



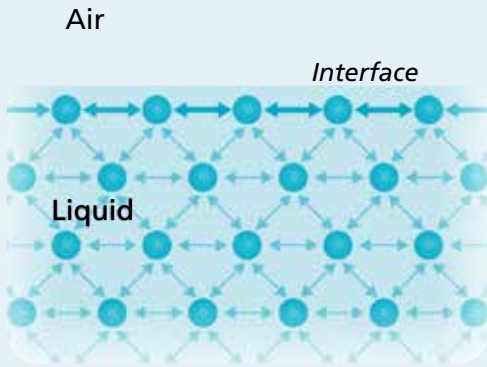
Surface and interfacial tension

- What is it and how to measure it?

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[Figure 1] (On the left) Surface molecules have net attractive force into the liquid creating the phenomena called surface tension. The forces acting on the molecules at the interface are illustrated.

(On the right) Water strider is taking advantage of surface tension to walk on the air-water interface.

Surface Tension	mN/m
Ethanol	22.4
Glycerol	63.4
Water	72.8
Toluene	28.5
Mercury	468.5

[Table 1] Examples of surface tension values at 20 °C².

Surface and interfacial tension play an important role in our everyday life. Whether you are washing laundry or painting a wall, you are utilizing interfacial tension phenomenon. With this it is easy to see that surface and interfacial tension are also important in many different industrial applications where liquid-gas or liquid-liquid interfaces are of interest.

With this white paper, we would like to introduce you to world of surface and interfacial tension and their measurement techniques. We discuss the theory behind the techniques as well as go through some of the advantages and limitations of each method.

What is surface tension?

In 1805 English physicist Thomas Young showed that surfaces behave as if a membrane were stretched over them tending to become spherical, like a soap bubble^[1]. This phenomenon can be considered to be a starting point to understand surface tension and its importance in our everyday life and in many industrial applications.

On a molecular level, the cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension (ST). In the bulk, molecules are interacting equally with each other in all directions. However, at the surface molecules do not have the same neighbors on all sides. Thus, a net inward force pulls the molecules toward the bulk. This forms a surface "film" which makes it more difficult to move an object through the interface versus moving an object while it is completely immersed (Figure 1).

The same situation also applies at the interface of two immiscible liquids (liquids that do not mix together). Interfacial tension (IFT) arises from differences between the intermolecular forces at the two liquid surfaces in contact with each other.

If the surface area of the liquid is increased, more molecules are present at the surface, and work must be done for this to occur. Therefore, the surface has excess Gibbs energy relative to the interior of the liquid. Surface tension is the excess energy per unit area (force per unit length; SI unit is Nm⁻¹). Typically mN/m (which is equivalent to dynes/cm) is used as the unit for surface and interfacial tension.

Surface tension values for some pure liquids are shown in (Table 1).

It should be noticed that surface tension of water is high compared to most of the organic liquids. Only glycerol has surface tension close to that of water. Both water and glycerol are highly polar liquids containing hydrogen bonds which explain the high surface tensions.

Surface tension depends on temperature and pressure

One of the main factors affecting surface tension of pure liquids is the temperature. Experimentally it has been found that the surface tension decreases almost linearly with temperature (see surface tension of water as a function of temperature in **figure 2**). When temperature increases, the molecular thermal activity increases causing a decrease in cohesive interaction. This causes decrease in surface tension.

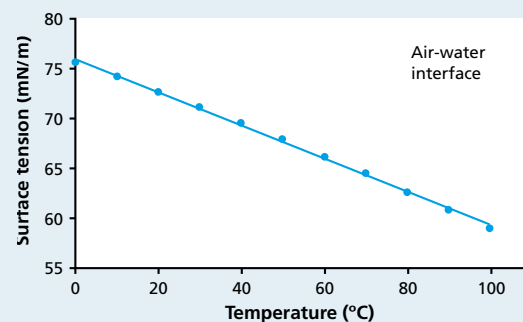
Another factor affecting the surface tension is pressure. In most applications the pressure does not play a role, but needs to be considered when processes that happen under high pressures are studied. These include for example enhanced oil recovery (EOR) and supercritical fluids. In general, dissolution of the gas in liquid increases with the increasing pressure, decreasing the surface tension. Interfacial tension between CO₂ and brine/water at different pressures are presented in **figure 3**. The interfacial tension decreases as pressure increases reaching a plateau at around 120 bars.

Surface tension is modified by surfactants

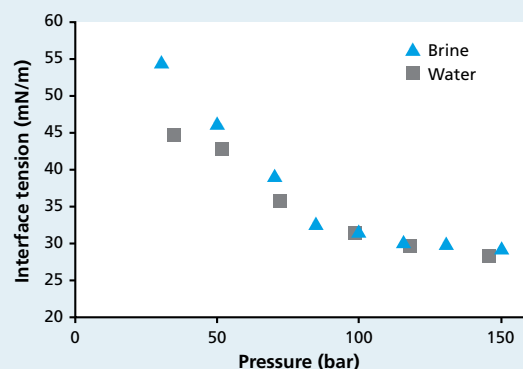
Surface tension of pure liquids is easily affected by certain impurities, called surfactants. Surfactants are amphiphilic molecules that include both hydrophobic (non-polar, water insoluble) and hydrophilic (polar, water soluble) segments (**Figure 4A**). When surfactants are dissolved in water they orientated at the surface so that hydrophilic parts are in water and hydrophobic parts are in air (**Figure 4B**). The surface tension is reduced as some of the water molecules are replaced by the surfactant molecules and interaction forces between surfactant and water is less than between two water molecules. The effectiveness of surfactant molecule is determined by the amount of surfactant needed and the minimum surface tension value that can be reached. This can be studied with critical micelle concentration (CMC) measurements⁴ as micelles (**Figure 4C**) are formed when the surfactant concentration is high enough to saturate the surface.

In addition to efficiency of the surfactant, the speed of the surface active agent is also of high importance in industrial processes. That is the rate at which the molecules are able to arrange themselves at the interface. Usually large molecule surfactants are slower, taking them more time to arrange at the interface and thus more time until the equilibrium surface tension is reached.

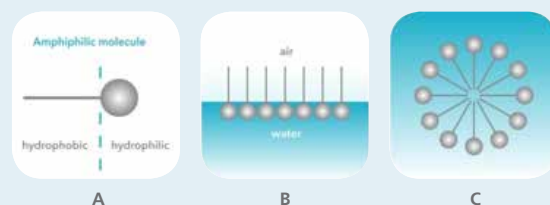
Surfactants are routinely used in industry to lower the surface and interfacial tension. Lower surface tension yields to better spreading of the liquid which is important for products like paints and detergents. To optimize the formulations, measurement of surface and interfacial tension is mandatory.



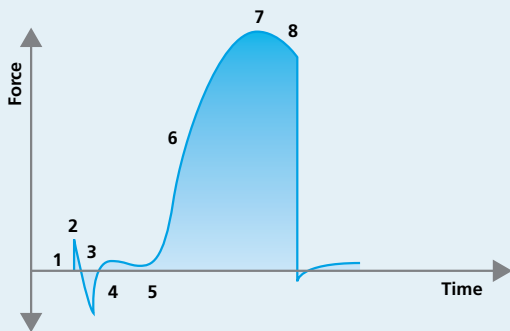
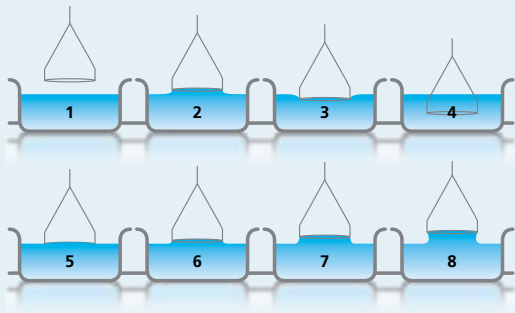
[Figure 2] Surface tension of water as a function of temperature (Data from³).



[Figure 3] Interfacial tension between CO₂ and brine/water as a function of pressure at 45 °C.



[Figure 4] (A) Cartoon of surfactant molecules containing hydrophilic and hydrophobic parts. (B) Surfactant molecules oriented at the air-water interface with hydrophilic head in the water and hydrophobic tail in the air. (C) Micelle that forms when surfactant concentration reaches high enough value for micelles to form.



[Figure 5] From force vs. time curves different stages of the experiment can be identified:

- 1) At the beginning, the ring is above the interface and the force is zeroed.
- 2) The ring touches the interface and there is a slight positive force due to the adhesive force between the ring and the surface.
- 3) The ring must be pushed through the interface (due to the surface tension which will cause a small negative force).
- 4) The ring breaks through the interface and a small positive force is measured due to the supporting wires of the ring.
- 5) When lifted through the interface the measured force starts to increase.
- 6) The force keeps increasing.
- 7) The maximum force is reached.
- 8) After the maximum there is a small decrease of the force until the lamella breaks, or the ring is pushed back below the surface.

Techniques for measuring surface and interfacial tension

Thomas Young developed the relationship between capillarity and surface tension; the capillary-rise method was the first method used to measure surface tension. Today, force and optical tensiometry are the most widely accepted methods to measure static surface and interfacial tension due to automation and disposable sample vessels enabling faster measuring cycles.

Force tensiometry

Measurement of surface and interfacial tension can be performed with force tensiometer. These instruments are based on measuring the forces exerted on a probe that is positioned at the liquid-gas or liquid-liquid interface. The probe is connected to a very sensitive balance and the liquid interface of interest is brought into contact with the probe. The forces measured by the balance as the probe interacts with the surface of the liquid can be used to calculate the surface tension. The force depends on the following factors: size and shape of the probe, contact angle between the probe and the liquid, and the surface tension of the liquid. The size and the shape of the probe are easily controlled. Probes are typically made of platinum which helps to ensure a zero degree contact angle between the probe and the liquid to be studied. Two configurations of probes are commonly used; the du Noüy ring and the Wilhelmy plate. A metal rod can also be used instead of a Wilhelmy plate when sample volume is limited. Force tensiometry is the most common method used in international standards to define surface tension.

Du Noüy ring

This method utilizes a platinum ring as the probe⁵. The ring is submerged below the interface by moving the stage where the liquid container is placed. After immersion, the stage height is gradually decreased and the ring eventually pulls through the interface bringing with it a meniscus of liquid. If the container is lowered further eventually 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 process is described in Figure 5.

The calculation of the surface or interfacial tension is based on the measurement of the maximum force. The depth of immersion of the ring and the level to which the ring is raised when it experiences the maximum pull are irrelevant to this technique. Original calculations are based on a ring with an infinite diameter (or wire) and do not consider the excess liquid that is pulled up due to the proximity of one side of the ring to the other. The portion of the fluid which is directly under the ring is not there due to surface tension forces – but rather capillary forces. This liquid however contributes to a force reading given by the balance and would

thus increase the measured surface tension value by approximately 7 %. Today correction factors are routinely used by automated software calculations to subtract and account for this excess liquid^{6,7}. When using a correction factor, the density of the liquid, or in case of interfacial tension measurement density difference between the two liquids, must be known.

Wilhelmy plate

This method utilizes a rough platinum plate as the probe. The calculations of this technique are based on the perimeter of the fully wetted plate in contact with the liquid. In this method the position of the probe relative to the surface is significant. As the liquid surface is brought into contact with the probe, the instrument will detect the exact moment of contact by registering a change in force on the probe. This position will thus be labelled the “zero depth of immersion”. The plate is then immersed to a set depth below this value (typically a few mm into the interface). When the plate is later returned to the zero depth of immersion, the force is recorded. By looking at figure 6, the equation for force affecting on the Wilhelmy plate can be written as, **Equation 1**.

$$F = \rho_p g l w t + 2\gamma(w+t)\cos\theta - \rho_l g t w h$$

where the first term is due to the mass of the plate, second is the wetting force and third is due to buoyancy. As the Wilhelmy plate is assumed to be wetted completely with the liquid the term $\cos\theta$ will go to one and the equation can be rewritten as **Equation 2**.

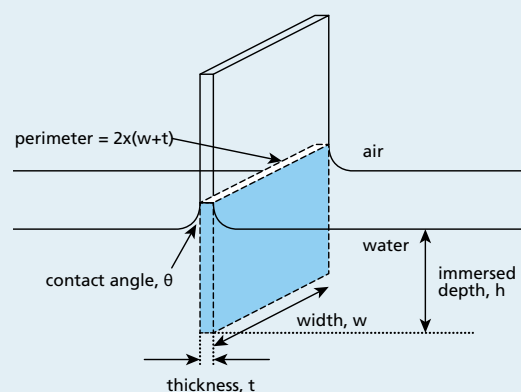
$$\Delta F = 2\gamma(t+w) \Rightarrow \gamma = \frac{\Delta F}{2w}, \text{ if } w \gg t$$

Wilhelmy plate measurements can also be done in so called static or continuous mode where Wilhelmy plate remains in contact with liquid during the entire measurement cycle.

Platinum rod

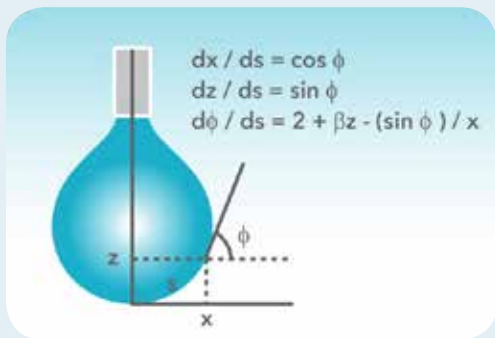
Both of the above mentioned approaches require a relatively large amount of the liquid (typically above 10 milliliters) to be used to ensure complete wetting of the probe. It is possible to use a sample vessel with a smaller diameter to decrease the total volume required. However, there is a limit. When the edges of the sample vessel and the probe are too close to each other, the balance can be affected by the meniscus that forms between the liquid and the edge of the vessel. To avoid this problem, the user must allow enough room between the probe and the side wall of the sample container, ~ 2 mm or so. In any of these techniques, the accuracy of the measurement is affected by the accuracy with which one measures the geometry of the probe. The measurement accuracy of the platinum rod is likely to be less than the du Noüy ring or the Wilhelmy plate which translates to larger errors in the surface / interfacial tension results. Therefore the platinum rod approach is only recommended when the volume of the sample is limited.

The method and calculations are based on the same principle as the Wilhelmy plate-method.



[Figure 6] Wilhelmy plate





[Figure 7] Pendant drop method based on optical drop shape analysis allows using very small sample volumes (~5 to 20 microliters).

Optical tensiometry

Surface and interfacial tension measurements can be performed optically using pendant drop shape analysis⁸. The shape of the drop hanging from a needle is determined from the balance of forces which include the surface tension of the liquid being investigated. The surface or interfacial tension can be related to the drop shape by Equation 3.

$$\gamma = \frac{\Delta\rho g R_0}{\beta}$$

where γ is the surface tension, $\Delta\rho$ is the density difference between fluids, g is the gravitational constant, R_0 is the drop radius of curvature at the apex and β is the shape factor. β can be defined through the Young-Laplace equation expressed as 3 dimensionless first order equations as shown in Figure 7.

Modern computational methods using iterative 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 droplet is important and it should have a tear or pendant shape. Care must be taken to ensure that the needle tip is not influencing the drop shape. When measuring surface tension, the density difference between liquid and gas (usually air) is large enough that volumes between 5 μl to 20 μl are generally sufficient to provide pendant or tear shapes. When measuring interfacial tensions, both density difference and interfacial tension have an effect on the required volume to achieve a pendant or tear shape drop. As a guideline, the smaller the density difference, the larger the volume required.

Comparison of methods

Force and optical tensiometers are excellent tools for surface and interfacial tension measurements. They provide fast and simple measurement methods for wide range of applications. As with any measurement methods, all the above discussed techniques have their advantages and disadvantages⁹.

With all the force tensiometry techniques the geometry of the probe is especially important. Wilhelmy plate and platinum rod are relatively robust but du Noüy rings are very delicate and deform easily. For correct surface and interfacial tension measurements it is crucial that the plane of the ring remain parallel to the interface. With the proper handling of the du Noüy ring, deformation of the ring can be avoided.

Another important factor with all the force tensiometry measurements is the wetting of the probe. Proper cleaning and in case of Wilhelmy plate also roughening of the probe are used to ensure perfect wetting. There is however a possibility that the wettability changes during measurement due to molecule adsorption on the probe surface. This is especially an issue with the Wilhelmy plate measurements. On the other hand, viscosity of the liquid also affects significantly on the wettability. In case of viscous samples, Wilhelmy plate is the best choice as there is a possibility to

do long measurements with Wilhelmy plate being stationary at the interface. This will give viscous liquid time to wet the Wilhelmy plate properly. Force tensiometer is very established instrument and many of the industrial standards are based on the du Noüy ring or Wilhelmy plate measurement. Force tensiometer also enables automated critical micelle concentration measurements.

Pendant drop is an excellent method especially for quick check of surface and interfacial tension. As optical tensiometers are often utilized for contact angle measurement, the pendant drop method offers a possibility to do surface tension measurements in conjugation with contact angle.

One additional thing to consider, especially when measuring surface tension of surfactant solutions, is whether the measured surface tension is really an equilibrium value. When the surface tension is measured by using du Noüy ring the interface is stretching which means that new interface is constantly created. With pure liquids this possesses no issue but as surfactant solutions are measured interesting dilemma arises. With increase in interfacial area, the surfactant molecules have larger interface to go to and thus the equilibrium state is not reached during the measurement. How big is the effect, depends on the speed of your surfactant molecules. Larger surfactant molecules are usually slower and require more time to arrange themselves at the interface. For this reason, the surface tension of surfactant solution measured by du Noüy ring tends to be higher than that measured with the Wilhelmy plate which is a stationary measurement. While this is not a major issue in most of the cases, it is something to keep in mind when choosing between du Noüy ring and Wilhelmy plate.

For interfacial tension measurements the use of du Noüy ring is justified as with the Wilhelmy plate the measurement needs to be done in two steps to compensate the buoyancy effect. Also the wetted length of the typical du Noüy ring is usually about 3 times more than the wetted length of the plate. This will lead the measured force to be three times higher and thus more accurate result.

Conclusions

In this white paper, we have given a short introduction to surface and interfacial tension as well as reviewed the most common measurement techniques. We have also discussed the advantages and limitations related to each measurement type. The instrument should be chosen according to your application. For more information on the selection of the best method for your application please refer to white paper titled "How to select the best measurement method for your application?".

[References and further reading]

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