

## Module 4: "Surface Thermodynamics"

### Lecture 21: ""

The Lecture Contains:

- Effect of surfactant on interfacial tension

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Surface Thermodynamics: Roles of Surfactants and solutes

## Effect of surfactant on interfacial tension

A surfactant or a surface active agent is an organic molecule which is amphiphilic in nature, that is, contains two distinct parts.

1) Hydrophilic part (the head group)

2) Hydrophobic part (the tail group)

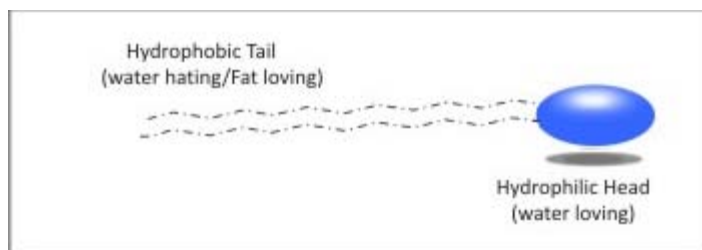


Fig 6.1: Schematic of a surfactant molecule

The hydrophilic (water-loving) head is attracted to water molecules while the lipophilic (fat-loving) tail attaches itself to oil and grease, repelling water. An effective surfactant is usually considered to be one with a hydrophobic tail > 8 Carbon atoms.

While surfactants may be further classified as nonionic (eg. Fatty alcohols), cationic (eg. Cetyl trimethyl ammonium bromide or CTAB), anionic (eg. Sodium dodecyl sulfate or SDS) or zwitterionic (Cocamidopropyl hydroxysultaine) based on the charge of the head group let us focus here on its effect on surface tension that renders it invaluable to us.

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When a surfactant is used as a solute all the surfactant molecules do not acquire the interface. There is always equilibrium between diffusion and thermodynamics. At the same time, it is also interesting to note that a small amount of surfactant is sufficient for the desired result because the effect does not depend on their bulk concentration but on the concentration at the interface.

Beyond a critical concentration known as critical micelle concentration (CMC), aggregate formation of the surfactants in the bulk phase called micelle formation starts because the interface becomes saturated.

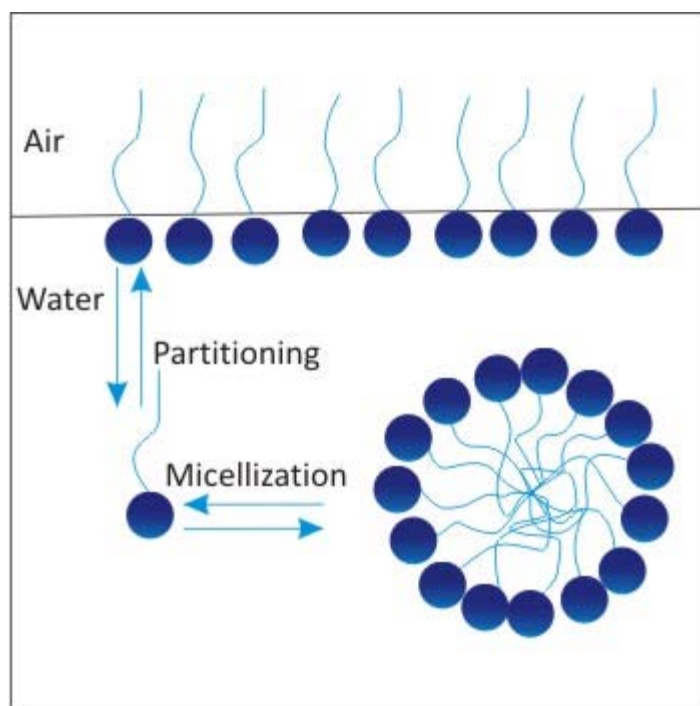


Fig 6.2: Micelle formation

The modified interfacial tension is expressed as a function of interfacial concentration of the surfactant.

$$\gamma = \gamma_0 - \Gamma$$

where  $\Gamma$  is the interfacial concentration of surfactant molecule.

$$\Gamma = (\text{number of moles on interface}) / \text{Area}$$

Interfacial concentration of component  $i$  is defined as the number of moles of  $i$  on the interface per unit area. There is a problem in defining  $\Gamma$  like this as in reality there is no zero thickness interface. Instead there exists an interfacial zone, so we choose any arbitrary interface in the interfacial zone using which we define  $\Gamma$ . Volume of this surface is assumed to be zero. Model of such an interfacial zone is shown below.

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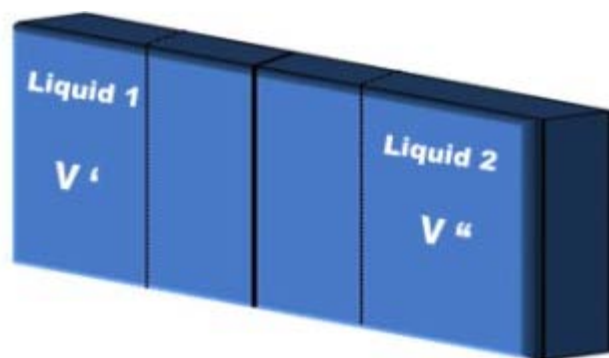


Fig. 6.3: Interface between two phases

If  $V$  is total volume then

$$V = V' + V''$$

Also

$$n_i^s = n_i - (n_i' + n_i'')$$

where  $n_i^s$  is number of moles of species  $i$  assigned to the interface,  $n_i$  is total number of moles of  $i$  and  $n_i'$  and  $n_i''$  are the number of moles of  $i$  assigned to bulk phases of liquid 1 and liquid 2 respectively. Therefore

$$\Gamma_i = \frac{n_i^s}{A} \quad (6.1)$$

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Now, we calculate the effect of surfactants on interfacial tension. Gibbs Duhem equation for bulk is

$$S' dT - V' dp' + \sum n'_i d\mu'_i = 0$$

Gibbs Duhem equation for interface is given by

$$S^s dT + A d\gamma + \sum n_i^s d\mu_i^s = 0$$

Assuming system is in thermal and chemical equilibrium at constant temperature  $T$ . We get,

$$dT = 0$$

$$d\mu'_i = d\mu_i'' = d\mu_i^s = d\mu_i$$

$$\text{Hence, } d\gamma = - \sum_{i=1}^N \left( \frac{n_i^s}{A} \right) d\mu_i = - \sum_{i=1}^N \Gamma_i d\mu_i \quad (6.2)$$

$$V' dp' = \sum n'_i d\mu'_i$$

$$V'' dp'' = \sum n_i'' d\mu_i''$$

$$dp' - dp'' = \frac{\sum n'_i d\mu'_i}{V'} - \frac{\sum n_i'' d\mu_i''}{V''}$$

$$n = CV$$

where  $C$  is concentration. Therefore

$$dp' - dp'' = \sum_1^n (C'_i - C''_i) d\mu_i$$

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If we assume that the interface is a flat surface then from the Young Laplace equation

$$dp' - dp'' = 0$$

Without loss in generality we can assume species '1' as the solvent for the system assuming it is present in excess amount.

$$(c_1' - c_1'')d\mu_1 = \sum_2^n (c_i' - c_i'')d\mu_i$$

$$d\gamma = -\Gamma_1 d\mu_1 - \sum_2^n \Gamma_i d\mu_i$$

$$d\gamma = \Gamma_1 \frac{\sum_2^n (c_i' - c_i'')d\mu_i}{c_1' - c_1''} - \sum_2^n \Gamma_i d\mu_i$$

$$d\gamma = \sum_2^n \left( \Gamma_i - \frac{\Gamma_i (c_i' - c_i'')}{c_1' - c_1''} \right) d\mu_i$$

$$-d\gamma = \sum_2^n \Gamma_{i,1} d\mu_i \quad (6.3)$$

where  $\Gamma_{i,1} = \Gamma_i - \Gamma_1 \frac{\Delta c_i}{\Delta c_1}$  = surface excess concentration of species  $i$  with respect to 1.

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We choose the interface such that  $\Gamma_{i,1} = 0$

then  $\Gamma_{i,1} = \Gamma_i$  (for  $i > 1$ ).

The idea is, change in surface tension  $d\gamma$  should not depend on the solvent concentration (species 1) i.e  $d\gamma$  should be independent of  $\Gamma_1$

This  $\Gamma_1 = 0$  is known as the *Gibb's convention*. It can be proved that  $d\gamma$  calculated above is independent of the position of the surface.

$$n_i^s = n_i - C_i' V' - V'' C_i''$$

$$n_i^s = n_i - C_i' V - V'' (C_i'' - C_i')$$

for  $i = 1$  (solvent) we have

$$n_1^s = n_1 - C_1' V - V'' (C_1'' - C_1')$$

Thus,

$$V'' = \frac{n_i^s - n_i + C_i' V}{(C_i' - C_i'')} = \frac{n_1^s - n_1 + C_1' V}{(C_1' - C_1'')} \quad (6.4)$$

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$$\frac{n_i^s}{A} - \frac{n_i^s}{A} \frac{\Delta C_i}{\Delta C_l} = \frac{n_i - VC_i'}{A} + \frac{(VC_i' - n_l)}{A} \frac{\Delta C_i}{\Delta C_l}$$

$$A\Gamma_{i,1} = (n_i - VC_i') + (VC_i' - n_l) \frac{\Delta C_i}{\Delta C_l} \quad (6.5)$$

where  $\Delta C_i = C_i' - C_i''$ ,  $\Delta C_l = C_l' - C_l''$  and  $A$  is the area of interface. RHS of the above equation is independent of the surface property hence  $d\gamma$  is independent of choice of surface. There is no uncertainty in this RHS since, being bulk properties, all are known measurables. Thus, if the interface is chosen in such a way that  $\Gamma_l = 0$  (Gibb's convention) we have,  $\Gamma_l = \Gamma_{l,1}$

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