INTERFACIAL PHENOMENA

Assist. Prof. Dr. Özge İNAL

Spring Course; 2020

What is interface?

Interface is the **border /surface** between the immiscible phases in systems consisting different phases such as;

Liquid-gas

Liquid-liquid

Liquid-solid

Solid-gas

Solid-solid

Interface is the border /surface between the immiscible phases in systems consisting different phases

Phases	Types of interface
Gas/ Gas	Interface do not exist
Gas / Liquid	Liquid surface exist; surface of liquid in contact with atmosphere
Gas / Solid	Solid surface exist; surface of table in contact with atmosphere
Liquid / Liquid	Liquid-Liquid interface exists; EMULSIONS
Liquid / Solid	Liquid-solid interface exists; SUSPENSIONS
Solid / Solid	Solid-solid interface exists; POWDERS

If two different liquids are completely miscible, this means that **there is not any interfacial tension between them**.

In heterogeneous systems it is important to understand how the phases will behave when they contact with each other.

Liquid can show tendency to spread on a surface or contrarily can remain in the form of a drop.
These behaviours are explained with cohesion and adhesion forces.

There are cohesive forces between the molecules of a liquid. Thus, the liquid molecules are drawn equally in each direction.

However, in the air-contacting surface of the liquid (liquid-gas interface), adhesional forces are the issue. Thus, the surface is shrunk to try to pass through the spherical shape and reduce its energy to a minimum (The surface of the liquid is minimum).

Cohesional forces are the intermolecular attraction between molecules of the **same species**. For example; forces between molecules inside a glass of water

Adhesional forces are the intermolecular attraction between **different types of molecules**. For example; forces between water molecules and table surface

cohesional >adhesional forces;

Liquids do not wet the surface and stays as drops.

adhesional forces > cohesional forces,

Liquids spread as a film and wets the surface.

⇓

miscibility will occur and the interface will disappear.

Surface tension

- **is defined as the force applied to the unit length to increase the surface by 1 cm^2.**
- If the surface tension is expressed in terms of energy, it is the energy required to expand the surface area of a liquid by 1 cm^2.

⇨ *the work required to create a unit area of surface is known as **surface free energy** and it is equivalent to the surface tension of a liquid system.*

The interfacial tension

- is defined as the force per unit length in the interface present between the two non-miscible liquids.

	CGS unit system	SI unit system
surface tension	dyne/cm	miliNewton/meter
surface free energy	erg/cm^2	mili Joule/ m^2

- **Surface tension is generally explained by a movable wire frame containing a film of liquid being expanded with a force (F).**
- Here, a rectangular wire with one movable side is assumed. After dipping into a liquid (for example a soap solution), a film of liquid will form within the frame when it is removed.
- When in contact with air this liquid surface will tend to contract with force (F). To keep the movable side in equilibrium an equal force must be applied.
- From this force and the distance of application surface tension can be calculated by using the equation below:

$$\gamma = F/2\,L$$

ɣ = surface tension
F = force which liquid surface tend to contract
2L = distance of surface which F is operating

2 surfaces will exist above and below the plane of the wire

Importance of surface/interfacial tension

- It is a characteristic feature that determines the quality of the mixture in multi-phase systems.
- It is an important criterion for the preparation of homogeneous and reproducible formulations.
- It informs about amount of substance collected on the surface during the adsorption.
- It is an important criterion for determining the size of the drop.
- It is important in the penetration of molecules from biological membranes.

Factors affecting the surface/interfacial tension

Concentration

- Substances with a tendency to aggregate at the interface reduce the surface tension.

Impurity

- A pure substance is the substance with the highest surface tension.
- Increased impurity reduces surface tension.

Temperature

- Increasing in medium temperature decreases surface tension.
- Therefore, temperature must be kept constant during surface/interface tension measurements.

Surface and Interfacial tension determination methods

1- Capillary rise method

2- Wilhelmy plate method

3- Du Nouy ring method

4- Drop methods
    ** Donnan pipette method
    ** Pendant drop method
    ** Sessile drop method

5- Maximum bubble pressure method

6- Oscillating jet method

Capillary rise method

The liquid begins to rise in the pipe due to surface tension. The upward movement of liquid, stops when the force of gravity, which tries to pull the liquid downward with the surface tension, comes to a balance.

$$\gamma = \frac{1}{2}\, r\, h\, \rho\, g$$

r = radius of the capillary tube
h = height at which the liquid is raised
ρ = density of liquid
g = gravitational acceleration (981 cm/s^2)

- **For obtaining correct results from the method, the tube radius must be constant, must remain same at all points and the material must be clean**
- **Thus, contact angle must be θ =0).**

Contact angle (ϴ)

- This is the angle between the surface of a drop of liquid on which it is spread.

- The contact angle can be between 0-180°.

0° there is full wetting
180° there's no wetting

Wilhelmy plate method

$$WL - W = 2(L+T)\,\gamma$$

WL: Value read just before the scale detaches
W : Weight of plate in the air
L : Plate's length
T : Plate's thickness
γ : Surface tension

- **In this method, a thin mica or platinum plate is immersed in water.**
- **This plate is attached to a scale on the other side.**
- **The value when the plate breaks from water surface (or liquid-liquid interface) is read out from the plate and is used to calculate the surface tension.**
- **Interfacial tension can be measured.**
- **For this, the plate must be in the bottom of the liquid and from it must be detached to the upper liquid.**

Du Nouy ring detachment method

$$\gamma = (F / 2 \times 2\pi r) \times \beta$$

F : Detachment force read from the dial
2πr : Ring circumference
β : Correction factor of field
γ : surface or interfacial tension

Surface and interfacacial tension can be measured.

- **Method is based on measurement of the force required to detach a platinum/iridium wire ring from the surface/interface of liquid(s).**
- **Results can be given as dyn or mNewton**
- **The radius of the wire and the volume of the bulk liquid is effective on measurement.**

Drop methods

The force that holds a drop at the tip of a dropper's wedge pipette is proportional to the surface tension of the liquid that influences the circle through which the drop contacts the dropper. The surface tension is exactly equal to the weight of the drops when the drop is completely removed from the tip.

In this method,

- A liquid drop from the tip of a narrow tube held in a vertical position is slowly removed.
- The breaking drops are either weighted, or the volume drops are detected.
- The drop volume of a liquid with a known surface tension is determined by the number of droplet weight drops. It is compared to the unknown liquid in the same conditions.

Drop methods

1-Donnan pipette method

Uses drop numbers

2-Pendant drop method

Uses drop size

3-Sessile drop method

Uses drop radius

$$\gamma = \frac{\phi . m . g}{2\pi r} = \frac{\phi V \rho g}{2\pi r}$$

m: Weight of drop

V: Volume of drop

ρ: Density of liquid

r: Radius of tube

ϕ: Correction factor

- Equation is established with reference to a known liquid, for example water

$$m_0/m = \gamma_0/\gamma$$

m, m_o are droplet weight of reference and sample

γ, γ_0 are surface tension of reference and sample

Donnan pipette

- Interfacial tension of liquids which do not mix with each other is detected.
- Liquid with low density is taken with the pipette and this pipette is immersed in other liquid (which has higher density).
- The pipette upper air tap is opened to allow a certain amount of liquid having a low density to flow out to the surface of the second liquid dropwise.
- The number of drops is counted.
- The liquid outerside in first step is then poured into the pipette to determine the interface tension against the external liquid and the previous procedure is repeated.
- The interface tensions are proportional to the drop numbers.

Pendant (Hanging) Drop method

- It is a method with sensitivity and reproducibility.
- Hanging drops are either photographed or projected.
- The surface tension is calculated from the size of the droplet.
- Dirty surface is not a problem.

Sessile Drop method

- The diameter of the droplet is examined by microscopic examination or by projection of the photograph of the liquid droplet on a non-wetting surface ($\theta > 90°$) which is immiscible with the liquid drop.

Oscillating jet method

- It is a dynamic method that measures surface tension in a very short time like 0.01 sec.
- The liquid is passed through a small hole with pressure.
- From the photograph of the circular cross-section of that hole, the dimensions and the surface tension are associated while the liquid is passing.

Maximum bubble pressure method

- It is used for surface tension measurement.
- The capillary tube dips into the liquid to a known depth and the minimum pressure is determined at which bubbles of an inert gas are just able to grow and detach from the tip.
- If the bubble forms a spherical curvature, the curvature is maximum when it takes the shape of a hemisphere. At that point pressure is maximum.