Attension® | White Paper

Surface and interfacial tension

- How to select the best measurement method

Author: Susanna Laurén, PhD, Biolin Scientific

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Surface and interfacial tension

- How to select the best measurement method for your application?

With a wide variety of surface and interfacial tension measurement methods available, it can be difficult to determine which one is best suited for your application. You have probably already heard about force and optical tensiometers and maybe also du Noüy rings and Wilhelmy plates, but why have so many different techniques if the outcome is essentially the same? As surface and interfacial tension measurements are utilized in many different applications, the samples studied are also very different from one another. When selecting a measurement method, you need to consider the properties of your sample as well as the application you are working with.

With this white paper we would like to offer you a tool for method selection. By asking some simple questions about your sample and application, we can decide the best method for you.

Quick overview of measurement methods

The most commonly used equilibrium surface and interfacial tension measurement methods are du Noüy ring, Wilhelmy plate and pendant drop, of which the first two use force tensiometers and the last one is an optical method.

Force tensiometer measurements are based on measuring the forces exerted on a probe positioned at the liquid-gas or liquid-liquid interface. The probe is connected to a highly 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 platinum rod can also be used instead of a Wilhelmy plate when the sample volume is limited.

Surface and interfacial tension measurements can be performed optically using 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 liquid being investigated. 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 more information on surface and interfacial tensions and their measurement methods, please see our white paper titled "Surface and interfacial tension – what is it and how is it measured?".*

Questions to ask when selecting the measurement method

To select the best method for your application, there are few things that need to be considered. Below, we have gathered some simple questions for you to answer to facilitate the selection of the method.

Do you need a standardized measurement method?

Force tensiometry has been the most common method used in international standards to define surface tension, though some standards for optical tensiometers also exist. A list of tensiometry standards is presented in Table 1. If your application requires you to follow a certain industrial standard, the method needs to be selected accordingly.

Is your sample volume limited?

In some applications, especially with biological samples, the sample volumes can be limited due to either high costs or limited availability of the sample. When this is the case, a measurement method that enables the use of small quantities of the sample must be chosen.

With all force tensiometer measurements, the sample volumes required are in the milliliter range. The exact volume is dependent on the selected sample vessel, as the liquid height has to be sufficient for the immersion of the probe. The sample vessel diameter must be chosen such that the probe is not affected by the edges of the vessel. With the force tensiometer, platinum rod should be chosen when only small quantities of sample is available. With the small diameter of the rod, a small diameter sample vessel can be chosen and thus the volume required to achieve the necessary height is less than with the larger diameter vessel. The measurement accuracy of the platinum rod dimensions is not as precise as with the ring or the plate, which causes additional errors to surface tension values. Thus, in the case of small sample volumes, the pendant drop method is recommended, where as little as 10 µl can be enough to achieve a measurement.

Are you working with surfactant solutions?

Measuring surfactant solutions poses an interesting dilemma. As shown in Table 1, there are two standards available for measuring the surface tension of solutions with surface active agents. Both of these standards utilize either the ring or the plate method. However, the ring method in particular can be problematic with surfactant solutions, as the interface is stretched during the measurements. This means that the equilibrium state is not achieved in the measurement, as a new surface area for surfactants to go to is constantly created. The measured surface tension values are higher than what would be measured in the true equilibrium state.

Standard	Name of standard	Method
ASTM D1331-11	Standard test methods for surface and interfacial tension of solutions of surface active agents	Force/Ring
ASTM D971-12	Standard test method for interfacial tension of oil against water by the ring method	Force/Ring
ISO 1409-2006	Plastics/rubber -polymer dispersions and lubber latices - Determination by the ring method	Force/Ring
OECD 115	OECD Guideline for the testing of chemicals - surface tension of aqueous solutions	Force/Ring
EN 14210	Surface active agents. Determination of interfacial tension of solutions of surface active agents by the stirrup or ring method	Force/Ring
EN 14370	Surface active agents - Determination of surface tension	Force/Ring & Wilhelmy plate
ISO19403-1	Paints and varnishes - Wettability - Part 1: Terminology and general principles	Optical / Pendant
ISO 19403-3	Paints and varnishes - Wettability - Part 3: Determination of surface tension of liquids using the pendant drop method	Optical / Pendant
ISO 19403-4	Paints and varnishes - Wettability - Part 4: Determination of polar and dispersive fractions of the surface tension of liquids from an interfacial tension	Optical / Pendant
ISO 19403-5	Paints and varnishes - Wettability - Part 5: Determination of polar and dispersive fractions of the surface tension of liquids from contact angles measurements on a solid with only a disperse contribution to its surface energy	Optical / Contact angle

[Table 1] *List of standards for surface and interfacial tension measurements.*

Sample	Viscosity (mPa*s)
Water	1
Milk	3
Engine oil	1000
Honey	10 000
Sour cream	100 000

[Table 2] *Approximate viscosities of some common liquids at room temperature*

With Wilhelmy plate, on the other hand, the equilibrium state can be achieved as the plate can be kept stationary throughout the measurement. However, the unwanted adsorption of surfactants on the plate surface can occur, changing the wettability of the plate. For these reasons, the pendant drop method may well offer the best solution for surface tension measurements of surfactant solutions, unless a certain standard needs to be followed. Another reason to choose either of the force tensiometer techniques is the possibility to perform automated critical micelle concentration (CMC) measurements.

What is the viscosity of your liquid?

As the force tensiometer measurements are based on the wetting of the probe, i.e. the meniscus must be formed, the viscosity of the sample needs to be considered. When viscosity is high (> 1000 mPa*s), the liquid needs more time to wet the probe properly. This is most readily achieved with a continuous Wilhelmy plate measurement, where the Wilhelmy plate is kept stationary at the interface for long periods of time. The du Noüy ring is not suitable for such measurements, as the amount of viscous liquid pulled with the ring is hard to control. Although the pendant drop method can be used with viscosities higher than 1000 mPa*s, it is not possible to give an exact viscosity limit as the density of the liquid also affects the measurement. When considering whether surface tension measurements on your sample are possible, you should test whether there is a flow of liquid (in some reasonable time scale) when you try to pour the sample out from the vessel. Approximate viscosities for some common liquids can be seen in Table 2.

Is your sample contaminating and thus difficult to clean?

When measuring surface or interfacial tension with the force tensiometer, the proper cleaning of the probe and sample vessel are highly important. Most typically, the probe is first rinsed with an appropriate solvent and then flamed before the experiment to ensure good wetting. The sample vessel has to be cleaned with the same solvent and rinsed properly with de-ionized water to ensure a clean vessel for the next measurement. Cleaning the probe and the vessel can thus, in some cases, take much more time than the actual measurement. To avoid the time-consuming cleaning procedure, there is a possibility to perform surface tension measurements with a Theta optical tensiometer and disposable tip dispenser.

Do you want to control the temperature during measurement?

As with most material properties, surface tension is affected by temperature. In such circumstances, depending on your application, a temperature control might be needed. For example, if you are studying the effectiveness of a surfactant used in a laundry agent, you might want to measure the surface tension as a function of temperature.

On the other hand, with biological samples, accurate results often require the measurements to be performed at 37 degrees C. In principal, all surface tension values should be reported with the temperature. Both Theta optical and Sigma force tensiometers are equipped with temperature control but Sigma provides the most convenient method.

Do you want to measure your sample at different pressures?

In some applications, especially the ones related to enhanced oil recovery (EOR), pressure plays an important role. As surface and interfacial tension are dependent on the pressure, the measurements should be performed at an appropriate pressure for your application. Attension Theta High Pressure allows measurements to be performed at elevated pressures and temperatures.

Would you like to perform additional measurements with your system?

Both the Theta optical tensiometer and the Sigma force tensiometer can be utilized for several other measurements in addition to surface and interfacial tension. If both of the techniques are equally suitable for you, you might want to consider the additional benefits you could gain by choosing one instrument over the other. One often used measurement with surfactant solutions is critical micelle concentration (CMC). CMC measurements can be utilized to study the efficiency of the surfactants and are most easily achieved using Sigma Force tensiometers and automated dispensers. Contact angles are also routinely measured with tensiometers. However, the Theta optical tensiometer provides the most versatile tool for contact angle measurements. The Theta optical tensiometer can also be equipped with a pulsating drop module, enabling interfacial rheology measurements that are of high importance when working with foams and emulsions.

Attension Theta Optical Tensiometers

Attension Sigma Force Tensiometers

Summary

The best measurement method for your application depends first of all on your sample properties and your desired measurement conditions. Also take into account if there are additional measurements or future needs that the system could be used for. In Table 3, the suitability of the methods and instruments is reviewed.

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	Optical Tensiometry	Force tensiometry		
	Pendant	du Noüy ring	Wilhelmy plate	Platinum rod
Standardized method	●	●	●	NA
Small volume	R	●	●	●
Surfactant solution	●	●	●	●
High viscosity sample	●	●	R	●
Contaminating sample	R	●	●	●
Temperature control	●	R		
Pressure control	●	NA		
Static contact angle	●	NA		
Dynamic contact angle	●	●		
Interfacial rheology	●	NA		
Automated CMC	NA	●		

[Table 3] *Comparison chart of different measurement techniques*

About us

Biolin Scientific is a leading Nordic instrumentation company with roots in Sweden, Denmark and Finland. Our customers include companies working with pharmaceuticals, energy, chemicals, and advanced materials, as well as academic and governmental research institutes. Our precision instruments help discover better drugs faster, develop better solutions for energy and materials, and perform research at the frontiers of science and technology.

Contact us at info@biolinscientific.com

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