Surface tension, Theory and characterization technics

Introduction:

Surface tension is the force that exists at the interface between a liquid and a gas. Because molecules at the surface prefer to be surrounded by similar molecules, the system tends to minimize the contact area between the two phases. This phenomenon explains, for example, the spherical shape of soap bubbles, the curved meniscus of an overfilled glass of water, and the droplets that form and fall from a tap.

This force can be altered by molecules called surfactants, which reduce the interfacial energy between the two phases. Surfactants are amphiphilic molecules, meaning they have a dual affinity: an apolar lipophilic tail (soluble in fatty substances) and a polar hydrophilic head (soluble in water).

1. The phenomenon of surface tension

Several simple observations highlight surprising phenomena. For example, a steel paper clip can rest on the surface of water without sinking, even though its density is much higher than that of water. Similarly, Gerris (water striders), small insects, can move at high speed (around 1 m/s) across the water's surface as if it were a flexible, elastic membrane. These observations suggest that a special force exists at the surface of water, giving it properties distinct from those of the bulk liquid.

Flotation of objects denser than water occurs their weight is small enough to be borne by the forces arising from surface tension.

Surface tension gives droplets their near-spherical shape, because a sphere has the smallest possible surface area to volume ratio.

1.1 Definition

In a liquid, a molecule undergoes forces of attraction from its neighbours that compensate each other by symmetry (Figure 1). At the water / air interface, the resulting intermolecular forces of attraction this time directed towards the inside of the liquid. The superficial layer will therefore tend to sink by compressing the liquid that reacts to maintain a balance at its free surface, this compensating force is called the surface tension, denoted by γ\gammaγ. When the liquid is in contact with another immiscible liquid, the corresponding force is referred to as interfacial tension.

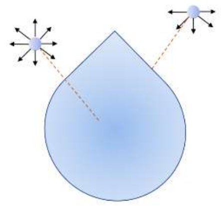

Figure 1: Attraction forces between molecules inside a liquid and at the interface

Because the forces at the interface are not fully compensated, a molecule at the surface is less stable than one inside the liquid. The liquid therefore tends to minimize its free surface area to reduce its energy. Increasing the surface area requires an input of energy. To illustrate this, consider a soap film stretched on a rectangular frame ABCD, in which one side is movable without friction (Figure 2).

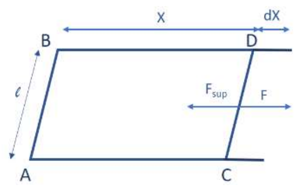

Figure 2: Soap film formed in a metal frame with one mobile side

To move the side CD, a force F must be applied to enlarge the surface of the frame. This applied force counteracts the surface tension force, which tends to restore the system to equilibrium. The energy required to increase the surface area corresponds to the work of the applied force:

$$F = \gamma \cdot \ell$$

Where ℓ is the length of the movable side. Surface tension can therefore be defined as the force per unit length acting along a surface element.

In many situations, such as thin films, soap bubbles, or membranes (Figure 3), two surfaces are present. Since the expression of the force is valid for a single interface, the total force must account for both surfaces, leading to:

$$F = 2\gamma \cdot \ell$$

Figure 3: Forces applying on a soap film

The concept of surface tension can also be considered from an energy perspective. A soap film with two interfaces has a total surface area of $2 \cdot \ell$. If the side CD is displaced by a distance dx, the work required per unit surface area created is therefore:

$$\frac{dW}{dA} = \frac{F.dx}{2.\ell.dx} = \frac{2\gamma\ell}{2\ell} = \gamma$$

Thus, surface tension may be interpreted either as a force per unit length or as the energy required per unit area to create new surface. It is expressed in N.m-1 which is the equivalent of J.m-2 or dyne / cm. The origin of this force lies in the intermolecular forces of Van der Walls.

The origin of these are forces is electrostatic, they appear because of the polarity of some molecules (interaction between polar molecules, induced polarity ...). When the temperature of a liquid increases, its interfacial tension decreases, because thermal agitation reduces the effectiveness of intermolecular cohesion.

1.2 Examples and applications

1.2.1 Orders of Magnitude (Liquid–Air Interface)

Interface	***Temperature***	***γ (mN·m⁻¹)***
Water–air	20 °C	72.86 ± 0.05
Water–air	25 °C	71.99±0.05
Ethanol–air	20 °C	22.39
Olive oil–air	20°C	33 [2]
Ethanol–Mercury	20 °C	389

1.2.2 Laplace's law

Consider a spherical gas bubble within a liquid. The resultant of the surface tension forces acts to compress the bubble, reducing its surface area. As a result, the pressure inside the bubble is higher than the external pressure. Let P_i denote the internal pressure and P_e the external pressure; the pressure difference is given by:

$$\Delta P = P_i - P_e$$

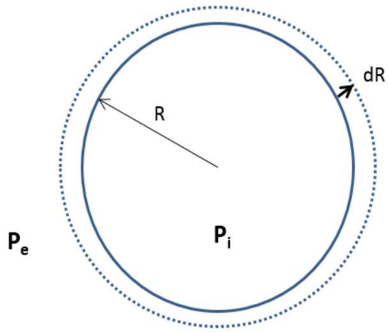

Figure 4: Spherical gas bubble subjected to forces of internal and external pressure

This overpressure can be expressed as a function of the bubble's radius R and the surface tension γ:

$$\Delta P = \frac{2\gamma}{R}$$

This relationship, known as Laplace's law, shows that smaller bubbles require a greater internal pressure to balance the same surface tension.

1.2.3 Soap bubble

A soap bubble consists of a thin layer of liquid enclosing a pocket of air (Figure 5).

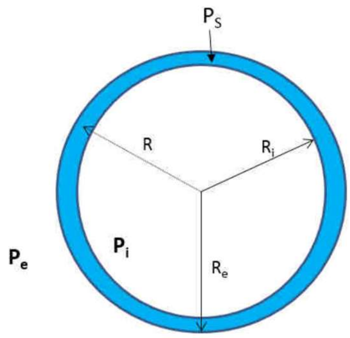

Figure 5: Soap bubble subjected to internal and external pressure forces

The liquid layer maintains its cohesion due to surface tension. For a bubble, the pressure differences across each surface of the thin liquid film can be expressed as:

$$P_i - P_s = \frac{2\gamma}{R} \quad (1)$$

$$P_s - P_e = \frac{2\gamma}{R} \quad (2)$$

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where $R \approx R_e \approx R_i$ for a thin film. By combining these expressions, the total pressure difference between the inside and outside of the bubble is:

$$\Delta P = P_i - P_e = \frac{4\gamma}{R}$$

This shows that as the radius R increases, the pressure difference ΔP decreases: smaller bubbles have higher internal pressure than larger ones. Consequently, if two bubbles come into contact, the smaller bubble tends to deflate into the larger one.

2. Surfactants

2.1 definition

Surface-active molecules are amphiphilic molecules that are used to lower the value of surface tension. They are composed of a hydrophilic head and a hydrophobic tail. Surfactant molecules have a high affinity for water-air and water-oil interfaces. When present at an interface, surfactant molecules decrease the interfacial energy and hence the surface tension. They are used for their properties as wetting agent, foaming agent, detergents, emulsifiers, ...

2.2 concept of HLB

The hydrophilic or hydrophobic character of surfactants depends on their molecular structure. To quantify their predominant nature, the concept of **HLB (Hydrophilic–Lipophilic Balance)** is used. This index provides a numerical estimate of the balance between the hydrophilic and lipophilic portions of a molecule.

The HLB scale ranges from 0 to 40: the higher the value, the greater the solubility of the surfactant in water (i.e., the more hydrophilic it is). Several calculation methods are described in the literature but the most used one is based on the ratio between the molecular mass of the hydrophilic portion and that of the lipophilic portion:

$$\mathrm{HLB} = 20\mathrm{x}\frac{\text{Molecular mass of hydrophilic part}}{\text{Molecular mass of lipophilic part}}$$

However, the HLB method has limitations. It only considers the chemical structure of the surfactant, without accounting for intermolecular interactions (e.g., Lewis forces, van der Waals interactions, etc.).

2.3 Function of surfactants

Surfactants exhibit different properties and applications depending on their molecular structure and HLB (Hydrophilic–Lipophilic Balance) value:

- Detergents (13 < HLB < 15): Compounds capable of removing dirt or grease from solid surfaces due to their solubilizing power.
- Solubilizing agents (18 < HLB < 20): Above the critical micelle concentration (CMC), surfactant molecules self-assemble into micelles. In these aggregates, the hydrophilic parts remain in contact with water, while the hydrophobic parts form a core that can trap and solubilize otherwise water-insoluble substances.
- Foaming agents (3 < HLB < 8): These surfactants stabilize thin liquid films around air bubbles, enabling the formation and persistence of foam.
- Dispersing agents: They allow the dispersion of hydrophobic solid particles in water by reducing surface tension. Surfactants prevent flocculation (clumping) of particles, which would otherwise aggregate and sediment.
- Emulsifying agents: Surfactants stabilize emulsions between two immiscible liquids by forming an interfacial film around dispersed droplets. Two main types of emulsions exist:
    - O/W (oil-in-water): obtained with surfactants of higher HLB values (HLB > 10).
    - W/O (water-in-oil): obtained with surfactants of lower HLB values (HLB < 6).

2.4 Structure of surfactants

There are four main categories of surfactants (Figure 6): anionic, cationic, zwitterionic and non-ionic depending on the nature of their hydrophilic head.

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Figure 6: categories of surfactants

When they are introduced into water, Surface-active molecules that are initially present in the bulk volume, migrate and adsorb at the interface (Figure 7).

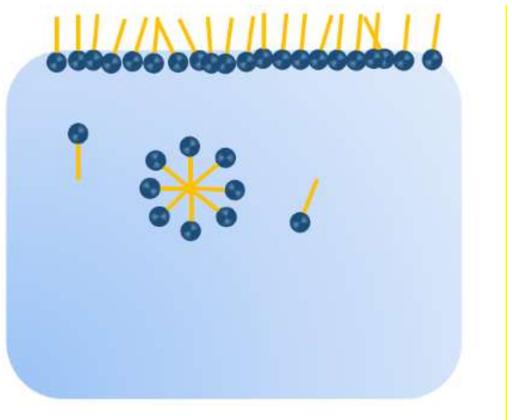

Figure 7: Behaviour of surfactants in solution and at the water / air interface.

When the concentration of surfactants increases, the number of surfactants per surface area at the interface increases until reaching the CMC (Critical Micellar Concentration). Above the CMC, the interface is saturated in surfactants, the surface tension is constant and equal to its minimum value and surfactant molecules aggregate and form micelles.

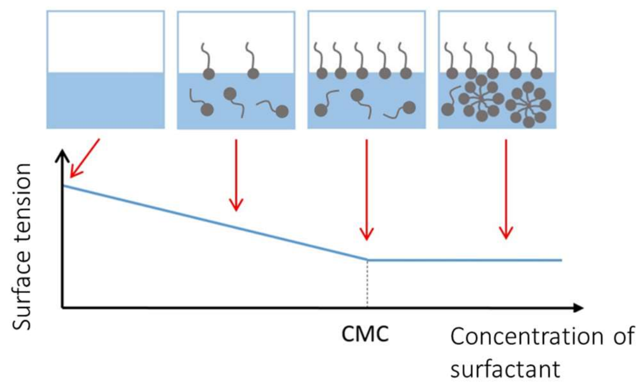

Figure 8: Critical Micellar Concentration

The CMC corresponds the limit in terms of surfactants concentration in the solution above which no further reduction of surface tension is expected. Increasing the concentration to values above the CMC results hence in a “waste” of surfactants.

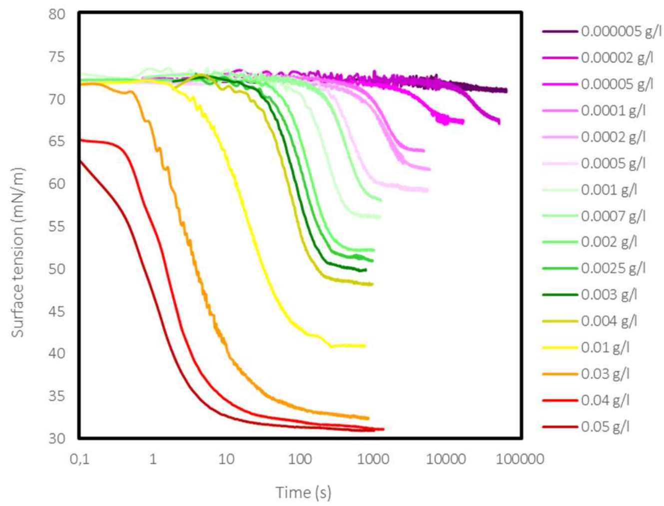

Figure 9: Example of dynamic surface tension measurements using a non-ionic surfactant at different concentrations: C12E6, Hexaethylene glycol monododecyl ether CH3(CH2)11(OCH2CH2)6OH

3. Surface Tension Measurement

3.1 Pendant drop method

The shape of the drop is determined by the combination of interfacial tension and the effects of gravitation. The interfacial tension makes the drop take a spherical shape while the effects of gravity tend to lengthen it to give a pear shape. Knowing the density of the liquid, the surface tension is then calculated by fitting the shape of a bubble or a drop (pending/rising or deposited) to a Laplacian profile parametrized by surface tension γ.

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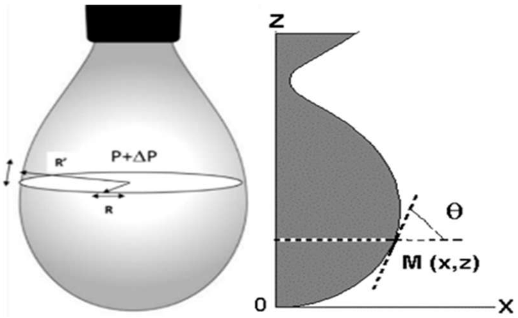

$$\Delta P = \gamma \cdot \left(\frac{1}{R} + \frac{1}{R'} \right)$$

The pressure difference caused by the curvature of the interface is proportional to the mean curvature, the proportionality coefficient being precisely the interfacial tension.

The Pendant/Rising Drop method is more versatile and accurate. Image analysis avoids uncertainties from wetting or adhesion to a solid object. Very small droplets (microliters) can be used, making it suitable for precious or rare liquids.

Dynamic measurements are possible by tracking the evolution of droplet shape, allowing studies of surfactant adsorption and transient surface effects.

By analyzing the exact droplet profile using image analysis, surface tension can be measured very accurately, even for low-tension liquids.

3.2 Method of weighing drop.

The weighing drop method is a classic technique for determining the surface tension of a liquid by measuring the mass of droplets that detach from a capillary or tube. The principle is based on the balance between gravitational forces and surface tension forces at the moment a drop separates from the tube.

The surface tension γ is related to the mass of the drop by the formula:

$$\gamma = \frac{mg}{2\pi r}$$

This method is simple and cost-effective but requires precise measurement of drop mass and accurate knowledge of the capillary radius.

3.3 De Nouÿ Ring Method

In this method, a thin ring, typically made of platinum, is submerged below the liquid surface and then slowly lifted. The force required to detach the ring from the surface is measured using a tensiometer. The surface tension is calculated from the maximum force F at detachment:

$$\gamma = \frac{F}{2\pi r}\, x\, f$$

where r is the radius of the ring and f is a correction factor accounting for the ring's geometry and wetting effects. This method is widely used due to its precision and suitability for a range of liquids.

3.4 Wilhelmy Plate Method

A thin, vertical plate (usually platinum) is partially immersed in the liquid. The force F exerted by the liquid on the plate, measured with a sensitive balance, is proportional to the perimeter P of the plate in contact with the liquid:

$$\gamma = \frac{F}{P}$$

De Nouÿ Ring and Wilhelmy Plate are simple and robust for static measurements but are less precise for small volumes, dynamic studies, or liquids with complex wetting behavior.

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