Experiment 446.8

SIZE OF A MOLECULE FROM A VISCOSITY MEASUREMENT

Theory

Viscous Flow. Fluids attempt to minimize flow gradients by exerting a frictional force, the so-called viscous force. The force is proportional to the area of contact, $A$, between regions flowing past each other at different rates. The force is assumed to be proportional to the velocity gradient, $dv/dx$, across the sample. The constant of proportionality is called the coefficient of viscosity, \( \eta \), or just the viscosity:

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

The common unit of viscosity is the poise, 1 gm cm\(^{-1}\) s\(^{-1}\). The SI unit of viscosity is the Pa-s. 1 poise = 10\(^{-1}\) Pa-s. Because of the values of viscosities of typical fluids, one sees viscosities expressed in units of centipoise or millipoise (or mPa-s when expressed in SI units).

Measuring Viscosity. To measure the coefficient of viscosity, one must measure flow in the presence of a velocity gradient. One way is to measure the flow through a tube. Poiseuille\(^2\) derived a formula for the volume, $\Delta V$, of an incompressible liquid of viscosity, $\eta$, moved through a tube of length $l$ and radius, $r$, in a time, $\Delta t$, subject to a pressure drop, $\Delta P$:\(^3\)

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

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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 Jena Louis Marie Poiseuille, a 19th century French physicist who derived the formula for the flow of fluid through a pipe that bears his name.

This equation, known as Poiseuille’s law, indicates that a measurement of the time for a specific volume to move through a tube, usually with a radius of no more than a few millimeters, under a constant pressure drop is a measure of the viscosity of the flowing material. Many designs for measurement of viscosity involve measurement of flow through a capillary.

There are other ways to measure viscous behavior than to measure flow through a tube. All methods require a measurement of the rate of flow in the presence of a known velocity gradient. For example, a measurement relying on Stokes Law relates the viscous drag on a falling object to the viscosity of the medium through which it falls. The technique is known as falling-ball viscometry.

In this experiment, the viscosity is determined with the Anton Paar SVM 3000 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 from the fluid, although the motion in this case is circular rather than linear. The frequency is converted directly into viscosity by software in the instrument and reported on the screen.

The quantity of interest in this experiment is the viscosity, which is sometimes called the dynamic viscosity. In the literature, one also finds another quantity, the kinematic viscosity. It is defined as the ratio of the dynamic viscosity to the density, and is useful in defining parameters of a material such as the Reynolds number. The kinematic viscosity is also reported by the viscometer, as well as the solution density.

Viscosity of Solutions. The properties of a solution depend not only on the materials that comprise it, but 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 uniform spherical particles in a continuous solvent:  

\[ \eta = \eta_0 (1 + 2.5\phi). \]  

(8.3)

\( \eta \) is the viscosity of the solution of volume fraction, \( \phi \), of the spheres. \( \eta_0 \) is the viscosity of the pure solvent. For particles of other shapes, a similar relationship is valid, but the numerical coefficient of the volume fraction is different.\(^5\)

One may criticize the use of this equation for measuring solutions in which the solvent and solute molecules are comparable in size, because the solvent molecules do not represent a continuous medium, as was assumed to derive equation (8.3). The use of this equation for measurement of very large biomolecules in small-molecule solvents is closer to the assumption underlying the derivation of this equation, but we use this equation as a practical means to relate viscosity to structure in the solutions in this experiment.

Equation (8.3) can be reduced to a more practical equation for analysis of the experimental data. The specific viscosity of a solution is the fractional increase of the viscosity over that of the pure solvent.

\[ \frac{\eta - \eta_0}{\eta_0} = 2.5\phi \]  

(8.4)


By Einstein’s relation, as seen in Equation (8.4), the specific viscosity is directly proportional to the volume fraction of the solute in an ideal solution of the kind that Einstein modeled. Substituting for the volume fraction in terms of the molarity, $c$, one obtains the following expression for the dependence of specific viscosity on the molar concentration of solute:

$$\frac{\eta - \eta_0}{\eta_0} = 2.5 V_{\text{solute},m} c,$$

(8.5)

where $V_{\text{solute},m}$ is the molar volume of the solute. Equation (8.5) predicts that, for an ideal solution, a plot of the specific viscosity versus molar concentration is linear, the slope of which is $2.5 V_{\text{solute},m}$. In principle, once known, one may describe the volume per molecule, and if one defines a shape for the molecule, a parameter relating to the shape such as the radius of a sphere. If the solute molecule is considered to be a sphere, the radius of a solute molecule is found from equation (8.6).

$$r = \sqrt[3]{\frac{3 V_{\text{solute},m}}{4 \pi N_0}},$$

(8.6)

where $r$ is the radius of the “spherical” molecule and $N_0$ is Avogadro’s number.

**Dependence of Viscosity on Concentration for Real Solutions.** The dependence of viscosity on concentration is often more complex than that predicted by Eq. (8.5). For one thing, the solvent is not appropriately considered a continuous medium, because the solute molecule is of similar size to the solvent molecule. For another, interactions between the solute and solvent molecules change the average volume needed by a solute molecule, making the concentration dependence more complex than Equation (8.5).

A time-honored means of dealing with the complexity of the dependence on concentration is to examine the limiting value of a parameter, often in the limit of very dilute solutions. In this experiment, the experimental parameter of interest is the derivative of the specific viscosity with respect to concentration, $\frac{d}{dc}\left(\frac{\eta - \eta_0}{\eta_0}\right)$, which should be a constant according to Equation (8.5), *i.e.* the specific viscosity should be linear in the concentration. In general, it is not. However, one may take the limit of the ratio of the specific viscosity to the concentration as the concentration approaches zero, which is the derivative at infinite dilution.

$$\lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} = 2.5 V^0_{\text{solute},m},$$

(8.7)

where $V^0_{\text{solute},m}$ is the molar volume of the solute in an infinitely dilute solution. From this quantity, one can calculate the molecular volume and parameters such as the apparent molecular radius, as shown in Equation (8.6). It is important to remember that this calculation gives the features of the molecule under conditions that a solute molecule is surrounded only by solvent molecules, with other solute molecules being infinitely far away.
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 continue the experiment for a second week, save 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 Solution.** The molecule to be investigated is glycerol. Into a 100-mL volumetric flask add 25 mL of glycerol. Rinse all of the material into the flask, if necessary, by washing the excess into the flask with methanol. Dilute the glycerol in the 100-mL flask to volume with methanol by successive aliquots, until the volume is exact. This forms the stock solution.

It takes time to mix the two components properly so one should mix the solution manually by gentle agitation after adding an aliquot of methanol; turning the flask up and down, being sure to hold the stopper properly, works well. There should be no bubbles in the final solution. Be sure to make the solution very carefully and that you can precisely know the molarity of the stock solution.

**Creating Dilute Solutions.** The extrapolated parameter is determined from measurements of the viscosity coefficients of several solutions of different concentrations. These concentrations are obtained by dilution of the stock solution. To get enough data to make a reasonable extrapolation, one needs 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.

Create the diluted solutions by pipetting an appropriate amount of the stock solution into the flask, adding methanol to bring the solution to volume, as was done in making the stock solution. Always start with the stock solution and dilute to create the solutions to be measured.

**Viscosity Measurement.** Make measurements of solutions in random order to avoid any systematic error. Perhaps one should work with the pure methanol first, but it takes a long time for the viscometer to measure the viscosity of methanol with this instrument. The higher the concentration, the more viscous the solution and the easier the instrument locks onto the viscosity. Measure each solution at least three times to get information on the uncertainty in the measurement. Be sure you also know the uncertainty in each concentration.

**Using the Anton-Parr Viscometer SVM 300.**
1. If it has not already been done, turn on the **Power** switch of 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. Bring 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 SVM 3000. 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 SVM 3000 are clean, turn off the power to the SVM 3000.

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 the SVM 3000 thoroughly after use; your grade may depend on it. If glassware or the SVM 3000 is found to contain residual material, 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 each value of the viscosity, $\eta$, measured. This can be conveniently done in a table. Also report the average viscosity and the specific viscosity for each solution, as well as the uncertainty in these average parameters. There should also be quoted uncertainties of the molarities of all solutions.

2. One may consider, for not too concentrated solutions, that the specific viscosity may be expanded as a Taylor series in the molarity: $\left( \frac{\eta - \eta_0}{\eta_0} \right) = Ac + Bc^2 + \cdots$. Make a plot of specific viscosity versus concentration. Give indications of error as error bars on your graphs for each measurement.

3. In a second graph, plot $\left( \frac{\eta - \eta_0}{\eta_0c} \right)$ versus concentration. This plot should be reasonably linear. Fit these data to a linear function of concentration, obtaining the intercept and the uncertainty in the intercept. If the data are not linear, then fit to a second-order function, but be careful to be sure the fit does not turn up at lower concentrations.

4. From the limiting value of the function plotted in question 3 (the intercept), calculate the molecular volume, and from the molecular volume, obtain a value for the radius of the sphere having the same volume as glycerol at infinite dilution in methanol.

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6 If the plot is not linear, it is likely that the data at highest concentration are in a region in which intermolecular interaction among solute molecules affect the system. If this is the case, neglect points at highest concentrations determined, but make sure that there are at least four data points on the graph after that neglect. If there are not at least four points after neglect of highest concentrations, make additional measurements at lower concentrations.
Discussion Questions

1. From a structure of glycerol (either from the literature or calculated with a program like GAUSSIAN), what is the predicted volume of the glycerol molecule and the estimated radius of the molecule treated as a sphere? Explain clearly how this value is determined, including a reference to any book, journal article, or other information used to make the estimate of this quantity.

2. Suppose that glycerol cannot be considered a sphere, but that the molecular volume determined by the method described above is correct. If glycerol is considered a prolate ellipsoid with an axial ratio of 1.5, what are the diameters of glycerol along the long axis and the short axis, as determined from the value of the molecular volume determined above?

3. **Stokes law** relates the diffusion coefficient and the viscosity coefficient

   \[ D = \frac{k_B T}{6\pi \eta r} \]

   where \( D \) is the diffusion coefficient, \( \eta \) is the viscosity of the environment, \( r \) is the radius of the molecule, \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature in kelvins. In this experiment, the radius of glycerol has been estimated at infinite dilution. Using the viscosity of pure methanol (Why?) and the radius of glycerol determined at infinite dilution in this experiment, estimate the diffusion coefficient of glycerol at infinite dilution in methanol by Stokes law. Is this a reasonable value for the diffusion coefficient of glycerol? Explain.

4. From the literature, find the self-diffusion coefficient of glycerol at 298.15 K. How does this value compare with the value determined in question 3 for glycerol at infinite dilution in methanol? Assuming Stokes law is correct, what is the viscosity of pure glycerol from this diffusion coefficient?

5. Explain the difference between Newtonian viscosity and non-Newtonian viscosity.

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7 For ellipsoidal molecules, the coefficient in equation 8.5 or 8.7 is not 2.5, but some larger number, as discussed in ref. 5. However, for purposes of the question, use 2.5.