

Module 4: "Surface Thermodynamics"

Lecture 22: ""

The Lecture Contains:

- Examples on Effect of surfactant on interfacial tension

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Example

Consider liquid, its vapors and the solute as a two-phase two-component system. Let the properties of the vapor be represented by $[]'$ and the properties of the liquid phase by $[]$.

(1) represents solvent and

(2) represents solute.

If the solute is non-volatile (surfactants are usually non-volatile), then $C_2' \approx 0$. Further, since concentration of solvent in vapor phase is very small compared to that in the bulk liquid phase, we have $C_1'' - C_1' \approx C_1''$.

From the above discussion we have

$$-d\gamma = \Gamma_{2,1} d\mu_2$$

$$A\Gamma_{2,1} = n_2 - n_1 \frac{C_2''}{C_1''}$$

If we consider the bulk solubility of the surfactant to be small then $C_2 \approx 0$.

$$\Gamma_{2,1} = \frac{n_2}{A}$$

This is a limiting case implying that all the surfactant has gone to the surface.

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$$\mu_2 = \mu_2^0 + RT \ln a_2$$

where a is activity of surfactant.

$$-d\gamma = \Gamma_{2,1} RT \frac{da_2}{a_2}$$

For an ideal solution activity of solute is equal to its concentration ($a = C$). So,

$$-d\gamma = \Gamma_{2,1} RT d \ln C_2$$

Thus with the increase in surfactant concentration, the interfacial tension decreases. Γ is not independent of C and it also increases with the bulk concentration of the solute. This dependence is captured by the adsorption isotherm.

$$-\int_{\gamma_0}^{\gamma} d\gamma = \int_0^C \Gamma_{2,1} RT d(\ln C_2)$$

Here, γ_0 is the interfacial tension for the pure surface, i.e. when no solute was present. A linear adsorption isotherm implies that γ varies linearly with the bulk solute concentration.

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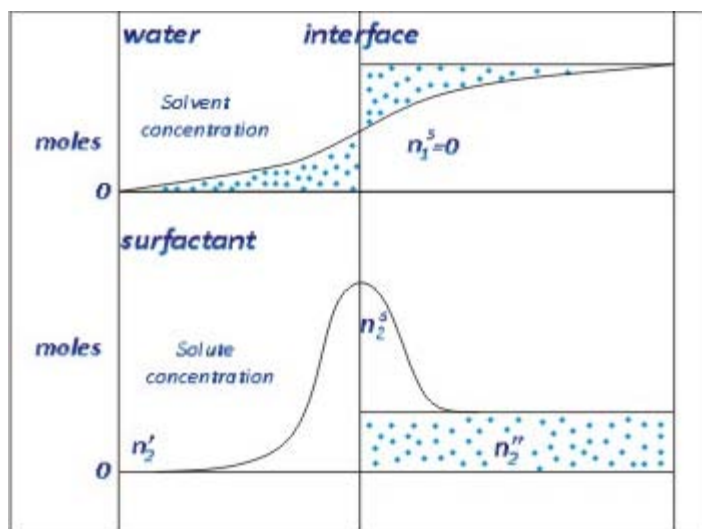


Fig. 6.4: Gibbs's convention

$n_2^s = n_2 - n_2'' - n_2' > 0$ for surfactants which crowd around the interface.

$$-d\gamma = \sum_{i=2}^N \Gamma_{i,1} d\mu_i$$

The above is the Gibbs equation.

Any solute which is extremely hydrophilic (like common salt and sugar) would have a negative surface concentration Γ implying it is present more in the bulk than at the surface.

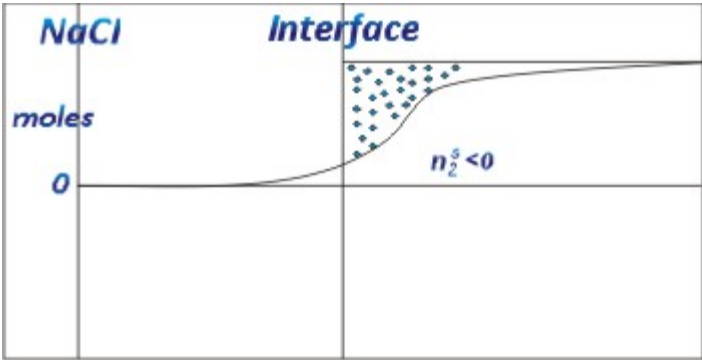


Fig. 6.5: Profile for a hydrophilic solute (NaCl)

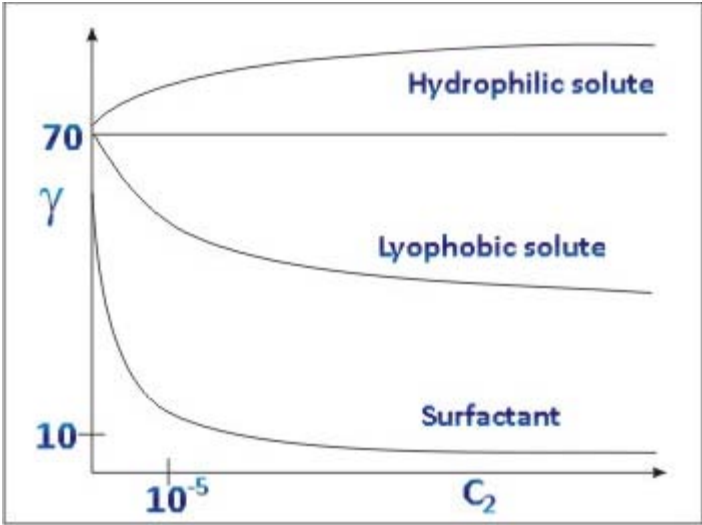


Fig. 6.6 : Interfacial tension versus solute concentration.

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$$-d\gamma = \Gamma_{2,1}RTd \ln C_2$$

Fig 6.6 shows the effect of adding different materials on the surface tension of water (72.8 mJ/m^2). On adding hydrophilic solutes that are present more in the bulk than the interface, the surface tension increases. While lyophobic solutes, that dislike the bulk aqueous phase, decrease the surface tension somewhat, huge reduction of surface tension takes place through surfactant addition. Cosurfactant addition further reduces the surface tension, while it is seen that alcohol, if added along with surfactant and cosurfactant can lead to ultra low surface tension.

At high concentration of solute (surfactants), interfacial tension does not change much due to formation of micelles. Hence $d \ln C$ may not be a good representation and needs to be replaced with activity. Micelles form only after a particular concentration of solute (i.e. surfactants) called critical micelles (delete) concentration (CMC). CMC is achieved because there is an energy penalty in micelles formation. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tension change becomes very small. Thus from a graph of concentration of surfactant versus the change in surface tension, the CMC for the system can be evaluated.

[2] For $C > \text{CMC}$, micelles form as a result of saturation and the activity of monomer surfactant remains constant.

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Example

Consider an electrolyte (RSO₃ONa) adsorbing at water air interface. It can be represented as chemical equation as

NaA ⇌ Na⁺ + A⁻ where A represents RSO₃O. Using Gibbs equation we can write

$$\sum_{i=2} \Gamma_i d\mu_i$$

$$d\gamma = -\Gamma_{Na^+} d\mu_{Na^+} - \Gamma_{A^-} d\mu_{A^-}$$

Assuming surface is neutral i.e. equal number of anion and cation at the surface so

$$\Gamma_{A^-} \approx \Gamma_{Na^+} \approx \Gamma$$

$$d\gamma = -\Gamma RT d \ln(a_{Na^+} a_{A^-})$$

$$a_m^2 = a_{Na^+} a_{A^-} \tag{6.6}$$

a_m is mean ionic activity which is practically more easy to measure then a_{Na} and a_A.

$$\begin{aligned} d\gamma &= -2\Gamma RT d \ln a_m \\ &= -2\Gamma RT d \ln C_{NaA} \end{aligned} \tag{6.7}$$

where C_{NaA} is the concentration(amount) of salt put in. Reduction in surface tension depends on how much molecules are adsorbed on the surface.

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For same mean activity (or same concentration of pure salt added), the reduction in γ for the case of dissociating salts will be twice as compared to that for the non-dissociating salts case.

But if NaA is present in large amounts, its dissociation will decrease and the reduction factor for γ will be lowered. This has implications in the case of detergency. In hard water, there are many salts present. Let us say NaCl is present in excess along with NaA . Concentration of sodium ion and chloride ion remain almost constant on adding small amount of NaA so the chemical potential of both sodium and chloride ions remain constant. Thus, dmNa term will disappear and the lowering in the interfacial tension reduces. Hence, it is difficult to wash clothes in hard water and thus water softening is needed to remove these impurity ions before using the detergent.

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