First Ten Ångstroms **ApplicationNotes**

Sessile Drop Interfacial Tension Measurements

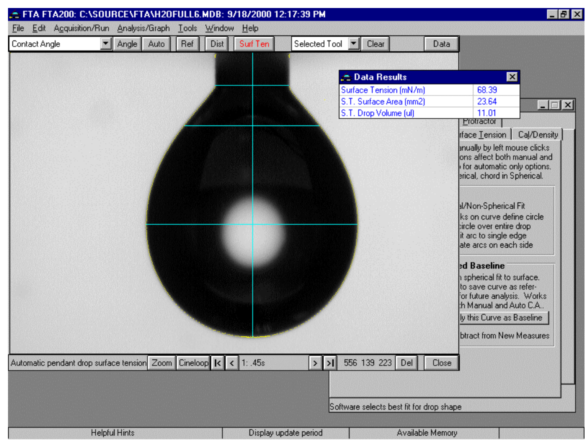
November 2, 2000

Interfacial tensions can be measured on sessile drops using the same mathematics as used for pendant drops, but the experimental conditions are different. In general, for reasons discussed below, it is more difficult to obtain the same level of accuracy in a sessile drop measurement as in a pendant drop measurement. Therefore, the obvious question is: why use this setup?

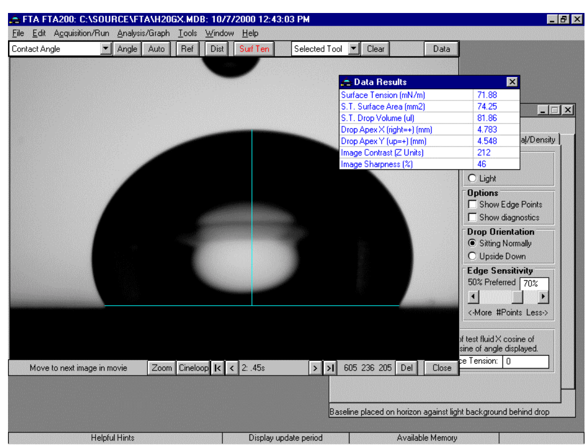
- some materials are difficult to make into pendant drops but sessile drops can be. Examples are molten solder and glass.
- sometimes the interaction of the test fluid with a substrate is of interest. An example is a surfactant desorbing from the substrate and therefore changing the liquid's surface tension.

Both pendant and sessile drop measurements assume an drop symmetric about the central vertical axis. In the case of the pendant drop, the needle from which the drop is suspended is normally small compared to the maximum drop diameter. If the liquid wets the needle, which it may or may not, and it wets it unevenly (i.e., the *contact angle* varies around the wetting line), then a distortion or strain is introduced into the drop shape. However, in the typical pendant drop case the needle is small and so the drop is distorted only in the immediate region of the needle. Then most of the drop profile, where the curvature is measured for the interfacial tension calculation, is *not affected by the needle*.

Now consider the typical sessile drop. The wetting line between the liquid and the substrate is large compared to the maximum diameter of the drop. More specifically, if the contact angle is 90° or less, the wetting line *is* the maximum diameter. Now the maximum diameter, *per se*, is not the issue, but if the drop is distorted by any substrate variation, *the region where the curvature is measured is distorted*. This distortion, or strain, leads to measurement error. The following two figures illustrate typical drop shapes in pendant and sessile drop measurements.



Pendant Drop



Sessile Drop

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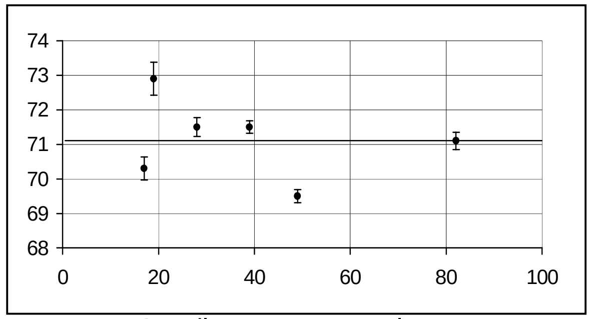
The images illustrate how the sessile drop is more susceptible to uneven strain within the measurement region from an uneven wetting line. Both pendant and sessile drops require a drop that is "tall" enough to be distorted away from a sphere by gravity. Another way of looking at this is that there must be sufficient hydrostatic pressure difference between the top and bottom of the drop to shape the drop. The difference between the pendant and sessile drop is the volume of fluid required to obtain this height (water γ_{LV} requires ≈2mm in height). In the drops illustrated above, the pendant drop has 11µl but the sessile drop has 81µl volume. The difference in volume is a result of the much larger support area of the sessile drop.

Example Data

Water interfacial tension was measured both by the pendant and sessile drop methods. The same liquid was used in both cases. More importantly, the same magnification was used for both drops. The average of ten pendant drops was 71.4mN/m with a COV of 0.2%.

A PTFE substrate was used for the sessile drop measurements. Only the *uniformity* of the substrate is important in the sessile drop method, because we assume the drop is the same from any viewing angle (no uneven strain). Contact angle does affect, however, the volume of liquid required to obtain the necessary drop height. Lower contact angles therefore mean larger volumes and a drop which might spread beyond the image.

A sequence of sessile drops was placed on the substrate. In practice, the preceding drop was made larger by adding additional liquid. This yielded a sequence of tensions for each volume. For each individual drop, ten images were captured, analyzed, and averaged to reduce the effects of vibration and camera noise. The following figure is a plot of measured sessile drop interfacial tension as a function of drop volume in µl.



Sessile IFT versus Volume

Error bars are shown for ±σ for each of the six sessile drops measured and the overall data set mean µ is shown by the horizontal line. The µ's for the individual sessile drops vary from 69.5 to 72.9mN/m. The σ's for the drops vary from 0.19 to 0.48mN/m, whereas σ for the *set mean* of six drops is 1.16mN/m. This shows the individual measurements are relatively noise free *but any particular drop can be distorted*. While not necessarily clear from this example, the variance from the set mean for small drops is in general larger than for large drops. That is, larger drops will fall closer to the "true" mean value than will small drops. This is a direct consequence of measuring closer to the strained region when the drop is small. The overall µ for the sessile drop set is 71.1, which compares favorably with the pendant drop µ = 71.4mN/m.

Summary

Sessile drop measurements can obtain accuracy similar to pendant drops if

- large drop volumes are used
- many drops are averaged