

Viscous Samples

January 5, 2001

Viscosity is resistance to flow. Viscous samples require special consideration. There are several separate issues, and these apply whether one desires to measure interfacial tension or contact angles. Viscosity is measured in milli Pascal seconds (mPa s) which is numerically identical to centi Poise (cp). Water has a nominal viscosity of 1cp or 1mPa s. Viscosity is a strong function of temperature, dropping rapidly as temperature rises. A good place to get reference values for viscosity is the CRC Handbook of Chemistry and Physics (www.crcpress.com).

The first consideration is dispensing the drop. As liquid is forced out the dispense needle or tip, a pressure is built up inside from viscosity. This pressure can be substantial and cause the syringe or pump to expand and will limit flow velocity. Perhaps even more bothersome is the effect of this pressure on any air trapped inside the pump. Trapped air is compressed easily and means that less liquid flows out of the tip than one expected from the movement of the pump. In other words, there is effectively a loss of volume to compressed air. Eventually the pressure is relieved when the pump stops and the "lost" volume flows out. So you get less than expected while the pump is running and more than expected after it stops!

The excess pressure from viscosity in the situations we encounter is proportional to the length of the needle and inversely proportional to the needle radius to the fourth power. This means that making the diameter twice as large divides the pressure by $2^4 = 16$. Therefore larger needles decrease viscosity pressures dramatically. Pressure is also proportional to flow rate.

To give some idea of the numbers involved, dispensing water through a 25mm long 22GA needle (0.71mm internal diameter) has no noticeable pressure, ΔP , at 1 μ l/s ($\Delta P=4.2$ Pa) but does begin to have at 10 μ l/s ($\Delta P=42$ Pa). As a rule-of-thumb, limiting the internal pressure increase ΔP to 50Pa ensures acceptable syringe pump control, even in the presence of some air bubbles. Conversely, if all air is removed, higher pressures may be tolerated, up to several hundred Pascals. Users can dispense glycerol, with a nominal viscosity of 1000cp, with an automatic pump by using a larger 18GA needle (1.27mm diameter) and limiting the rate to 1 μ l/s ($\Delta P\approx 400$ Pa) and ensuring no air is present. Smaller, glass syringes are useful in these situations as they are stronger than the disposable plastic ones.

Manual dispense systems can accommodate higher viscosities, because the user can apply significant pressure to the pipette, but maintaining adequate control over the amount dispensed will be an issue. As a convenient test, go into the lab and see if you can pipette the desired liquid with a disposable tip pipette, such as from Rainin or Eppendorf. If you can form a small drop on the tip and hold it, you will be able to control the liquid in an FTA system.

Once you have dispensed a drop, you must consider how long the drop will take to assume its equilibrium shape, which is what you want to measure to determine contact angle or interfacial tension. With water, equilibrium is reached in 10 milliseconds or so. The exact time depends on

how much kinetic energy must be dissipated by vibration. Glycerol, by comparison, having a viscosity one thousand times as great, will take a number of seconds to reach equilibrium. In fact, the careful experimentalist will take measurements through the first several minutes with glycerol, just to be sure all motion has stopped. This leads us to an important conclusion: viscous fluids and rapid absorption experiments do not mix. By that we mean that absorption will be viscosity limited rather than determined by surface tension and capillary forces. The latter are normally the object of such measurements.

Again, it is well to go into the lab and dispense a sample of any viscous fluid you wish to use. See how easy it is to form a pendant drop. Place a small sessile drop on a surface and see how long it takes to equilibrate. Make sure you can form a small sessile drop that is axisymmetric (i.e., round) when viewed from above.

What can you do if the above tests fail?

1. If you are in a position to heat the sample, you can do one of two things. Higher temperature will lower viscosity rapidly. Viscosity is affected much more rapidly with temperature than interfacial tension or contact angles, so some measurements become practical by raising the sample temperature. Other materials, such as solders and many polymers, are solids (frozen) at room temperature. As an alternative to dispensing them through a heated needle, cut a small cube, a millimeter or two on the side, and place it in a heated chamber. As the temperature rises and the sample melts, it will draw up into a sessile drop. Interfacial tension, γ_{LV} , can be measured using the sessile drop technique and the contact angle can be measured against whatever substrate is used. Other FTÅ application notes discuss these techniques.
2. If you need the γ_{LV} interfacial tension of a very viscous material, you can obtain an *approximation* by treating it as a solid and then measuring its surface energy using any of the built-in models (Girifalco, Owens geometric mean, Lewis acid/base model, etc.). Surface energy is obtained by measuring the contact angles of known fluids against the sample and then using the models, with the software performing the calculations.