

## Experiment 446.5

### VISCOSITY OF POLYMER SOLUTIONS

#### Theory

Fluids resist a flow gradient. This resistance produces a frictional force known as a **viscous force** proportional to the area of contact,  $A$ , between the flowing regions and to the velocity gradient,  $dv/dx$ . The constant of proportionality is called the **coefficient of viscosity**,<sup>1</sup>  $\eta$ , as given in Eq. (5.1).

$$F = \eta A \frac{dv}{dx} \quad (5.1)$$

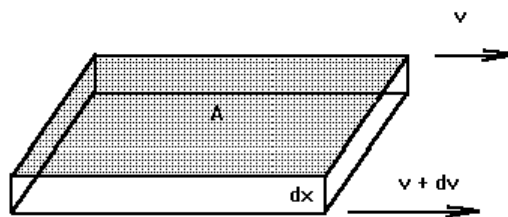
The unit of viscosity is a **poise**,  $1 \text{ gm cm}^{-1} \text{ s}^{-1} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$ .

To measure viscosity, one must determine flow in the presence of a velocity gradient. Poiseuille<sup>2</sup> derived a formula for the volume,  $\Delta V$ , of an incompressible fluid of viscosity,  $\eta$ , moved through a tube of length  $l$  and radius,  $r$ , in a time,  $\Delta t$ , subject to a pressure drop,  $\Delta P$ , Eq. (5.2).<sup>3</sup>

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{8\eta l} \Delta P. \quad (5.2)$$

From this equation, one sees that a measure of the time it takes 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.

There are many other other ways to measure viscous behavior. Another measurement of viscosity relies on **Stokes Law**, which relates the viscous drag on a falling object to the viscosity of the medium through which it falls, **falling-ball viscometry**.



**Figure 5.1. Differential flow in a system.**

<sup>1</sup> The measured quantity is often called the viscosity, although the major 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 perfectly acceptable to use the word “viscosity” to mean “the coefficient of viscosity.”

<sup>2</sup> The poise is named in honor of Poiseuille.

<sup>3</sup> See, for example, J. H. Noggle, *Physical Chemistry*, 3<sup>rd</sup> Ed., Addison-Wesley-Longmans, 1996, p. 479.

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. This is converted directly into a viscosity by the software of the instrument and reported on the screen.

### Origins of Viscosity

Viscosity is a property of fluids, *i.e.* liquids and gases. For liquids, it is dominated by short-range attractive intermolecular forces, the effects of which are hard to model. For gases, viscosity arises from momentum transfer between layers of moving molecules. The kinetic theory of gases gives the following formula for the viscosity of a gas:

$$\eta = \sqrt{\frac{MRT}{\pi^3 \sigma^4 L^2}}, \quad (5.3)$$

where  $M$  is the molar mass,  $R$  is the gas constant,  $\sigma$  is the molecular diameter, and  $L$  is Avogadro's number. For example, for helium gas at 298.15 K, this equation predicts a coefficient of viscosity of 198 micropoise. Perhaps the most important result of the kinetic-theory derivation is the prediction that the viscosity of a gas **increases** with temperature and molar mass.

It is well known that the viscosity of a typical liquid **decreases** with temperature. Eyring's model of dynamics in liquids treats a molecule in motion as passing through an energy barrier caused by the cage of molecules surrounding it. If there were not a barrier, the jump rate would occur at a frequency of approximately  $kT/h$ , where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $h$  is Planck's constant.<sup>4</sup> Because of the barrier the jump rate is reduced by a Boltzmann factor. In the absence of any stress (pressure drop), jumps occur equally in both directions over the barrier. However, the presence of a stress makes jumps easier in one direction than another. Calculating the net jump rate in one direction gives the net flow velocity. Using the definition of the viscous force in equation (5.1), this gives the theoretical prediction for the viscosity coefficient

$$\eta = che^{\varepsilon/kT}, \quad (5.4)$$

where  $c$  is the concentration in molecules per cubic centimeter, and  $\varepsilon$  is the barrier energy. Eyring's theory predicts that the viscosity is proportional to the number density and is roughly inversely proportional to temperature. Qualitatively, this equation reproduces the observation variation of viscosity with these parameters.

### Viscosity of Polymer Solutions

Solution properties depend not only on the materials mixed, but on the amount of each present in the mixture, as Eyring's theory shows. A particularly important example is the viscosity of a solution of a polymeric material in a small-molecule solvent. The basis for explaining the concentration dependence of the viscosity of a polymer solution is Einstein's relationship for the viscosity of a dilute solution of spherical particles:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi. \quad (5.5)$$

---

<sup>4</sup> A. Adamson, *A Textbook of Physical Chemistry*, 3<sup>rd</sup> Edition, Academic Press, San Diego, CA, 1986.

$\eta$  is the viscosity of a solution of volume fraction,  $\phi$ , of the spheres.  $\eta_0$  is the viscosity of the pure small-molecule solvent. For particles of other shapes, a similar relationship is valid, but the numerical coefficient of the volume fraction is different.

It is usual to define the **specific viscosity**,  $\eta_{sp}$ , of a polymer solution by Eq. (5.6).

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad (5.6)$$

The specific viscosity is the fractional increase in the viscosity over that of the pure solvent caused by the addition of the polymer. According to the Einstein relation, Eq. (5.5), for a theoretical solution of perfect spheres, the specific viscosity is can be related to the concentration:

$$\eta_{sp} = \frac{10\pi r^3}{3m} c_m \quad (5.7)$$

$r$  is the radius of the “spherical” molecule,  $m$  is its mass, and  $c_m$  is the mass concentration. Thus, by this simple theory, the specific viscosity is predicted to be linear in mass concentration.

For real polymer solutions, the dependence of the specific viscosity on mass concentration is often more complex than this simple theory predicts. The polymer molecule is not necessarily a sphere nor is it large compared to solvent molecule, so that the treatment as a sphere in a continuum is appropriate. To parameterize the concentration dependence of specific viscosity, one defines the **intrinsic viscosity**,  $[\eta]$ , as:

$$[\eta] = \lim_{c_m \rightarrow 0} \frac{\eta_{sp}}{c_m} \quad (5.8)$$

Like other parameters extrapolated to infinite dilution, the intrinsic viscosity describes the interaction of a single average polymer molecule with a sea of solvent. For a spherical molecule,  $[\eta]$  should be proportional to the molecular volume. For many synthetic polymers in dilute solution, the chains tend to adopt a tight, ball-like configuration in solution, the average structure of which is defined by a **radius of gyration**,  $R_G$ . For such molecules, one predicts that:

$$[\eta] = K' \frac{R_G^3}{M} \quad (5.9)$$

where  $M$  is the molar mass and  $K'$  is a constant. For a polymer that adopts a random-coil conformation, theory predicts that  $R_G \propto M^{1/2}$ . Thus, one predicts the dependence of intrinsic viscosity on molar mass of the form:

$$[\eta] = KM^{1/2} \quad (5.10)$$

This generally applies to polymer solutions under what are known as theta conditions.<sup>5</sup> In practice, one can describe the dependence more accurately by the empirical **Mark-Houwink equation**:

$$[\eta] = KM^\alpha \quad (5.11)$$

where  $K$  and  $\alpha$  are two parameters that depend on the solvent and polymer. Values of these coefficients for several polymers and solvents are given in Table 5.1. Once  $K$  and  $\alpha$  are known for a combination of polymer and solvent, one may use the intrinsic viscosity to give the **viscosity-average molar mass** of a material,  $M_v$ .

---

<sup>5</sup> P. J. Flory, *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, New York, 1953.

**Table 5.1. Mark-Houwink Parameters for Various Polymers and Solvents<sup>a</sup>**

Polymer	Solvent	Temperature/°C	K/(cm <sup>3</sup> /gm)	$\alpha$
Atactic polystyrene	Benzene	25	.034	0.65
Atactic polystyrene	Toluene	25	0.00848	0.748
Atactic polystyrene	Cyclohexane	28	.108	0.479
Poly(isobutylene)	Benzene	25	0.083	0.53
Poly(isobutylene)	Toluene	25	0.087	0.56
Poly(isobutylene)	Cyclohexane	25	0.040	0.72
Atactic polypropylene	Benzene	25	0.027	0.71
Atactic polypropylene	Toluene	30	0.0218	0.725
Atactic polypropylene	Cyclohexane	25	0.016	0.80
Poly(vinyl alcohol) <sup>b</sup>	Water	25	0.0002	0.76

<sup>a</sup> From J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2<sup>nd</sup> Edition, Wiley-Interscience, New York, 1975.

<sup>b</sup> P. J. Flory and F. S. Leutner, *J. Polym. Sci.*, 3, 880 (1948).

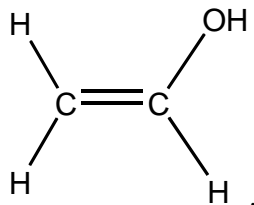
Polymer samples tend to be mixtures of molecules of different mass (*i.e.* they are polydisperse). The average quantity that represents the molar mass depends on how the average is calculated. The quantity calculated with the Mark-Houwink equation is the **viscosity-average molar mass**,  $M_v$ . Another measure is the **number-average molar mass**,  $M_n$ . The relationship of these two depends on the distribution of molecules of different masses in a sample. For a log normal distribution one has the relation in equation (5.12):

$$\frac{M_v}{M_n} = [(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha}, \quad (5.12)$$

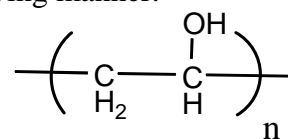
where  $\Gamma(x)$  is the gamma function evaluated at  $x$ . Another sort of average is the **weight-average molar mass**,  $M_w$ . It turns out that the viscosity-average and the weight-average molar masses are similar. In fact, they will be identical if  $\alpha = 1$ .

### Degradation of the Polymer and Viscosity of the Solutions<sup>6</sup>

One kind of polymer is made from additions across the double bond of a material. Polyethylene is such a vinyl polymer, as are polypropylene, polystyrene and poly(vinyl chloride). A particularly interesting and useful material is vinyl alcohol:

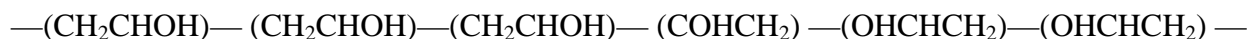


Polymers made from it are commercially useful. In this experiment, you measure viscosities of poly(vinyl alcohol) solutions and solutions of degradation products of this material. Poly(vinyl alcohol) is often written in the following manner.



<sup>6</sup> P. J. Flory and F. S. Leutner, *J. Polym. Sci.*, 3, 880 (1948).

The formula in parentheses is the monomer unit. The monomer unit has a *head* (the CHO group) and a *tail* (the CH<sub>2</sub> group). This formula does not indicate how adjacent monomer groups are oriented with respect to each other. One might suppose that they form regular chains, with the head of one monomer bonded to the tail of its neighbor, and so on, down the chain. Nothing is that perfect, so the chains often contain runs of regularly arranged monomers, with occasional head-to-head defects. One finds chains of the sort shown below, where the central linkage is a head-to-head, 1,2-glycol structure.



A measure of the polymer's structure is the fraction,  $\Delta$ , of monomer linkages that are head-to-head. In this experiment, treatment with periodate specifically cleaves 1,2-glycol linkages, making smaller chains. The size of the smaller chains will depend on the number of head-to-head linkages in the particular sample of poly(vinyl alcohol), which can be estimated from the number-average molar masses of the polymer and its cleaved products.

**Table 5.2. Numerical Values of the Gamma Function**

x	$\Gamma(x)$	x	$\Gamma(x)$
1.00	1.00000000	1.52	0.88703878
1.04	0.97843820	1.56	0.88963920
1.08	0.95972531	1.60	0.89351535
1.12	0.94359019	1.64	0.89864203
1.16	0.92980307	1.68	0.90500103
1.20	0.91816874	1.72	0.91258058
1.24	0.90852106	1.76	0.92137488
1.28	0.90071848	1.80	0.93138377
1.32	0.89464046	1.84	0.94261236
1.36	0.89018453	1.88	0.95507085
1.40	0.88726382	1.92	0.96877431
1.44	0.88580506	1.96	0.98374254
1.48	0.88574696	2.00	1.00000000

<sup>a</sup>Taken from CRC Standard Mathematical Tables and Formulae D. Zwillinger, ed., CRC Press, Boca Raton, Florida, 1996, p. 497.

Thus, one examines the structure of the polymer indirectly through a chemical reaction. A reaction that acts specifically at the 1,2-glycol linkages to cleave a polymer breaks it into smaller units, the size of which is determined by the number of monomer units between these sites. Treatment with periodate can cause this cleavage. On the assumption that all 1,2-glycol linkages are cleaved and that none of the head-to-tail linkages are cleaved during treatment with periodate,  $\Delta$  is equal to the increase in the number of molecules after cleavage divided by the total number of monomer units, as in equation (5.14):

$$\Delta = M_m \left( \frac{1}{M_n'} - \frac{1}{M_n} \right), \quad (5.14)$$

where  $M_m$  is the molar mass of the monomer,  $M_n$  is the number-average molar mass of the polymer before cleavage, and  $M_n'$  is the number-average molar mass of the polymer after cleavage. Using the Mark-Houwink equation, one may calculate the number-average molar

mass from the viscosity-average molar mass, to obtain a value of the head-to-head fraction for a polymer sample.

### Procedure

This experiment requires attention to detail to give very good results. Therefore, you must use time wisely. 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 a stoppered flask. Be sure to label the flask clearly. The cleaved solution can also be left to cool and used the following week with any uncleaved dilutions left from the first week. Be sure that the laboratory instructor knows you have stored materials for use (to prevent things from being thrown away!!).

### Stock Solution

Prepare a stock solution of PVOH with a concentration of approximately 1 g PVOH per 100 mL. The preparation of the stock solution takes about one hour.

- (1) In a 600 mL beaker, place 200 mL of distilled water with a large magnetic stirring bar.
- (2) Heat this with slow stirring to 90°C.
- (3) **SLOWLY** add approximately 5 grams of the poly(vinyl alcohol) over about 30 minutes with sporadic stirring. Use sporadic stirring to avoid frothing. (Be sure to record the weight you added.) Add the polymer **slowly**; it may not all dissolve, but try to add it so as not to produce agglomerate or frothing. When the solution is clear (which may take perhaps an hour), the polymer has all dissolved.
- (4) Turn off the heat and allow the solution to cool to room temperature.
- (5) After cooling, transfer the solution to a 500 mL volumetric flask, being sure to use washing to get all of the material into the flask.
- (6) Add distilled water to bring the solution to volume.

### Preparing Solutions of the Cleaved Polymer

The cleaved solution is made by adding ~1.0 g  $\text{KIO}_4$  to 200 mL of the stock solution and heating to about 70°C with stirring. An Erlenmeyer flask is a good cleaving vessel since the solution can be stored in it (after removing the stirring bar).

### Creating Dilute Solutions

To obtain the information, you must measure the viscosity coefficients of several solutions of both the original polymer and the cleaved polymer over a range of concentrations. These concentrations are obtained by successive dilution, and you must be very careful in this procedure to minimize errors that will propagate through your data. To get enough data to make a reasonable line, the following minimum approximate dilutions are suggested:

Original polymer -- stock, 3/4, 1/2, 1/4, and 1/8

Cleaved polymer -- stock, 3/4, 1/2, 1/4.

(If you have sufficient time, you should examine other dilutions, as that makes your extrapolation better.)

Unused solutions may be stored in Erlenmeyer flasks. **Do not prepare all solutions at once.** Use 100 mL of each solution for a viscosity measurement. Make sure that you dilute properly so that the concentrations are well known.

### 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  $0.0011 \text{ gm/cm}^3$  for air. If not, see your laboratory instructor.
3. Get an aliquot of the material into a disposable syringe. Make certain there are **NO BUBBLES!**
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. Press **Start** to get a viscosity reading.
6. You **MUST** clean the system **IMMEDIATELY** after each experiment.
  - (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 for the measuring cell by attaching an air hose to push 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.
7. After you finish all measurements and ensure that all glassware and the SVM3000 is clean, turn off the power to the SVM3000.
8. **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 polymer solution, report the concentration,  $c$  (in gm PVOH per 100 mL of solution) and the viscosity,  $\eta$ , you measured. This can be conveniently done in a table.
2. Always include uncertainties. Give estimates of:
  - The relative uncertainty in each concentration,  $\Delta c/c$ . Is this a negligible error?
  - The relative uncertainty in each viscosity.
3. Plot  $\eta_{sp}/c$  versus  $c$  for the uncleaved and the cleaved polymer. 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 analyses of these plots obtain  $[\eta]$  for each material. Record the uncertainty limits on  $[\eta]$  (obtained by propagation of uncertainty) in your Results section.
5. Calculate  $M_v$  and  $M_n$  for the original polymer and the degraded polymer. Always report uncertainties with the values.
6. From the molar-mass results, obtain a value for  $\Delta$ . Report this value and any uncertainty in it.

**Discussion Questions**

1. What are the principal commercial uses of poly(vinyl alcohol)?
2. Write out a general equation for the cleavage reaction of poly(vinyl alcohol).
3. Cleavage occurs only at 1,2 glycol structures, but two successive backward additions do not result in two 1,2 glycol structures. How is this taken into account in the calculation of  $\Delta$ ?
4. A statistical fit to  $\eta_{sp} = Ac + Bc^2$  might be an appropriate way to analyze for  $[\eta]$ . Carry out this analysis on your data for the uncleaved polymer, and compare the answer to that determined by plotting  $\eta_{sp}/c$  versus  $c$ . In your view, which procedure is more accurate? Explain.
5. Does the uncertainty in  $[\eta]_{cleaved}$  or the uncertainty in  $[\eta]_{uncleaved}$  contribute more to the uncertainty in  $\Delta$ ? Explain.
6. Are systematic errors important in this experiment? If so, identify any sources of systematic error and provide estimates of how significant they may be.