

# Considerations Before Making Non-equilibrium Surface Tension Measurements

Technical Note #307e

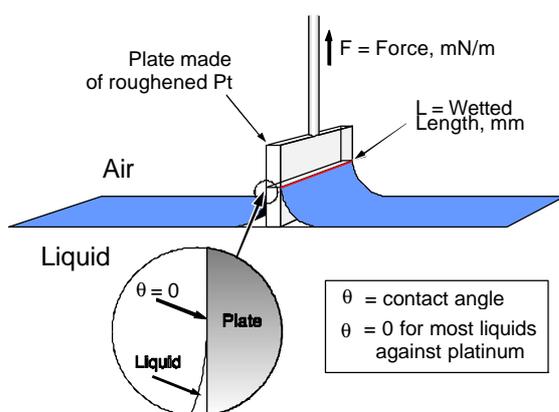
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## Abstract

There are many applications that can benefit from the measurement of non-equilibrium surface tensions. These instances range from the basic study of surfactant diffusion and adsorption coefficients to the application of line-speed dependent coatings on moving substrates to the behavior of spray droplets in flight and upon adsorption to an appropriate substrate. The measurement of non-equilibrium/dynamic surface tensions by the maximum bubble pressure method has been known for many years. However, the measurement of non-equilibrium tensions by the Laplace solution to pendant drops has only recently become of interest due to the advent of higher speed computer processors. Three common methods for the measurement of surface tension (Wilhelmy plate method, pendant drop analysis, and the maximum bubble pressure method) are compared here for the measurement of non-equilibrium tensions for various applications.



The Wilhelmy plate method is the most prominent method for measuring equilibrium surface tensions of liquid samples. A small platinum coupon is attached to a force-measuring sensor and precisely dipped into a liquid and withdrawn to the point where the bottom edge of the coupon is exactly parallel with the surface of the bulk fluid itself. At this point, the surface tension is related to the force exerted by the liquid wetting it by the following equation:

$$\sigma = F / (\cos\theta * L)$$

where:

$\sigma$  = surface tension

$F$  = force

$\theta$  = contact angle of the sample against the Pt coupon

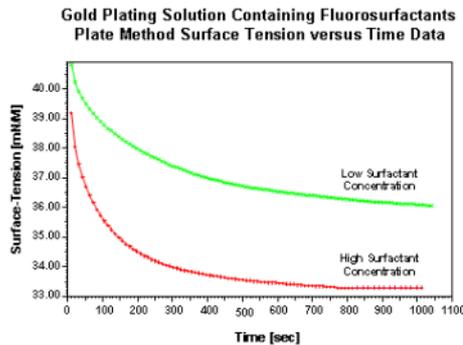
$L$  = wetted length of the Pt coupon

For almost all liquids against Pt,  $\theta=0$  and so the equation simplifies to:

$$\sigma = F / L$$

Although the plate method is most commonly used for measuring equilibrium surface tension, for certain samples the plate method can be used to measure non-equilibrium surface tensions. For examples, the time dependent surface tension lowering of solutions containing notoriously slow adsorbing fluorosurfactants can easily be

measured by the plate method as shown below.



If we look closely at the time scale, however, we can see that this is certainly an extremely slow adsorbing surfactant species. Neither solution has come to an equilibrium surface tension yet by the time 10 minutes has passed. However, the majority of interesting time-dependent behavior can be witnessed within the first few minutes, which can be easily measuring by the plate method.

### Pendant Drop Analysis

The solution of the Laplace equation for drops pending from a needle tip has also been accomplished for a considerable period of time. For this method, a drop is simply pushed out of a syringe needle until it almost detaches from the needle tip. At this point an image is snapped of the hanging drop and the contour of the profile of that drop is analyzed for its shape via the Laplace equation.

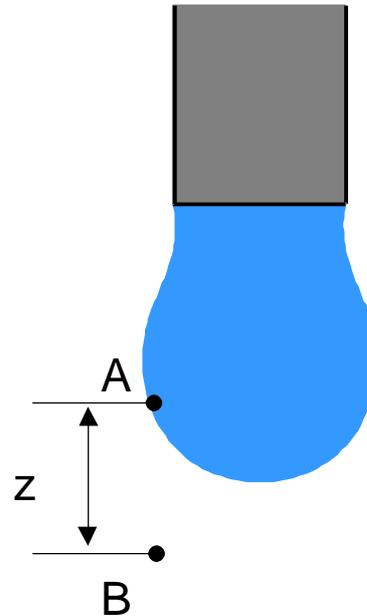
The actual mathematics of pendant drop analysis are based on the fact that pressure differences exist across curved surfaces. The pressure difference at any given point on the surface ( $\Delta P$ ) is equal to mean curvature of the surface at that point ( $1/r_1 + 1/r_2$ ), where  $r_1$  and  $r_2$  are the principal radii of curvature) multiplied by twice the tension ( $\sigma$ ) contained in the surface.

$$\Delta P = (1/r_1 + 1/r_2) 2 \sigma$$

For a pendant drop, the pressure difference within the drop between any two vertical positions is:

$$\Delta \rho g Z$$

where  $\Delta \rho$  = the difference in density between the liquid that is forming the drop and the bulk gas,  $g$  = gravity, and  $Z$  = the vertical distance between the two positions, as shown below.

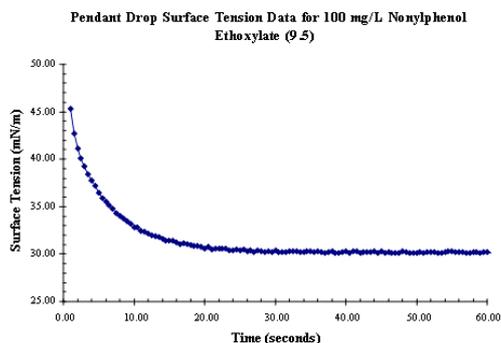


Those points are then used in pairs, with the equations given above, to solve for surface tension. In the following manner:

$$\begin{aligned} & \left( (1/r_1 + 1/r_2)_{\text{at A}} - (1/r_1 + 1/r_2)_{\text{at B}} \right) 2 \sigma \\ & = \\ & \Delta \rho g Z_{\text{between A and B}} \end{aligned}$$

Historically the equation has been solved by literally taking a photo of the drop and performing the mathematics at a later point by hand and calculator. The equation is much more easily solved today with the advent of modern computers. In fact, the calculation is solved within the DSA 1 software for a few hundred pairs of points on a single drop in less than one second. This kind of speed allows one to rapidly expel a new drop to the end of a needle tip and follow the surface tension

change (non-equilibrium surface tension) over relatively short time periods. An example of such data is given below.



### Maximum bubble pressure technique:

The maximum bubble pressure technique is the most common technique for measuring dynamic surface tensions. During the measurement, a gas (usually nitrogen or air) is expelled through a small orifice tube that is submerged into the liquid sample of interest. The bubbles that are blown out of the orifice have a back-pressure necessary to expel them from the tube and that back pressure is related to the surface tension by the following form of the Laplace equation:

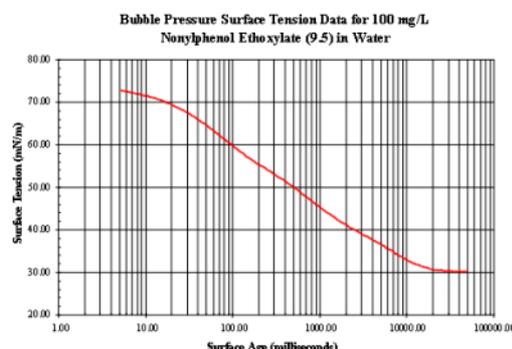
$$\sigma_d = 0.5 (P_{\text{max}} - P_o) r$$

where:

- $\sigma_d$  = surface tension (dynamic)
- $r$  = capillary radius
- $P_{\text{max}}$  = maximum pressure
- $P_o$  = hydrostatic pressure ( $r_L - r_G$ )  $g d$
- $r_L$  = density of liquid
- $r_G$  = density of gas
- $g$  = acceleration due to gravity
- $d$  = capillary immersion depth

So, for any given bubble the surface tension of the solution of interest can be determined. The non-equilibrium aspect of the experiment is created by varying the rate at which bubble are formed at the orifice. At the highest bubble rates less time is allowed for surfactant accumulation at the bubble surface and

thus shorter surface ages are realized. At slow bubble formation rates, the amount of time for surfactant accumulation at the bubble surface is increased and the equation above then solves for surface tension at longer surface ages. The data is usually plotted as surface tension vs.



log of surface age as shown below:

In practice, this surface age can be varied from about 5 ms to 1 minute. A few physical constraints of the measurement itself do not allow for surface ages outside of these limits to be tested.

### Surface Age Zero

For timed surface age measurements as shown in all of the above non-equilibrium examples, the relative accuracy of a proper "time zero" for the starting point of a newly formed, fresh surface is important to understand. The known accuracy of this time zero for each method can also help provide a sense of which experimental protocol is the most appropriate.

For the plate method, the accurate time zero can be assumed to be the point at which the solution is first still. Normally this would be after any pre-experimental stirring. Although this situation is complicated by the small mixing that occurs when the plate is immersed into the sample, we will assume that the zero point in time occurs when mixing is stopped. Depending on the procedure used, the time between the stoppage of

any mixing and the realization of the first measurement can range between 5-30 seconds. So, for non-equilibrium measurements in the time range of minutes, this delay and inaccuracy of time zero is acceptable. For shorter surface ages, the delay in the measurement itself outweighs the length of the measurement making the plate method not-useful for measuring shorter aged non-equilibrium tensions.

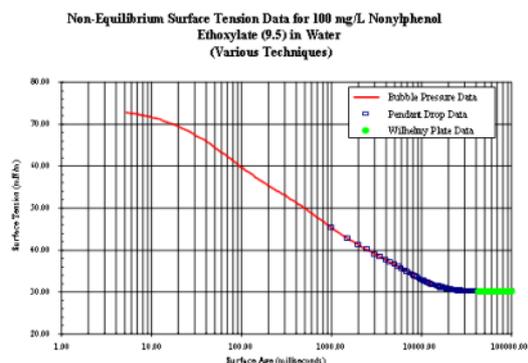
The time necessary to produce a new, fresh pendant drop for subsequent Laplace solution of non-equilibrium surface tensions is approximately 0.2-2 seconds depending on the method used for producing the drop. This shorter time frame and accuracy of a point of time zero allows for more accuracy in the measurement range of seconds to a minute. However, the delay in surface production still does not allow for surface ages under a few seconds to be accurately determined.

The bubble pressure method intrinsically accurately determines a time zero for a new, fresh surface. Time zero is determined to be the time at which the proceeding bubble released from the orifice. The time between this point and the point of surface tension measurement is accurately determined in the regime of microseconds. This accurate time zero allows for accurate surface tension curves down to surface ages as low as 5 ms.

## Which Method Should You Choose?

All 3 methods described above are compared for a very common Phenol Ethoxylate surfactant in the curve below:

As the curve demonstrates, the 3 methods show nicely contiguous data. In fact, the pendant drop data takes over where the bubble pressure technique



reaches it's upper limit in surface age. The Wilhelmy plate data continues on at longer time frames shown by the pendant drop method. In essence, the plot answers the question of which method to choose on its own. Samples that require quick data acquisition and a well defined time zero must be run by the bubble pressure method. Samples that do not require such speed can be run on and, in some cases, must be run by Pendant drop analysis. Very slow surface ages and samples that do not change surface tension within a minute or so can still be run by the Wilhelmy plate method, but there are few of these such samples.

**Summary**

the clearest path to solving your surface science problem!

Choose your technique and instrumentation carefully when pursuing non-equilibrium surface tension data. Below is a short key for general considerations:

Bubble Pressure	Pendant Drop	Wilhelmy Plate
basic surfactant kinetics ink jet studies sprays fast application of coatings	viscous inks slow adsorbing surfactants slow application of coating	ONLY for very slow adsorbing surfactant systems

With these basic rules in mind and a fundamental understanding of the measurements, you can make a more informed decision toward the most appropriate instrumentation, giving you