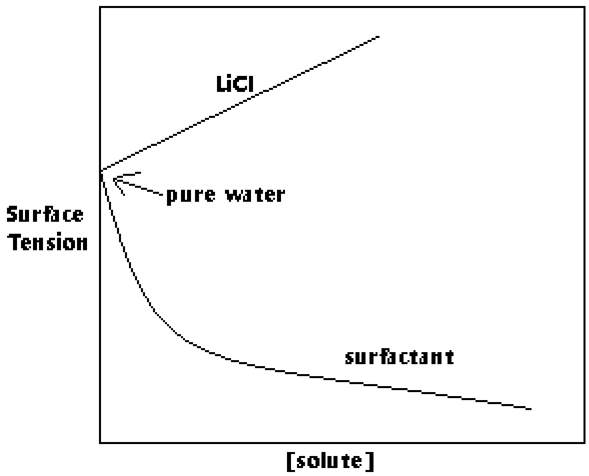
Lecture 15 8/0/07

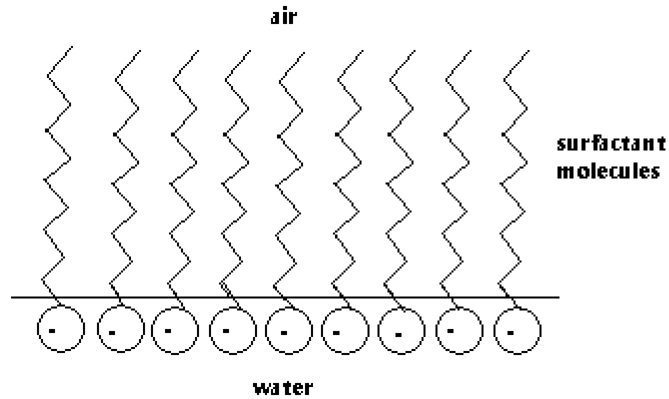
A. The Gibbs Isotherm Equation

- Returning to the thermodynamics of surfaces, we are left with the equation
$$dG = -SdT + VdP + \gamma dA + \sum_i \mu_i dn_i$$
- We need an equation which describes the relationship between the molar free energy of the surface, and properties of the surface that we can measure (e.g. surface tension). Consider an air-liquid interface where the liquid is a solution. A component i of the solution is distributed between the bulk solution phase α, the vapor phase β, and the surface σ. If i is in equilibrium between the three phases we have $\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma = \mu_i$.
- The total free energy is the sum of the free energies for acomponet of the system in the vapor, bulk liquid, and in the surface… $G_i = G_i^\alpha + G_i^\beta + G_i^\sigma$
- The free energy of i at constant P and T is $dG_i^\sigma = \gamma d\sigma + \mu_i dn_i^\sigma$
- This expression can be integrated to give $G_i^\sigma = \gamma\sigma + \mu_i n_i^\sigma$.
- Subsequent differentiation yields $dG_i^\sigma = \gamma d\sigma + \mu_i dn_i^\sigma + \sigma d\gamma + d\mu_i n_i^\sigma$.
- Comparing the two equations for dG^σ, we find $\sigma d\gamma + n_i^\sigma d\mu_i = 0$ This equation can be rearranged to give $d\gamma = -\frac{n_i^\sigma}{\sigma} d\mu_i = -\Gamma_i d\mu_i$ where Γ_i is the surface adsorption, and has units of moles per m^2.
- The relationship between surface tension and surface adsorption (i.e. surface concentration) is given by $\Gamma_i = -\left(\frac{\partial\gamma}{\partial\mu_i}\right)_T$. It will be shown later in the course that the chemical potential of a component of a solution is related to the concentration Ci of the component by $d\mu_i = RT\ln C_i$. Therefore
$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C_i}\right)_T = -\frac{C_i}{RT}\left(\frac{\partial\gamma}{\partial C_i}\right)_T$$
- This means that a graph of the surface tension of a solution versus logarithm of the bulk concentration of a given component gives the surface adsorption. This is called the Gibbs Isotherm Equation.

B. Surfactants

The surface tension of a pure liquid can be raised or lowered by the presence of certain solutes. The graph below shows typical behavior for some solutes.





- Inorganic salts generally raise the surface tension when they are added to water.
- Certain molecules drastically lower the surface tension when they are added to water. Such molecules frequently amphiphilic in the sense that they are linear molecules composed of a charged end that is attracted to water and a hydrophobic end that is repelled by water. Examples include organic acids like butanoic acid. $CH_3CH_2CH_2COO^-$ adsorbs to the surface of the water with the COO^- group solvated and the aliphatic chain directed away from the water surface (see diagram above, right). Such molecules are called surface-active molecules or surfactants. Other examples include lipids and detergents.
- The total concentration of the surfactant c_2 and the change in surface tension of the solvent $\gamma_0 - \gamma$ where γ_0 is the surface tension of the pure solvent. For aliphatic acids this relationship is $\gamma_0 - \gamma = a\log(1 + bc_2)$. The constants a and b are determined by the acid.

Acid	a (N/m)	b (L/mole)
Propanoic acid	0.0298	6.07
Butanoic acid	0.0298	19.64
Caproic acid	0.0298	232.70

Example: What is the surface tension of a 0.1M solution of caproic acid?
Solution:

$$\gamma_0 - \gamma = a\log(1 + bc_2) \Rightarrow \gamma = \gamma_0 - a\log(1 + bc_2)$$

$$\gamma = 0.07275 N/m - (0.0298 N/m)\log(1 + 232.70 \cdot 0.1)$$

$$= 0.07275 N/m - (0.0298 N/m)(1.385) = 0.03147 N/m$$

- The relationship between the concentration of surfactant molecules at the surface, called the surface adsorption Γ, and the change in surface tension per unit change in total concentration of surfactant c_2 is given by the Gibbs Isotherm Equation

$$\Gamma = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_{P,T}$$

- Example: Calculate the surface adsorption Γ for a 0.1M solution of caproic acid.
  - $\gamma = \gamma_0 - a\log(1+bc_2) = \gamma_0 - \frac{a}{2.303}\ln(1+bc_2)$

$$\Gamma = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_{P,T} = -\frac{c_2}{RT}\frac{d}{dc_2}\left(\gamma_0 - \frac{a}{2.303}\ln(1+bc_2)\right)$$

$$= \frac{c_2}{RT}\frac{ab}{2.303(1+bc_2)} = \frac{(0.1M)(0.0298J/m^2)(232.70M^{-1})}{(8.31J/mole\cdot K)(298K)(1+(232.70M^{-1})(0.1M))}$$

$$= \frac{0.693}{6.01\times10^4} moles/m^2 = 1.15\times10^{-5} moles/m^2$$