

Module 4: "Surface Thermodynamics"

Lecture 23: "Effects of surfactants on adsorption"

The Lecture Contains:

- ☰ Wettability
 - Special Cases
- ☰ Detergency

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Effects of surfactants on adsorption

Wettability

If surfactants are added to a liquid, its surface property changes due to adsorption of surfactant. This adsorption changes the liquid's surface tension and thus changes its equilibrium contact angle with any other surface. Hence its ability to wet a surface also changes. Therefore Contact angle ' θ ' of the liquid on a surface is a function of the surfactant concentration.

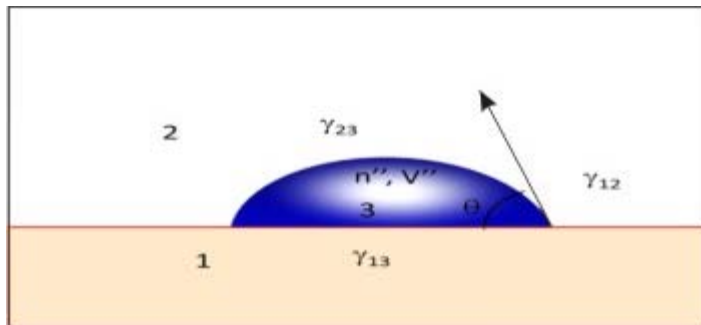


Fig. 6.7: Liquid drop on a surface.

From Young's equation we have

$$\gamma_{23} \cos \theta + \gamma_{13} = \gamma_{12} \quad (6.8)$$

Differentiating the above equation with respect to chemical potential (μ)

$$\cos \theta \frac{d\gamma_{23}}{d\mu} - (\sin \theta) \gamma_{23} \frac{d\theta}{d\mu} = -\frac{d\gamma_{13}}{d\mu} + \frac{d\gamma_{12}}{d\mu}$$

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Let us assume C to be the bulk concentration of the surfactant.

Changing the chemical potential by concentration by Gibbs adsorption equation

$$\frac{d\gamma_{12}}{d\mu} = -\Gamma_{12}, \frac{d\gamma_{13}}{d\mu} = -\Gamma_{13}, \frac{d\gamma_{23}}{d\mu} = -\Gamma_{23}$$

$$d\mu = RT d(\ln C) = RT \frac{dC}{C}$$

$$\gamma_{23} \sin \theta \frac{d\theta}{d \ln C} = RT(\Gamma_{12} - \Gamma_{13} - \Gamma_{23} \cos \theta) \quad (6.9)$$

The above expression gives the change in the contact angle when concentration is changed. If we want to decrease θ with increase in concentration then

$$\frac{d\theta}{dC} < 0, \text{ which implies,}$$

$$\Gamma_{12} - \Gamma_{13} - \Gamma_{23} \cos \theta < 0$$

Thus variation of θ depends on relative adsorption at the three interfaces. We can increase or decrease equilibrium contact angle (and hence the wettability) by changing Γ_{12}, Γ_{13} and Γ_{23} appropriately.

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Special cases

When 2 (fig. 6.7) is a gas and a surfactant added is non-volatile then the surfactant will not be present in gas phase. Thus

$$\Gamma_{12} \approx 0$$

$$\Gamma_{13} + \Gamma_{23} \cos \theta > 0$$

Γ_{13} and Γ_{23} are positive quantities (true if surface active) so for $0 < \theta < \frac{\pi}{2}$ contact angle will decrease on adding solute. Contact angle may increase on adding solute if contact angle was such that $\cos \theta$ became negative.

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Detergency is defined as removal of foreign material from the solid surfaces. This includes removal of dirt, oil or impure particle from clothes, metal surfaces etc.

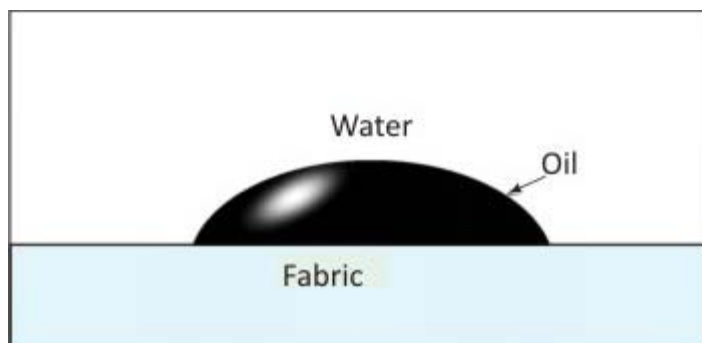


Fig. 6.8: Dirt (oil) on a fabric.

Soaps remove both liquid (oil) and solid (dirt) particles from the fabrics. When a dirt particle is removed from surface its configuration may look like as shown in figure below (6.9). For the detachment of dirt particle from the fabric surface to be thermodynamically favorable, the change in surface free energy ΔG should be less than zero.

$$\Delta G = \gamma_{sw} + \gamma_{wo} - \gamma_{so} < 0 \quad (6.10)$$

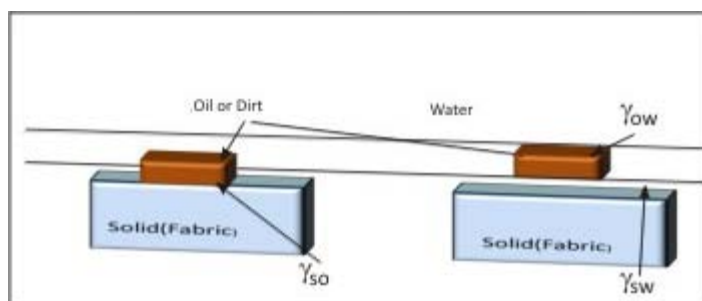


Fig. 6.9: Removal of dirt creates new surface.

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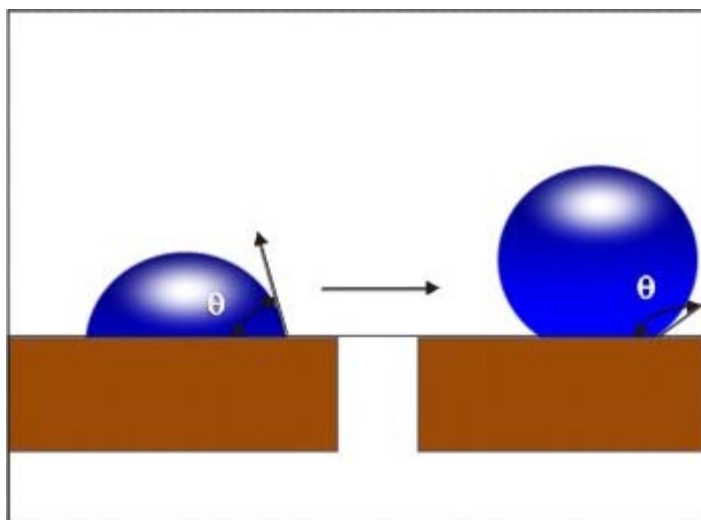


Fig: 6.10: Change of contact angle on addition of surfactant.

Removal of the oil particle from the fabric becomes difficult when the contact angle (θ) of the oil with the fabric surface is less. Surfactant facilitates removal of oil by increasing the contact angle of oil with the fabric. For this to happen, the following equation must be satisfied

$$\Gamma_{sw} - \Gamma_{so} - \Gamma_{ow} \cos \theta < 0$$

This equation reflects that the q increases with the increase in concentration of the surfactant. Surfactants make both the solid and the oil surface hydrophilic and hence oil particles dislodge from solid surface. Re-deposition of oil on a solid surface is a major concern in detergency and is prevented due to repulsion between hydrophilic ends of surfactant (fig: 6.11). If the surfactant is charged, electrostatic repulsions may also play a major role in preventing redeposition.

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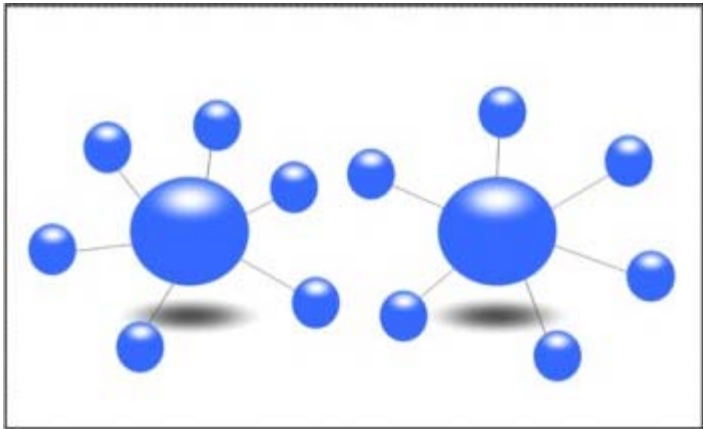


Fig. 6.11: Repulsion between hydrophilic heads

Agglomeration of particles is suppressed because of hydration pressure. It is often argued that surfactants alone are not responsible for removal of dirt from the fabric and mechanical agitation may be necessary for the purpose. However the undeniable and critical role of surfactants is not removal of dirt, but prevention of dirt redeposition. Formation of the foam also prevents re-deposition of oil and removes dirt from substrate (fig: 6.12). Foaming ability is not correlated to cleaning ability. But foam helps in preventing redeposition. Once both the particles and surface is coated with hydrophilic material(e.g. polymeric film), redeposition gets prevented.

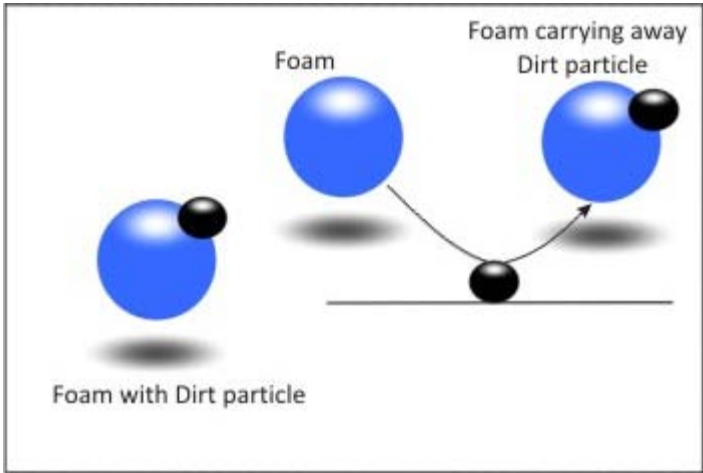


Fig. 6.12: Foam prevents re-deposition of oil.