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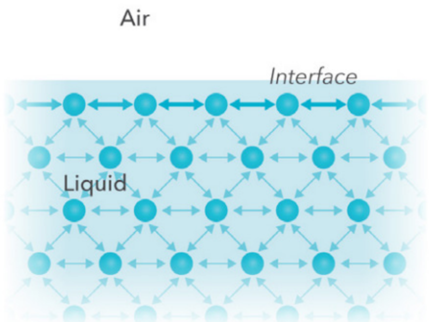
Attension [Technology Note] 2

Surface and interfacial tension and their measurement techniques

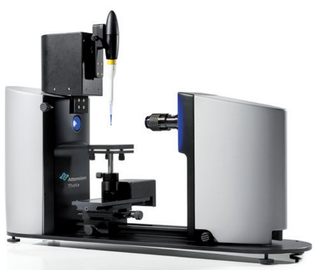
This technology note explains the concepts of surface tension and interfacial tension and goes through the measurements by using both optical and force tensiometer.

Introduction

The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension (ST). The molecules at the surface do not have the similar neighboring atoms on all sides and thus they cohere more strongly to those directly associated with them on the surface. This forms a surface "film" which makes it more difficult to move an object through the surface than move it when it is completely immersed (Figure 1). The same situation applies also at the interface of the two liquids that do not mix together. In this case the term interfacial tension (IFT) is used. There are several different units for surface and interfacial tension; typically mN/m (which is equivalent to dynes/ cm) is used.



[Figure 1]: Interactions between molecules in the bulk rule out each other whereas on the surface the interaction between neiboring atoms is stronger.



Attension Theta

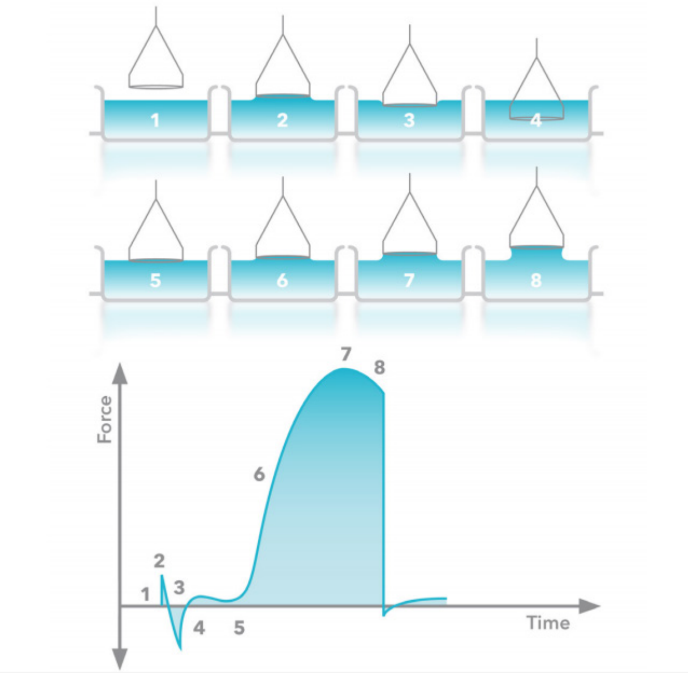
Attension Sigma

Measurement with force tensiometer

The measurement of the surface and interfacial tension can be done by using Sigma force tensiometer. It is based on the force measurements of the interaction of a probe at the liquid-gas or liquid-liquid interface. A probe is hang on the balance and brought into contact with the liquid interface tested. The forces experienced by the balance as the probe interacts with the surface of the liquid can be used to calculate the surface tension. The forces present in this situation depend on the following factors; size and shape of the probe, contact angle between the probe and the liquid and surface tension of the liquid. The size and the shape of the probe are easily controlled. The probe is made of platinum which ensures the zero contact angle between the probe and the liquid to be studied. Two types of probes are commonly used; the Du Noüy ring and the Wilhelmy plate. A metal rod can also be used when the sample volume is limited.

Du Noüy ring

This method utilizes the interaction of a platinum ring with the surface of the liquid [1]. The ring is submerged below the interface by moving the stage where liquid container is placed. After immersion, the stage is gradually decreased and the ring pulls up the meniscus of the liquid. Eventually the meniscus would 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 2.



[Figure 2]: Surface tension measurement by Du Noüy ring

In Figure 2, different stages of the experiment can be identified:

1) The ring is above the surface and the force is zeroed.
2) The ring hits the surface 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 surface due to surface tension which causes a small negative force.
4) The ring breaks the surface and a small positive force is measured due to the supporting wires of the ring.
5) When lifted through the surface 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.

The calculation of the surface or interfacial tension by this technique 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. The original calculations are based on the ring with the 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. Nowadays correction factors are routinely used by automated software calculations [2, 3]. For the utilization of the correction factor, the density of the liquid has to be known.

Wilhelmy plate

This method utilizes the interaction between the platinum plate (= the probe) and the surface of the liquid. The calculations of this technique are based on the geometry 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 surface is brought in contact with the probe, instrument will detect this by the change in force it experiences. It will register the height at which this occurs and set it to be "zero depth of immersion". The plate is then wetted to a set depth. When the plate is later returned to the zero depth of immersion, the force is registered and used to calculate the surface tension according to equation (1).

$$\text{Wetting force} = \gamma_l P\cos\theta \qquad (1)$$

Remember that the term cosθ goes to 1 since the contact angle between the probe and the liquid is considered to be zero.

Platinum rod

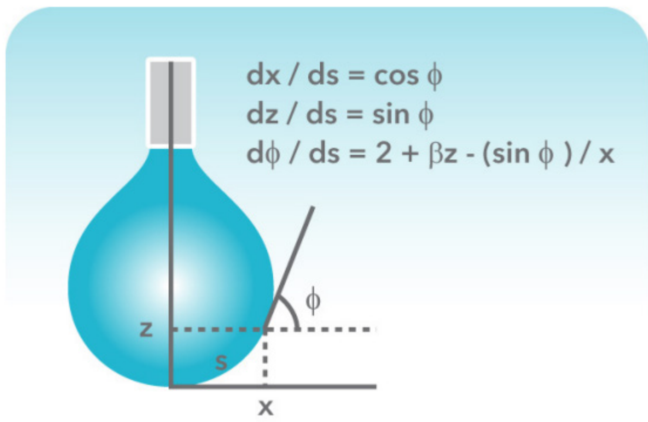
Both of the above mentioned approaches require a relatively large amount of the liquid (some ml) to be used to ensure complete wetting of the probe. It is possible to use a sample vessel with the smaller diameter to decrease the volume of the liquid. Limitation to this strategy occurs when the edges of the probe approach the edges of the measuring vessel. When the edges 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, it is possible to use the platinum rod which allows you to use much smaller in diameter sample vessel and thus less volume of the sample. In any of these techniques the accuracy of the measurement is affected by the accuracy of the geometry of your probe. The geometry of the fine probe is likely to be less accurate than the geometry of the ring or the plate which will lead to bigger error percentage of the surface/interfacial tension results. Therefore this approach should only be used when the volume of the sample is limited. Calculations are based on the same principle as the Wilhelmy plate method.

Measurement with optical tensiometer

Surface and interfacial tension measurements can be done with optical tensiometer by so-called pendant drop shape analysis (or reversed pendant drop). The shape of the drop hanging on the needle is determined from the balance of forces which include the surface tension of that liquid. The surface or interfacial tension can be related to the drop shape by the equation (2).

$$\gamma = \Delta\rho g \,(R_0^{\,2})/\beta \qquad (2)$$

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



[Figure 3]: Pendant drop method.

Modern computational methods using iterative approximations allow solution of the Young-Laplace equation for β to be performed. Thus for any two fluids in contact which densities are known, the surface or interfacial tension may be measured based on Young-Laplace equation. This method has advantages since it is able to use very small volumes of liquid (some μl) and it is possible to measure low interfacial tension values. What has to be considered when measuring surface and interfacial tension is the size of the droplet used. The droplet should have the suitable pendant shape to achieve reliable results. When measuring surface tension, the density difference between liquid and gas (usually air) is so big that the droplet size from 5 μl to 20 μl is usually sufficient depending on the surface tension of the liquid. When measuring interfacial tensions, both density difference and interfacial tension have an effect on the required droplet size. As a rule of thumb, smaller the density difference, bigger the droplet has to be. [4]

Comparison of the techniques

All of the above techniques are widely utilized in surface tension measurements. Du Noüy ring, Wilhelmy plate, platinum rod and pendant drop methods can all be used for measuring the surface tension but there are also applications where one technique is better than the other. Wilhelmy plate is for example thought to work a little bit better than Du Noüy ring with high surface tension liquids. Rod and pendant drop measurements on the other hand are most suitable when the amount of liquid is limited.

References:

[1] P. L. du Noüy, "A new apparatus for measuring surface tension", Journal of genetic physiology (1918-19) 521.

[2] C. Huh and S.G. Mason, "A rigorous theory of ring tensiometry", Colloid and polymer science 253 (1975) 566.

[3] H. H. Zuidema and G. W. Waters, "Ring method for the determination of interfacial tension" , Industrial and engineering chemistry 13 (1941) 312.

[4] C. E. Stauffer, "Measurement of surface tension by pendant drop technique", The journal of physical chemistry (1965) 1933.

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