

Experiment 446.8

SIZE OF A MOLECULE FROM VISCOSITY MEASUREMENTS

Viscous Flow

Fluids attempt to minimize flow gradients by exerting a frictional force known as a **viscous force** proportional to the area of contact, A , between regions flowing at different rates. The force is proportional to the velocity gradient, dv/dx , across the sample. The constant of proportionality is called the **coefficient of viscosity**,¹ η , or just the **viscosity**:

$$F = \eta A \frac{dv}{dx}. \quad (8.1)$$

The common unit of viscosity is the **poise**, $1 \text{ gm cm}^{-1} \text{ s}^{-1}$. The SI unit of viscosity is the Pa-s. $1 \text{ poise} = 10^{-1} \text{ Pa-s}$. Because of the size of viscosities of typical fluids, one often sees viscosities expressed in units of centipoises and mPa-s.

To measure the coefficient of viscosity, one must measure flow in the presence of a velocity gradient. One way to do this is to measure the flow through a tube. Poiseuille² derived a formula for the volume, ΔV , of an incompressible liquid of viscosity, η , moved through a tube of length l and radius, r , in a time, Δt , subject to a pressure drop, ΔP :³

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta l} \Delta P. \quad (8.2)$$

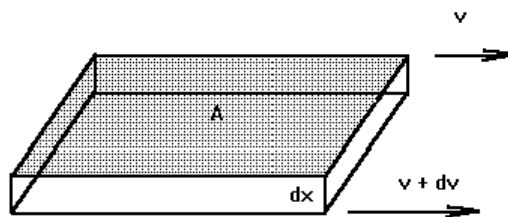


Figure 8.1. Differential flow of two sheets, showing the velocity gradient and the area of contact.

¹ The measured quantity is often called the viscosity, although the definition of viscosity is “the property of a fluid that resists the force tending to cause the fluid to flow.” So long as one is clear, it is acceptable to use the word “viscosity” to mean “coefficient of viscosity.”

² The poise is named in honor of Poiseuille.

³ See, for example, T. Engel and P. Reid, *Physical Chemistry*, Pearson-Benjamin Cummings, 2006, p. 869.

This equation demonstrates that a measure of the time for a specific volume to move through a tube, usually with a diameter of no more than a few millimeters, under a constant pressure drop is a direct measure of the viscosity of the flowing material.

There are many ways to measure viscous behavior other than flow through a tube. All methods require one to measure flow in the presence of a known velocity gradient. For example, another measurement relies on **Stokes Law**, that relates the viscous drag on a falling object to the viscosity of the medium through which it falls, **falling-ball viscometry**. In the experiment you are doing, the viscosity is determined with the Anton Paar SVM3000 viscometer. In this instrument, the **viscous torque** on a spinning object is monitored by measuring the rotation frequency of the object. In a sense, this is analogous to falling-ball viscometry, in that one is dragging an object through a liquid and measuring the retarding force due to viscous drag, although the motion in this case is circular motion rather than linear motion. The frequency is converted directly into viscosity by software in the instrument and reported on the screen.

Viscosity of Solutions

Solution properties depend not only on the materials that comprise the solution, but also on the amount of each present. The basis for explaining the concentration dependence of the viscosity of a solution is Einstein's relationship for the viscosity of a dilute solution of spherical particles in a continuous solvent:

$$\eta = \eta_0(1 + 2.5\phi). \quad (8.3)$$

η is the viscosity of a solution of volume fraction, ϕ , of the spheres. η_0 is the viscosity of the pure solvent. This formula was originally derived for the situation in which spheres of uniform size are in a continuous medium. For particles of other shapes, a similar relationship is valid, but the numerical coefficient of the volume fraction is different. Obviously, solutions of molecules in a molecular solvent do not approximate the condition that the medium appear to be a continuous fluid, but we use this equation as a practical means to relate viscosity to structure.

To begin, one can reduce Eq. (8.3) to a more practical equation for analysis. Note that the second term is the fractional increase in the viscosity over that of the pure solvent caused by the addition of the solute. The equation may be rearranged to give:

$$\frac{\eta - \eta_0}{\eta_0} = 2.5\phi \quad (8.4)$$

Substituting for the volume fraction in terms of the molarity, c , one obtains the following expression:

$$\frac{\eta - \eta_0}{\eta_0} = 2.5V_{solute,m} c, \quad (8.5)$$

where $V_{solute,m}$ is the molar volume of the solute. Thus, a plot of the left-hand side of Eq. (8.5) versus c is predicted to be linear with a slope that $2.5 V_{solute,m}$.

Once the molar volume is known, one may calculate the radius of a solute molecule (assuming it to be a sphere) by the simple equation:

$$r = \sqrt[3]{\frac{3V_{solute,m}}{4\pi L}}, \quad (8.6)$$

where r is the radius of the "spherical" molecule and L is Avogadro's number.

For real solutions, the dependence of viscosity on molarity is often more complex than that predicted by Eq. (8.5). For one thing, the solvent is not appropriately considered a continuous medium, since the solute is of similar size to the solvent molecule. For another, interactions between the solute and solvent molecules may change the average volume needed by a solute molecule.

In this experiment, we take the limiting-slope approach to determining the infinite-dilution “size” of the molecule. That is, we assume that

$$\lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} = 2.5 \frac{4\pi r^3 L}{3}, \quad (8.7)$$

from which one can extract the “size” of the molecule from a calculation of the radius. This is obviously a crude measurement, but – as will be seen – the result is reasonably in accord with our sense of the “size” of a molecule. As this is an extrapolation, the radius refers to the solute molecule surrounded by solvent molecules, *i.e.* the experiment gives a measurement of the molecular property at infinite dilution.

Procedure

This experiment requires attention to detail to give very good results. For the most efficient use of time, make solutions as needed; **making all solutions before they are needed wastes time and glassware.** If you must continue the experiment through a second week, save your materials in stoppered flasks. Be sure to label flasks clearly as to the material, the date, and the owner. Be sure that the laboratory instructor knows you have stored materials (to prevent them from being discarded!!).

Stock Solutions

The molecule which you are to investigate is glycerol. Into a 50-mL volumetric flask add 40 mL of glycerol. Dilute this glycerol to volume with methanol to produce the stock solution.

Creating Dilute Solutions

To obtain the information for the extrapolation, you must measure the viscosity coefficients of several solutions. These concentrations are obtained by dilution, and you must be very careful in this procedure to minimize errors. To get enough data to make a reasonable line, you need to measure at least six solutions (or more) over a range of concentrations from the pure solvent to the stock solution. Choose appropriate dilutions to make a set of solutions over this range.

Using 10-mL volumetric flasks, create the solutions by pipetting an appropriate amount of the stock solution into the flask, and then diluting this solution to volume for each of the concentrations you decide to make. Make measurements in random order; do not start with the most dilute solution.

Viscosity Measurement

1. Turn on **Power** switch on the SVM 3000. The switch is located at the back left side of the instrument.
2. The SVM 3000 conducts a self-test. Examine the first Measuring window. It displays, (a) dynamic viscosity, (b) kinematic viscosity, and (c) raw density. Make certain that the density (raw) reads 0.0011 gm/cm³ for air. If not, see your laboratory instructor.

3. Get an aliquot of the material whose viscosity is to be measured into a disposable syringe. Make certain there are **NO BUBBLES!** Bubbles result in incorrect readings.
4. Connect the syringe to the filling port of the SVM3000. Fill **SLOWLY** with at least 2 mL of sample going into the measuring cell.
5. Let the fluid sit in the cell for a while to settle.
6. Press **Start** to get a viscosity reading. The sampling begins until the system has made a consistent measurement, as indicated by diamonds to the right of the display.
7. You **MUST** clean the system **IMMEDIATELY** after each measurement.
 - (a) Remove the sample from the measuring cell by pushing air through the system with a disposable syringe.
 - (b) Fill the syringe with cleaning solvent and fill the measuring cell.
 - (c) Remove the cleaning solvent from the measuring cell by pushing air in, which pushes the solvent out.
 - (d) Press **Pump** to push solvent into the waste container. (Press **Pump** again to stop the pump.) Always use the proper solvent for cleaning the measuring cell.
8. After you finish all measurements and ensure that all glassware and the SVM3000 is clean, turn off the power to the SVM3000.
9. Do not forget that you must measure the density of both the glycerol and the pure solvent.
10. **Sign the logbook!**

IMPORTANT: Clean glassware and SVM3000 thoroughly after use; your grade may depend on it. If glassware or the SVM3000 is found to contain polymer, the grade of the group who used it last will be lowered. Do not let this happen to you!

Calculations

1. For each solution, report the molarity, c , and the viscosity, η , you measured. This can be conveniently done in a table.
2. Always include uncertainties. Give estimates of:
 - The fractional uncertainty in molarity. Is this a negligible error?
 - The fractional uncertainty in each viscosity.
3. Plot $\ln\left(\frac{\eta - \eta_0}{\eta_0 c}\right)$ versus c for the solutions. Give indications of error as solid error bars on your graphs for each measurement, and report the values you plotted in tabular form in the Results section.
4. From analysis of this plot (assuming it to be linear, which means you may have to neglect some points at higher concentrations), obtain the limiting value of $\ln\left(\frac{\eta - \eta_0}{\eta_0 c}\right)$, together with the uncertainty in this value.
5. From this limiting value, calculate the radius of the equivalent sphere that represents the glycerol molecule at infinite dilution.

Discussion Questions

1. What is the structure of glycerol?
2. What are the general commercial uses of aqueous glycerol solutions? Why might it be important to investigate the viscosity of such glycerol solutions?

3. Using a model of the glycerol molecule, estimate the radius of a sphere that just encloses the molecule. How does this value compare with the viscosity-determined radius?
4. Are systematic errors important in this experiment? If so, identify any sources of systematic error and provide estimates of how significant they may be.