SURFACE AND INTERFACE TENSION

Molecules in liquids interact with each other by cohesive forces. Due to this forces a molecule is pulled equally in every direction by neighbouring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have the same molecules on all sides of them and therefore are pulled inward (Figure 1). This creates internal pressure and forces liquid surfaces to contract to the minimum area. Therefore, liquid surface behave like a thin flexible layer.

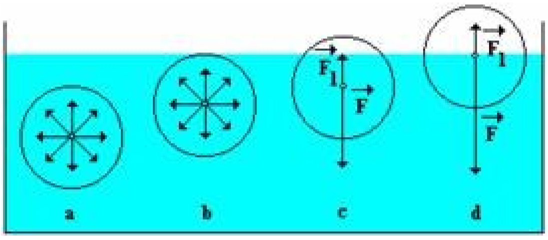

***Figure 1**: Cohesive forces in liquids*

The work which is required to increase the size of the surface of a phase is referred to as the surface tension. As a measure of work per unit area or force per wetted length, surface tension has the unit mN/m and is designated by the symbol σ. The surface tension is not influenced by the surface area of the liquid and decreases with increasing temperature. In a small temperature range, the surface tension decreases practically linearly with the increasing temperature.

The surface tension slightly decreases also with the increasing pressure, but the change in the value is negligible. Therefore, the influence of pressure can be usually neglected.

The surface tension of the purified water at the air interface is approximately 73 mN/m. In the case of solutions, the solute affects the surface tension value. The surface tension of water solutions of surfactants significantly decreases with increasing concentration of the surfactants. However, once the critical micellar concentration (CMC) is reached, the surface tension remains almost constant. At this point, the surface is fully overlaid with surfactant molecules and aggregates, so-called micelles, form in the volume phase. Any further addition of the surfactant monomers causes creation of new micelles that lack the surface activity. The dependence of surface tension on surfactant concentration is shown in Figure 2.

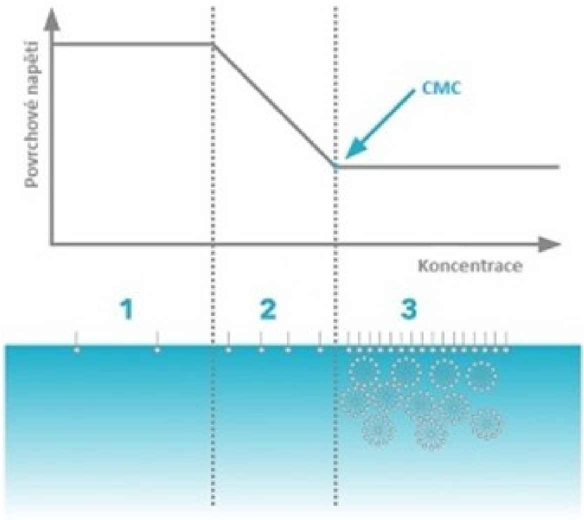

Figure 2: *The dependence of surface tension on the surfactant concentration divided into 3 phases*

In the case of solutions, the surface tension of a freshly formed surface (so-called dynamic surface tension) differs from the equilibrium tension (so-called static surface tension) differs due to the adsorption on the interface. Nevertheless, adsorption does not take place immediately and, therefore, the composition of the newly formed and equilibrium surface varies. Several methods have been introduced for the determination of the surface tension. These methods can be divided to:

- static methods
- semi-static methods (quasi-static)
- dynamic methods

Static methods

The static surface tension is the value of the surface tension in thermodynamic equilibrium independent of time. The establishment of the equilibrium value with respect to time can be pursued using static methods in which the size of the interface does not change.

Capillary rise method

Capillary rise results from the fact that the liquid wets the capillary walls. The surface (or interfacial) tension is then determined from the height of the raised liquid in the capillary (Figure 3). The capillaries used for the measurement are preferably made of materials that are perfectly wetted by a liquid (usually glass).

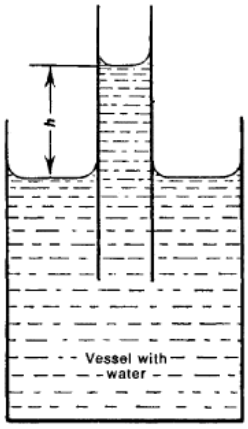

Figure 3: Capillary rise method

Pendant drop shape analysis

The shape of the drop hanging from a needle is determined from the balance of forces which include the surface tension of the investigated liquid (Figure 4). Modern computational methods using interactive approximations allow for solutions of the Young-Laplace equation to be found. Thus, the surface or interfacial tension between any two immiscible fluids with known densities can be determined. For optical tensiometry the size of the dromplet is important, and it should have a tear or pendant shape.

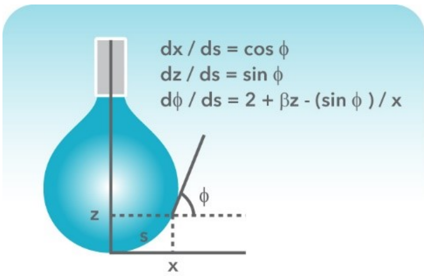

Figure 4: Pedant drop shape analysis

Semi-static methods

Semi-static methods, so-called quasi-static, are based on the achieving the equilibrium state of the system similarly to the static methods. However, in the case of semi-static methods, the equilibrium is unstable. The measurement of the surface tension using these methods is based on the determination of conditions under which the equilibrium state of the system is broken.

Maximum bubble pressure method

Maximum bubble pressure method was designed in 1851 by M. Simon. In this method a capillary that is completely wetted by the liquid, is placed vertically om the liquid under study. By bringing an extra pressure p_e on top of the meniscus the meniscus is pushed down against the capillary pressure and the hydrostatic pressure. Figure 5 sketches three successive stages. It is assumed that the meniscus of the liquid remans spherical. The external pressure p_e, needed to reach the sketched situation, is equal to the sum of the capillary and the hydrostatic pressure (b). In this situation, the pressure reaches the maximum value and the meniscus radius (r) is to a first order approximation equal to the capillary radius (R), whereas in situations (a) and (c) $r > R$. Another increase in pressure (c) leads to a spontaneous further growth and release of the bubble.

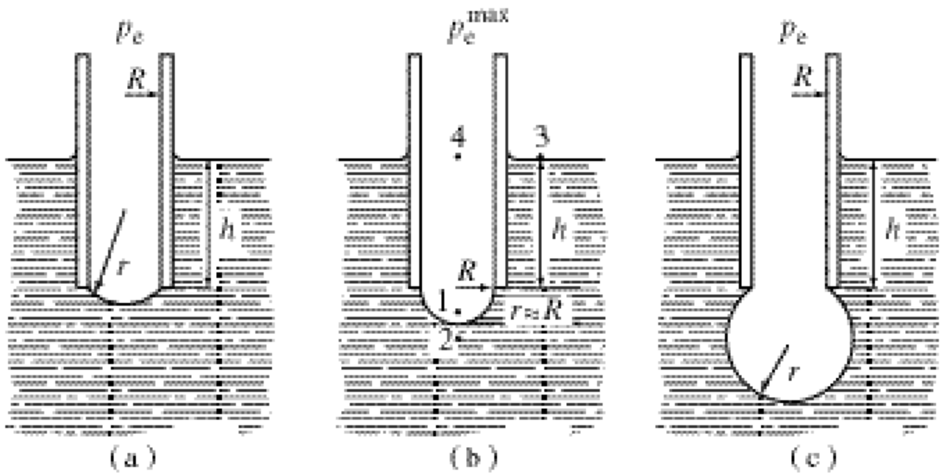

Figure 5: Maximum bubble pressure method

The wetting plays a major role in the maximum bubble pressure method. For capillaries that are well wetted (contact angle is lower than 90 °), the gas bubble is formed on the inner radius of the capillary (Figure 6). For poorly wetted capillaries (contact angle is grater than 90 °) the bubble forms on the outside wall.

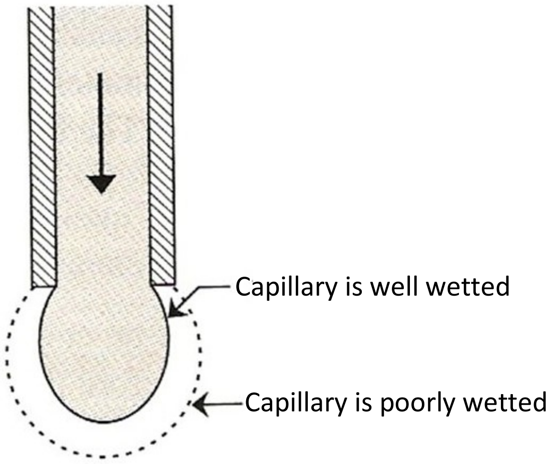

Figure 6: Growth of a gas bubble at low and high contact angle.

Tear-off methods

The tear-off methods are based on the evaluation of the force needed to tear off the thin ring (du Noüy ring method) or the thin plate (Wilhelmy method) from the interface. The suitably adapted analytical balances, torsion balances or preferably electrobalances are usually used to determine the force. The advantages of these methods include their speed and possibility to measure surface and also the interfacial tension.

Du Noüy ring method utilizes a platinum ring as the probe (Figure 7) that has to be completely wetted by the investigated liquid (contact angle is 0 °). With this method, a correction must be made to the measurement, as the weight of the liquid lamella increases the measured force, and because the force maximum does not occur at the inside and outside of the lamella at the same time. Various correction methods are already integrated to modern commercially available equipment (e.g. tensiometer Krüss K 100) and surface tension is the direct output.

Figure 7: du Noüy ring

Du Noüy ring method uses the interaction of the platinum ring with the surface of the investigated liquid. The ring is submerged below the interface by moving the platform on which the liquid container is placed. After immersion, the height of the platform is decreased, and the ring pulls through the interface bringing meniscus of liquid with it. If the container is lowered further, the meniscus will tear from the ring. Prior to this event, the volume (and thus the force exerted) of the meniscus passes through the maximum value and begins to drop before the actual tearing event. The calculation of the surface or interfacial tension is based on the measurement of the maximum force and the perimeter of the ring. The whole process is shown in Figure 8.

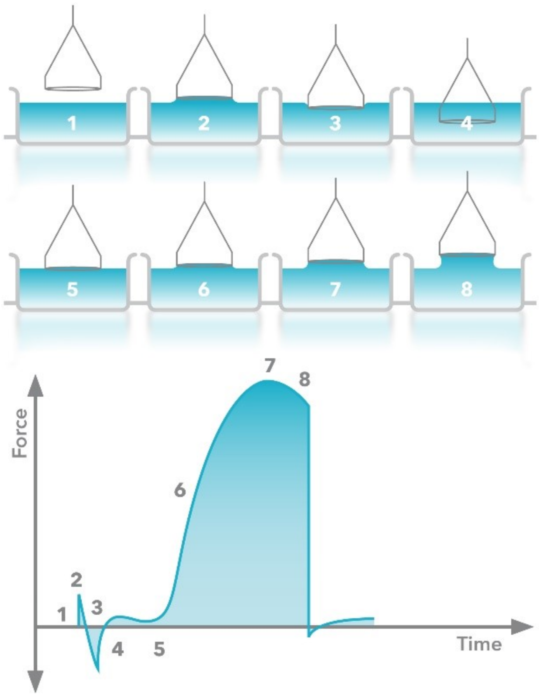

Figure 8: Evaluation of the surface tension using the du Noüy ring method

The Wilhelmy plate method utilizes a rough platinum plate as the probe. The calculations in this technique are based on the perimeter of the fully wetted plate in contact with the investigated liquid (it is not fully submerged). Meniscus is form on both sides of the plate during the measurement (Figure 9). The shape and height of the rise is given by the Laplace-Young equation. If the container is lowered, the meniscus will tear from the plate. Prior to this event, the force passes through the maximum value and begins to drop before the actual tearing event.

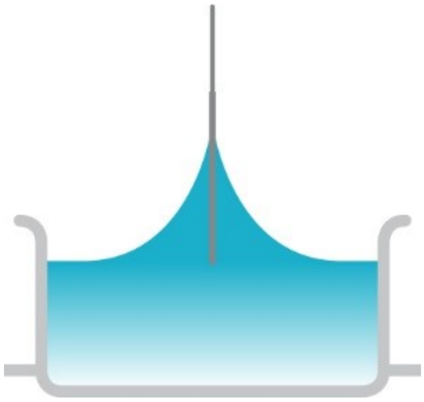

Figure 9: Meniscus on Wilhelmy plate

Similarly, it is possible to carry out the measurement by replacing the Wilhelmy plate with a platinum rod. The measurement principle stays the same, but the small diameter of the probe makes it possible to also measure smaller sample volumes. However, at the same time, the accuracy of the measurement is not as high with the standard Wilhelmy plate technique.

Drop weight or drop volume method

Another rather simple method to evaluate the surface tension is stalagmometric method using the stalagmometer (so-called stactometer or stalogometer) (Figure 10). The principle of this method is to measure the weight of drops of an investigated fluid falling from a capillary glass tube. When a liquid drop falls from a vertical capillary there is a relation between drop weight and surface tension.

Figure 10: Stalagmometer

Another possibility to determine the surface tension using stalagmometer is to measure the number of drops formed from a defined volume of investigated liquid. To calculate the surface tension (γ_T) of the sample, the relationship between the number of drops of water (P_V), the number of drops of the sample (P_T), the density of water (ρ_V), the density of sample (ρ_T) and surface tension of water (γ_V) is used:

$$\gamma_T = \frac{P_V \cdot \rho_T}{P_T \cdot \rho_V} \cdot \gamma_V$$

Dynamic methods

Dynamic methods for the determination of the surface tension are methods in which the surface quickly changes from shape and/or size during the measurement. In real dynamic methods the time scales are much smaller than a second. Dynamic interfacial tensions are of importance for the understanding of interfacial processed with the formation and stability of liquid interfaces (e.g. preparation and stability of emulsions and foams, flotation)

Oscillating jet

An oscillating jet of liquid is formed when a liquid is pressed through a non-circular orifice at a certain speed (Figure 11). Directly after leaving the orifice the capillary pressure tries to make the non-circular cross section circular and, therefore, the oscillation develops. Through the momentum of the liquid the circular situation passes, and a new non-circular cross section develops that is rotated by 90 ° compared to the original opening. In this way, oscillations arise in which there is a relation between the wavelength of the oscillation and the capillary pressure. By optical determination of the jet dimensions the wavelength of the oscillation can be determined and surface/interfacial tension can be found.

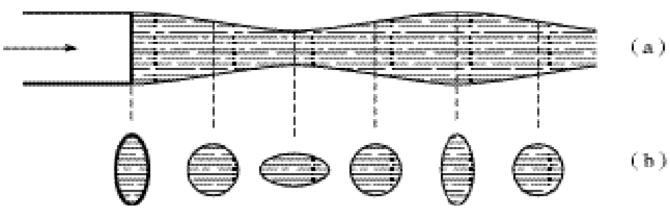

Figure 11: Oscillating liquid jet

Capillary waves

If the surface of the liquid is periodically disturbed by mechanical, acoustic or other impulses, so-called capillary waves arise. The velocity of the ripples and density it is possible to calculate the surface tension of the investigated liquid. Capillary waves method may be used also for the determination of the interfacial tension between to liquids.

Spinning drop

The spinning drop method is used for the determination of very low interfacial tensions between two liquids. In this method a drop of liquid A is suspended in a horizontal glass tube filled with liquid B. Surface/interfacial tension may be determined using the oscillation frequency, the known drop size and the viscosity of the investigated liquid

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