

Rings are for Fingers

– Plates are for Surface Tension

Technical Note #308e

by

Dr. Christopher Rulison, Augustine Scientific (www.augustinescientific.com)

Summary

This note explains some of the pitfalls of using ring tensiometry on surfactant solutions, without understanding the dynamics of ring situation, relative to the dynamics of surfaces. It answers, in some detail, the classic question of, "When do I use a ring and when do I use a plate?", and gives a prelude to another note in this issue on non-equilibrium tensiometry.

Background

The classic question from tensiometer users, the one surely heard thousands of times at Kruss, is, "Should I use the ring or the plate?" I refer, of course, to the DuNouy ring method for surface or interfacial tension measurement versus the Wilhelmy plate method. Historically, the ring method has been more widely used for both types of measurements (measurements of air/liquid interfaces = commonly referred to as surfaces and measurements of liquid/liquid interfaces = commonly referred to as interfaces). There are also several standards, perhaps most notably ASTM standards, which call for the ring method. These standards exist for historical reasons also. More old style manual ring surface tension instruments still exist in the world than any other type of tensiometer which has been developed since.

However, if you want to make the most use of your ring, you will put it in a jewellery box while you are measuring surface tension and only remove it for measurements of interfacial tension.

Ring Method

The ring method has three main issues which make it a less than good option for measuring exacting surface tensions. This is particularly true for surfactant based solutions, wherein the rate of surfactant diffusion to newly formed surfaces is particularly slow as is the case particularly for large molecule surfactants, amphoteric, and fluorosurfactants.

1) Most importantly, the ring method itself is designed to keep the surface in a non-equilibrium state during the measurement of surface tension. The ring is pulled through the surface to make the measurement (or in today's more sophisticated

tensiometers, at minimum, the ring expands and contracts the surface during the measurement - looking for the maximum force of the liquid meniscus). So the measurement of surface tension is really made on a surface which is in a non-equilibrium state. This does not matter to the measurement of surface tension if you are measuring a pure liquid. Because for pure liquids the surface tension is, at all times, the same. However, in surfactant solutions, wherein the surface tension is dependent on the presence and orientation of the surfactants at the surface, having the surface in a state of expansion during the measurement can make a huge difference in the measured surface tension.

As an example, witness the data below, all performed with an (as nearly as possible), true and round DuNouy ring and with the necessary Harkins and Jordan correction factors for the mass of liquid trapped under the ring not due to surface tension (two other issues we will discuss shortly). The only difference between these measurements of surface tension is the speed at which the ring is being pulled through the surface - as noted. However, two different liquids are tested. One is pure water, the other a solution of a simple non-ionic surfactant (nonyl-phenol ethoxylate with an average degree of ethoxylation of 9.5 units in water at 100 mg/l).

Note that the measured surface tension changes with the rate of ring pull through, in the case of the surfactant solution, but not in the case of the pure liquid. The actual equilibrium surface tension for this surfactant solution is 30.12 mN/m - which we establish shortly. But, regardless of that, this is what is deceiving about using the ring method for equilibrium surface tension measurement.

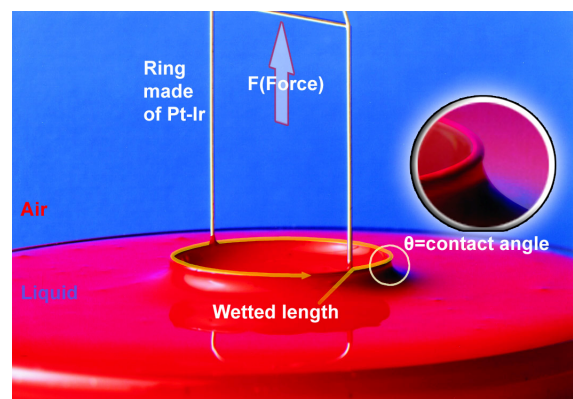
Ring Pull-Through Rate During Surface Tension Measurement (mm/min)	Surface Tension Measured (corrected) Pure Water (mN/m)	Surface Tension Measured (corrected) Nonyl-Phenol Ethoxylate Solution (mN/m)
10	72.51	36.34
5	72.50	35.24
2	72.53	34.02
1	72.54	33.19
0.5	72.50	32.34

Most people use pure liquids (water, typically) as justification that the surface tension measurements they are making on unknown solutions are accurate. They then ignore (or have no true control over in the case of manual ring tensiometers) the rate of ring pull through.

However, in a surfactant system, the true equilibrium surface tension is dependent on how the molecules of the surfactant are adsorbed at, and orienting at, the surface. This requires time and doesn't ever truly happen if the surface is being stretched (more surface created) during measurement of the surface tension. The problem can be minimized somewhat by reducing the rate at which the ring is pulled through the surface. However, a true equilibrium tension is never measured by the ring method. The surface tension measured is always somewhat higher than equilibrium – and the extent to which it is higher is based on rate of pull through (or oscillation in the case of sophisticated tensiometers of the Krüss type), as well as the slowness of the surfactant equilibration process. Particularly difficult applications for measurement include large molecule surfactants, amphoteric, and fluorosurfactants – known to be notoriously slow to reach final equilibration at surface.

2) I also mentioned briefly above a correction factor was necessary whenever surface tension is measured by the ring method. This is to account for the fact that the ring pulls a meniscus above the surface of liquid during measurement. The portion of the liquid pulled above the surface which is directly under the ring is not there due to surface tension forces – but rather capillary forces (see schematic below). But this liquid does contribute force to the force measuring device used to measure surface tension in a ring method experiment. So the resultant surface tension (or the force value from which it comes) needs to be

corrected for that extra force in order to measure a true surface tension. The amount of that force varies with meniscus height which, in turn varies with surface tension and density of the liquid being measured for surface tension. However, a typical error in surface tension due to not making the proper correction for this effect is about 7% (causing a further increase in the reported surface tension).

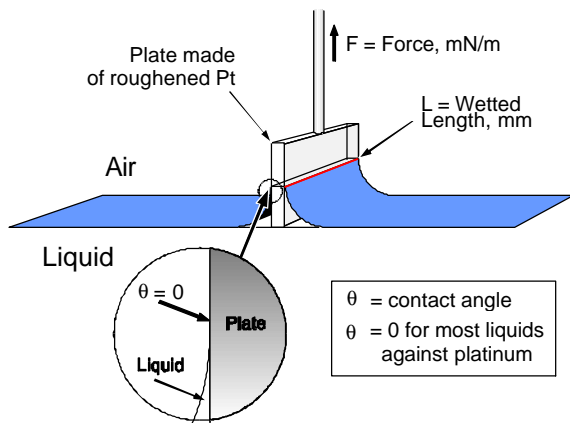


The third problem with the ring method is quite simply that the rings are difficult to keep true - circular and free of bending to the shaft - which causes the ring to be not absolutely parallel with the surface as the meniscus is pulled. This also typically results in more force being generated (higher than expected surface tensions measured) – and/or causes the meniscus to tear before the measurement can be made.

Plate Method

Another means of measuring “equilibrium” surface tension is the Wilhelmy plate method. This method is similar to the ring method except that the plate is a flat piece of platinum instead of a ring and that a meniscus is formed only on the perimeter of the plate. The plate does not have to be pulled above the surface to form the meniscus.

The plate can rather be placed right at the surface of the liquid being measured, and is not moved while surface tension is being measured.



These differences make the plate method vastly more accurate for determining the surface tensions of both pure liquids and surfactant solutions.

The lack of a pulled meniscus during the experiment means that the surface does not have to be in flux (being stretched) during measurement. The plate is simply touched to the surface (typically dipped into the liquid and brought back and held within 1.0 microns of the surface position – in high-end tensiometers), and then the surface is allowed to relax and come equilibrium with the plate present - without being stretched or perturbed. Thus, if surfactants are present, they are given as long as they need to reach an equilibrated state – typically one minute is used for most surfactant solutions unless the surfactants are known to be exceedingly slow. Then the force on the plate is measured and surface tension determined from the force. No

non-equilibrium state of the surface is present during measurement, and no corrections for volume of liquid hanging from the bottom of the plate (if the plate is flush with the surface) are necessary. Also, a Wilhelmy plate is easier to keep true and parallel with the surface – since it is a coupon of platinum rather than a ring. Platinum is ductile enough to be straightened and reformed by hand if necessary.

In the table below we add surface tension measured by the plate method for the nonyl-phenol ethoxylate solution we have been discussing to the former ring method data presented.

The 30.12 mN/m measurement of the surface tension of this solution can be verified by other methods (as discussed in a KRÜSS Technical Note TN307e by James Chamberlain) as the true equilibrium surface tension of this solution. The ring method measurements are all higher due to surface perturbation during the measurement of surface tension. And this surfactant in particular, nonyl-phenol ethoxylate, is **not** one that would be considered to be particularly slow to adsorb at surfaces. For other slower equilibrating surfactants, the increase in apparent surface tension measured by ring method would differ more widely.

Based on this, our laboratory **never**, unless specifically requested to do so to meet a customer's standard or follow an ASTM standard, uses the ring method. The chance for error, particularly to the high side or surface tension determination, is just too great unless you are working with a pure liquid or a simple mixture which you know will reach equilibrium surface tension in a short period of time.

Ring Pull-Through Rate During Surface Tension Measurement (mm/min)	Surface Tension Measured (corrected) Pure Water (mN/m)	Surface Tension Measured (corrected) Nonyl-Phenol Ethoxylate Solution (mN/m)
10	72.51	36.34
5	72.50	35.24
2	72.53	34.02
1	72.54	33.19
0.5	72.50	32.34
Zero –Plate Method	72.53	30.12

Interfacial Tension

Unlike for surface tension, for interfacial tension between two liquids the ring has its utility, and I would even recommend it over the plate method. This is mainly because the advantages of the plate method for surface tension are lost at the interface. The plate cannot be placed flush with an interface for the measurement of accurate interfacial tension – because for a plate wetted with a liquid, zero contact angle is not insured against another liquid. Thus, for proper plate method interfacial tension measurement, you must pull a meniscus to create a zero-degree contact angle and then you have all of the disadvantages of the ring method. Therefore, you may as well use the ring method, since a typical ring has approximately 3 times the wetted length of a standard plate, the force measured with a ring for interfacial tension will be at least 3 times greater than that measured for a plate. That means approximately 3 times more accuracy on interfacial tension measurements with the ring versus the plate, with the same force measuring system. However, even for interfacial tension, the issue of the interface not being at equilibrium during measurement still exists. (So please also have a read of James Chamberlain's paper on non-equilibrium surface and interfacial tension, Krüss Technical Note TN307e – to learn about more controlled methods of measuring non-equilibrium surface tension.)

Conclusions

1. Rings are for fingers and interfacial tensions
2. Plates are for equilibrium surface tensions
3. Non-equilibrium surface tensions and interfacial tensions can be measured and can be important – but you shouldn't measure them by accident and assume they are equilibrium values.