# APPENDIX

Experiments

Surface/Interfacial tension: Theory

The following is a short introduction to the concepts involved in the measurement of surface and interfacial tensions. Included is an introduction to the techniques involved and some practical advise. For those interested in further information a list of references appears at the end of this chapter.

<u>What is surface tension?</u>
Surface tension is a measurement of the cohesive energy present at an interface. The molecules of a liquid attract each other. The interactions of a molecule in the bulk of a liquid are balanced by an equal attractive force in all directions. Molecules on the surface of a liquid experience an imbalance of forces as indicated below.

Air

Liquid
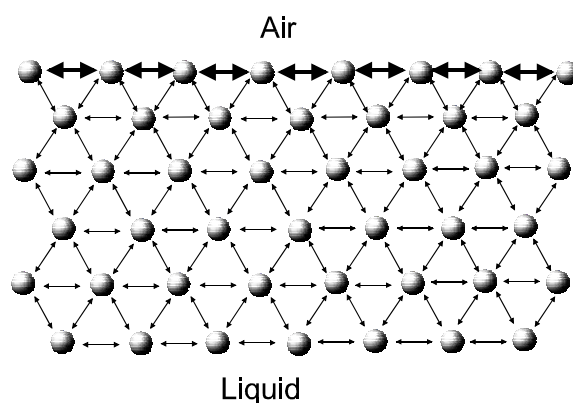
The net effect of this situation is the presence of free energy at the surface. The excess energy is called surface free energy and can be quantified as a measurement of energy/area. It is also possible to describe this situation as having a line tension or surface tension which is quantified as a force/length measurement. The common units for surface tension are dynes/cm or mN/m. These units are equivalent. Solids also may be described to have a surface free energy at their interfaces but direct measurement of its value is not possible through techniques used for liquids (see Contact Angle Theory section for advise on calculating solid surface free energies).

Polar liquids, such as water, have strong intermolecular interactions and thus high surface tensions. Any factor which decreases the strength of this interaction will lower surface tension. Thus an increase in the temperature of this system will lower surface tension. Any contamination, especially by surfactants, will lower the surface tension. Therefore researchers should be very cautious about the issue of contamination.

How is surface tension measured?

The measurement of surface and interfacial tension as performed by the Sigma 70 tensiometer is based on force measurements of the interaction of a probe with the surface or interface of two fluids. If one of the fluids is the vapor phase of a liquid being tested the measurement is referred to as surface tension. If the surface investigated is the interface of two liquids the measurement is referred to as interfacial tension. In either case the more dense fluid is referred to herein as the 'heavy phase' and the less dense fluid is referred to as the 'light phase'. With any of the techniques described herein you may perform interfacial tension measurements just like surface tension measurements by insuring that the bulk of the probe is submersed in the light phase prior to beginning the experiment.

In these experiments a probe is hung on a 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 surface tension. The forces present in this situation depend on the following factors: size and shape of the probe, contact angle of the liquid/solid interaction and surface tension of the liquid. The size and shape of the probe are easily controlled. The contact angle is controlled to be zero (complete wetting). This is achieved by using probes with high surface energies. KSV probes are made of a platinum/iridium alloy which insures complete wetting and easy and reliable cleaning.

The mathematical interpretation of the force measurements depends on the shape of the probe used. Two types of probes are commonly used, the Du Nouy Ring and the Wilhelmy Plate. Both are available from KSV Instruments.

Choice of probes:

Du Nouy ring: This method utilizes the interaction of a platinum ring with the surface being tested. The ring is submerged below the interface and subsequently raised upwards. As the ring moves upwards it raises a meniscus of the liquid. Eventually this meniscus tears from the ring and returns to it's original position. Prior to this event, the volume, and thus the force exerted, of the meniscus passes through a maximum value and begins to diminish prior to the actually tearing event. The process is shown in the diagram below:
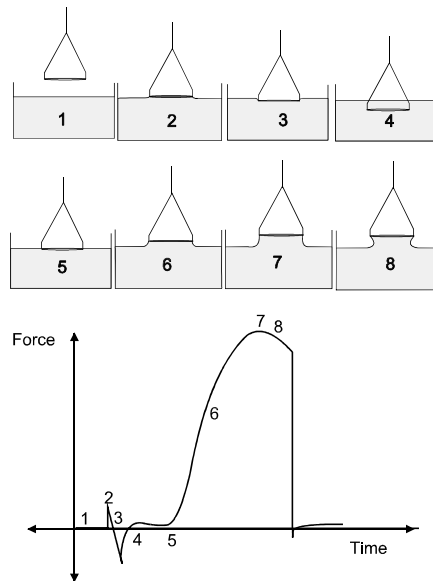
1. **The ring is above the surface and the force is zeroed.**
2. **The ring hits the surface and there is a slight positive force because of the adhesive force between the ring and the surface.**
3. **The ring must be pushed through the surface (due to the surface tension) which causes a small negative force.**
4. **The ring breaks through 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 until**
7. **The maximum force is reached**
8. **After the maximum there is a small decrease of in the force until the lamella breaks.**

The calculation of surface or interfacial tension by this technique is based on the measurement of this maximum force. The depth of immersion of the ring and the level to which it is raised when it experiences the maximum pull are irrelevant to this technique. The original calculations based on the ring technique were based on theories which apply to rings of infinite diameter and do not consider an additional volume of liquid which is raised due to the proximity of one side of the ring to the other. This additional liquid lifted is diagrammed below as the shaded portion:
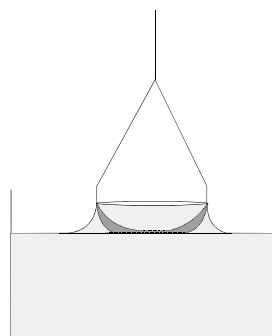
Mathematical corrections which compensate for this extra liquid have been produced. KSV software utilizes the corrections suggested by Huh and Mason from the reference cited below. There are also older corrections method suggested by Harkins and Jordan, or Zuidema and Waters, but the corrections according to Huh and Mason has been found to be the most suitable.

Wilhelmy Plate: This method utilizes the interaction of a platinum plate with the surface being tested. The calculations for this technique are based on the geometry of a fully wetted plate just in contact with, but not submerged in, the heavy phase. In this method the position of the probe relative to the surface is significant. As the surface is brought into contact with the probe your Sigma 70 will notice this event by the change in forces it experiences. It will register the height at which this occurs as the 'zero depth of immersion'. The plate will then be wetted to a set depth to insure that there is indeed complete wetting of the plate (zero contact angle). When the plate is later returned to the zero depth of immersion, the force it registers can be used to calculate surface tension.
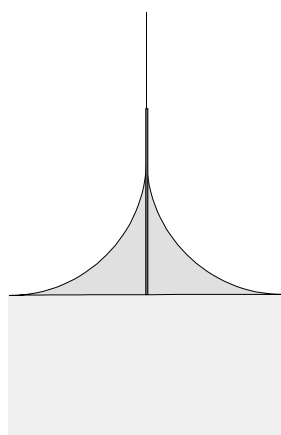
Metal rod: If you wish to measure surface tension of a liquid of which you have limited quantities you may consider using a platinum rod as your probe. With either of the probes discussed above the liquid required for testing may be more than you have available. The amount necessary to test with a certain probe must be sufficient to fill a vessel which accommodates the probe, to a depth which insures complete wetting of the probe is possible. With a given volume you can fill to a greater depth if the diameter of the vessel is smaller. Limitations to this strategy occur when the edges of the probe approach the edges of the measuring vessel. In that case the forces on the balance may be effected by the meniscus of the liquid as it contacts the vessel.

To avoid these problems you can choose to employ a metal rod as your probe. This allows you to use very much smaller volumes of your test liquids. In any technique the absolute accuracy of the measurement of the geometry of your probe effects the accuracy of your results. Measurement of the geometry of a fine rod are likely to be less accurate, on a % basis, than the measurement of your larger probes. Therefore this approach should only be used in situations where the volume of liquid available is an issue. The calculations for this technique are based on the same principles as the Wilhelmy plate method.