3.4.2 System of two components

The simplest application of the Gibbs adsorption isotherm is a system of two components, e.g., a solvent 1 and a solute 2. In this case we have

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{3.48}$$

The ideal interface is conveniently defined such that $\Gamma_1 = 0$. Then we get

$$d\gamma = -\Gamma_2^{(1)} d\mu_2 \tag{3.49}$$

The superscript "(1)" should remind us of the special choice of the interface. The chemical potential of the solute is described by the equation

$$\mu_2 = \mu_2^0 + RT \cdot \ln \frac{a}{a_0} \tag{3.50}$$

Here, a is the activity and a_0 is a standard activity (1 mol/L). Differentiating with respect to a/a_0 at constant temperature leads to

$$d\mu_2 = RT \cdot \frac{d\left(a/a_0\right)}{a/a_0} = RT \cdot \frac{da}{a} \tag{3.51}$$

Substituting this into Eq. (3.49) leads to

$$\Gamma_2^{(1)} = -\frac{a}{RT} \cdot \left.\frac{\partial \gamma}{\partial a}\right|_T \tag{3.52}$$

This is a very important equation. It directly tells us that when a solute is enriched at the interface ($\Gamma_2^{(1)} > 0$), the surface tension decreases when the solution concentration is increased. Such solutes are said to be surface active and they are called **surfactants** or surface active agents. Often the term amphiphilic molecule or simply amphiphile is used. An amphiphilic molecule consist of two well-defined regions: One which is oil-soluble (lyophilic or hydrophobic) and one which is water-soluble (hydrophilic).

When a solute avoids the interface ($\Gamma_2^{(1)} < 0$), the surface tension increases by adding the substance. Experimentally Equation (3.52) can be used to determine the surface excess by measuring the surface tension versus the bulk concentration. If a decrease in the surface tension is observed, the solute is enriched in the interface. If the surface tension increases upon addition of solute, then the solute is depleted in the interface.