

## Experiment 2: Characterization of polyacrylamide (PAM) by viscometry and gel permeation chromatography (optional)

**Aim:** (a) To determine the intrinsic viscosity and molecular weight of polyacrylamide (synthesized in experiment 1) using a Ubbelohde capillary viscometer.

(b) To measure the shear rate dependent viscosity of "concentrated" PAM solutions by using a coaxial cylinder (Couette) viscometer.

(c) To measure molecular weight and polydispersity index by gel permeation chromatography (optional)

### Materials and Apparatus:

Polyacrylamide synthesized in experiment 1.

Water containing 0.05 M NaNO<sub>3</sub> + 0.02% NaN<sub>3</sub>

Water bath with arrangements for maintaining constant temperature.

Ubbelohde capillary viscometer

Brookfield Couette viscometer or Bohlin 88 Couette viscometer

### Brief Background:

Methods to measure viscosity of polymer solutions: (See handout from Rabek, *Experimental Methods in Polymer Science*, Ch 9.)

The measurement of the viscosity of polymer solutions is called viscometry and the apparatus used is called the viscometer. We shall study about three viscometers: falling ball viscometer, capillary (Ubbelohde) viscometer and Couette viscometer. The falling ball viscometer was discussed in experiment 1.

Capillary viscometer, intrinsic viscosity, Mark-Houwink empirical correlation : A capillary viscometer is used to get a measure of the viscosity of very dilute polymer solutions. The solution is allowed to flow through a capillary of known diameter under the action of a pressure drop as a fully developed laminar flow and the time taken to flow through a given length is measured. For a dilute solution, the measured time ( $t_c$ ) at a given temperature is proportional to the viscosity of the solution ( $\eta_c$ ) at that temperature. At the same temperature, the flow time ( $t_s$ ) for the solvent through the same capillary is also measured.  $t_s$  is proportional to the viscosity of the solvent ( $\eta_s$ ). Thus,

$$\frac{\eta_c}{\eta_s} = \frac{t_c}{t_s} \quad (1)$$

Thus, capillary viscometry gives only a relative measure of the viscosity and not an absolute one. Let us define a couple of terms before proceeding.

$$\text{Specific viscosity} = \eta_{sp} = \frac{\eta_c}{\eta_s} - 1 \quad (2)$$

$$\text{Intrinsic viscosity} = [\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{1}{c} \ln \left[ \frac{\eta_c}{\eta_s} \right] \quad (3)$$

where,  $c$  is the concentration of the polymer solution. Thus, if the specific viscosity is determined experimentally for polymer solutions of different concentrations (but same molecular weight), then the intrinsic viscosity can be determined by extrapolating the plot of

$$\frac{\eta_{sp}}{c} \text{ vs. } c \quad \text{or} \quad \frac{1}{c} \ln \left[ \frac{\eta_c}{\eta_s} \right] \text{ vs. } c$$

to  $c=0$ . This intrinsic viscosity can be used to determine the molecular weight by using a previously determined Mark-Houwink empirical correlation for that polymer in a given solvent and temperature. The general form of the Mark-Houwink relation is

$$[\eta] = K' M^a \quad (4)$$

where,  $[\eta]$  is reported in  $\text{cm}^3/\text{g}$  and the molecular weight is obtained in units  $\text{g/mol}$ . The range of  $a$  is  $0.5 \leq a \leq 0.8$ . Consider some examples:

Polymer solution	$K'$	$a$
PAM in 0.05 M $\text{NaNO}_3$ at 30 C	0.0063	0.800
NaPAA in 0.05 M $\text{NaNO}_3$ at 30 C	0.0281	0.770
PEO in 0.05 M $\text{NaNO}_3$ at 30 C	0.0120	0.784

A short note on the  $\frac{\eta_{sp}}{c}$  vs.  $c$  and  $\frac{1}{c} \ln \left[ \frac{\eta_c}{\eta_s} \right]$  vs.  $c$  plots: These plots are typically found to be linear and describable by the following Huggins' equations:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (5)$$

$$\frac{1}{c} \ln \left[ \frac{[\eta]_c}{[\eta]_s} \right] = [\eta] + k'' [\eta]^2 c \quad (6)$$

$k'$  and  $k''$  are called the Huggins' constants.

#### Coaxial cylindrical Couette viscometer:

A Couette type viscometer consists of a rotating cylinder (cylinder radius,  $R_1$  and rotating at  $N$  rev per min) positioned coaxially inside a cylindrical cup (of a slightly larger radius,  $R_2$ ). The liquid of viscosity,  $\eta$ , is subjected to shear in the narrow gap between the two cylinders. Each rotating speed,  $N$ , corresponds to a particular strain rate,  $\dot{\gamma}$ , experienced by the liquid. The viscous drag exerts a torque,  $T$ , on the rotating cylinder. For such a system, the strain rate dependent viscosity can be written as,

$$\eta = \frac{60(R_2 - R_1) T}{4\eta^2 R_1^3 H N} \quad (7)$$

and the shear stress,  $\tau$  is given as,

$$\tau = \eta \dot{\gamma} = \frac{T}{2\eta H R_1^2} \quad (8)$$

where,  $H$  is the height of the cylindrical region of the rotating cylinder.

#### Shear stress vs. strain rate relationship:

If the liquid under study is Newtonian,  $T/N$  (and hence  $\eta$ ) will be constant and independent of the shear strain rate. Polymer solutions, however, are generally Newtonian only below some limiting shear strain rate. Above this limiting value, many behave as "shear thinning" fluids i.e.,  $\eta$  decreases as  $N$  decreases. One common empirical correlation used is the power law relation:

$$\eta = \eta_0 \dot{\gamma}^{n-1} \quad (9)$$

Note that the above relation works only at large strains and not at the zero-shear limit. What should be the value of  $n$  for a shear-thinning liquid?

#### **Precautions:**

No special precautions.

**Procedure:****A. Intrinsic viscosity determination by Ubbelohde viscometer:**

1. Keep ready the solvent for this experiment: 0.05 M NaNO<sub>3</sub> and 0.02% NaN<sub>3</sub>. Use previously prepared PAM solutions (C<sub>0</sub> = 4%, 8% or 12%) to form diluted solutions of concentration C<sub>i</sub> such that

$$C_1 = 0.0010 \text{ g/cm}_3$$

$$C_2 = 0.0015 \text{ g/cm}_3$$

$$C_3 = 0.0020 \text{ g/cm}_3$$

$$C_4 = 0.0025 \text{ g/cm}_3$$

The values of C<sub>i</sub> need not be exactly as shown, as long as you know what the real value is, e.g. C<sub>4</sub> = 0.00235.

2. Prepare the water bath such that the bath is at a uniform temperature of 30 C.

3. Use the Ubbelohde viscometer (as described below) to measure the flow time of the solvent (t<sub>s</sub>). Repeat the measurement. The two measurements of the flow time should agree within 0.5 sec.

**Using the Ubbelohde capillary viscometer:**

This method is used for dilute solutions. We shall be using Ubbelohde viscometer of size OC or OB. These sizes are used for solutions in the following viscosity ranges:

Size	$\eta$ (cStokes)/ t (sec)	$\eta$ range (cStokes)
OC	0.003	0.6 to 3
OB	0.005	1.0 to 5

Let us consider the case where a concentrated solution of C<sub>0</sub> is diluted to concentration C<sub>i</sub> by using a solvent and we are to determine the viscosity of the solution of concentration C<sub>i</sub>. The procedure is as follows (Note: in the following the sample could be solvent or any of the solutions):

a) Clean the viscometer using suitable solvents (water, then ethanol) and dry by passing clean, dry filtered air through the instrument to remove the final traces of solvents.

b) Charge the viscometer by introducing the sample through tube G into the lower reservoir; introduce enough

sample to bring the level between lines J and K (this is about 15 ml).

c) Place the viscometer into the holder, and insert it into the constant temperature bath. Vertically align the viscometer in the bath if a self-aligning holder has not been used.

d) Allow approximately 15-20 minutes for the sample to come to bath temperature.

e) With the side vent tube (B) closed (using a finger) use a suction bulb on tube A to pull liquid upward through the capillary measuring bulb (E) until it is above the top mark and half way into bulb C. Remove the suction bulb. Remove the finger from the side vent (B) and immediately place the finger over tube A until the sample drops away from the lower end of the capillary into bulb I. Then remove the finger and measure the efflux or flow time.

f) To measure the flow time, allow the liquid sample to flow freely down the mark D (start the stopwatch when the meniscus drops below this top mark) , measuring the time for the meniscus to pass from mark D to mark F (stop the stop watch when the meniscus drops below the bottom mark F).

g) Without recharging the viscometer, repeat the measurement of the flow time.

h) The flow times and concentrations are used to calculate the intrinsic viscosity.

4. Empty solvent from the viscometer and add 5ml of next PAM solution to be tested, swirl to collect drops of solvent and then drain the solution.

5. For each solution of concentration  $C_i$ : Use the Ubbelohde viscometer to measure the flow time ( $t_i$ ) of the solution of concentration  $C_i$ . Repeat the measurement. The two measurements of the flow time should agree within 0.5 sec. The flow times for the solutions will be greater than that of the solvent.

## B. Viscosity measurement using a Couette viscometer:

1. Keep ready the solvent for this experiment: 0.05 M NaNO<sub>3</sub> and 0.02% NaN<sub>3</sub>. Use previously prepared PAM solutions (C<sub>o</sub> = 4%, 8% or 12%) to form diluted solutions of concentration C<sub>i</sub> such that,

For C<sub>o</sub> = 4%, C<sub>i</sub> = 3%, 2%, 1%

For C<sub>o</sub> = 8%, C<sub>i</sub> = 4%, 2%, 1%

For C<sub>o</sub> = 12%, C<sub>i</sub> = 8%, 4%, 1%

Nine ml of each solution (so prepare 15-20 ml) is required for viscometry using the Brookfield viscometer. A lot more solution is required if you are using the Bohlin viscometer.

2. Equilibrate all solutions to room temperature before viscometry.

3. Now use the Couette viscometer (as described below) to measure the shear stress at several different RPMs (0.5, 1, 2.5, 5, 10, 20, 50, 100 RPM).

### Using the Brookfield Couette Viscometer:

This method is used for comparatively concentrated solutions. The procedure for measuring the shear stress is as follows:

a) Level the instrument by ensuring that the leveling bubble is at the center of the circle.

b) Turn POWER ON. Touch SPDL. Touch 21. (This is the spindle size.) Touch %. Touch AUTO ZERO.

c) Hang spindle # 21 via S-hook.

d) Position flow jacket to surround spindle. Lock to frame by thumb screw (back side of instrument).

e) Introduce 9 ml of sample solution into the sample chamber.

f) Slide sample chamber up through cylindrical hole in flow jacket, until top of the sample chamber is even with the top of the jacket. Twist to lock in place. Spindle should now be totally immersed. You should see 0.00 on the dial.

g) Touch SS. This will display the shear stress in dyn/cm<sup>2</sup>.

h) Turn MOTOR ON.

i) Increase RPM in steps. Measure and record the shear stress. Viscosity is then calculated using the torque and rpm.

j) Viscosity is then calculated using the torque and rpm.

Using the Bohlin viscometer:

a) Check if the instrument is connected to the mains. Press the ON/OFF button to switch on. "OFF" should appear on the display.

b) Check to see if it is necessary to zero adjust the residual torque of the motor. Press the START button to start motor. Press FUNCTION button until the torque value (in units of mN.m) appears on display. Run motor for 30 sec. Turn the SPEED switch. Read torques at speeds 1 to 4. If torque value at any speed is greater than 0.01 mNm, zero adjustment is needed. Press START button to stop motor.

c) Perform the zero adjustment. Press the START button. If motor is cold, let it run for 30 sec. Press START button to stop motor. Press FUNCTION button until "CAL" appears on the display. Hold the CAL button down until the motor starts. Doing the adjustment for one speed, does the same for all speeds.

d) Choose rotational speed from the following:

SPEED switch pos.	Rotational speed	
	(rpm)	(Hz)
1	20	0.33
2	35	0.58
3	61	1.02
4	107	1.78
5	187	3.12
6	327	5.45
7	572	9.53
8	1000	16.67

e) Choose measuring system using the SYSTEM switch.

Measuring system	System switch position	Est. sample vol. with bottom cover
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C14	1	10 ml
C25	2	14 ml
C30	3	17 ml
"infinite sea" C14	4	-
"infinite sea" C25	5	-
"infinite sea" C30	6	-
"wide gap" C14	7	-
"wide gap" C25	8	-

Check if optimum system by reading the torque value at a rotational speed. Lower the measuring cylinder into the sample until it is submerged about 10 ml below the surface of the sample. If the viscosity is time-dependedent, use a test sample for this check. Press START button to start the motor at the chosen speed. Press the FUNCTION button until the torque, M, appears on the display. Read the torque value and check that its is above 0.5 mNm and below 9.5 mNm. Press the START button to stop the motor. (If torque is below 0.5 mNm, use a larger diameter system or higher speed. If torque is above 9.5 mNm, use a smaller diameter or lower speed.)

f) Start measurements. Lower the measuring cylinder into the sample until it is submerged about 10 ml below the surface of the sample. This will position the temperature sensor about 5 mm into the sample. Indicate the measuring system chosen with the STSTEM switch. Using the SPEED switch, indicate the rotational speed chosen. Press the START button to start the motor and the measurement.

g) Read measured data on the display by pressing FUNCTION button. Note down:

rotational speed, V (rpm)

torque, M (mNm)

For calculations use:

$$\text{Shear stress (Pa)} = C1 \times M$$

$$\text{Shear rate (1/s)} = C2 \times V$$

$$\text{Viscosity (Pas)} = \text{shear stress/shear strain}$$

Measuring system	C1	C2
1	154.7	1.207
2	27.16	1.207

3	15.72	1.207
4	154.7	0.209
5	27.16	0.209
6	15.72	0.209
7	154.7	0.255
8	27.16	0.492

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h) End measurements. Press the START button to stop the motor. If all measurements are completed, the instrument can be shut off via the ON/OFF button.

C. Molecular weight determination by gel permeation chromatography (GPC) (optional):

The GPC should be set up beforehand and ready to go. The mobile phase is 0.05 M NaNO<sub>3</sub>/0.05 M NaN<sub>3</sub> in water. The columns are Ultrahydrogel models. To run a chromatograph, do the following:

1. In a glass vial, prepare 2 ml of solution of PAM in 0.05 M NaNO<sub>3</sub>/0.05 M NaN<sub>3</sub> water with a polymer concentration of 0.003 g/ml (record actual concentration).
2. Filter the solution through 0.45 μl syringe filters into a new glass vial.
3. On the GPC LCD screen, make sure that the computer is set to “Channel A” and the plot to “Auto”.
4. Check to make sure that the GPC injector is in the “Load” position.
5. Fill the GPC syringe (about 50-100 μl) with solution, being sure to remove any air bubbles. This can be done by turning the syringe upside down and allowing any bubbles to rise to the top of the syringe. It may be necessary to tap the syringe to dislodge the bubbles. Then, while the syringe is upside down, gently push the plunger until liquid comes out the end of the needle.
6. Place the syringe in the injector and inject enough solution such that it begins to come through the overflow tube on the injector panel. It may be necessary to use more than one syringe full of solution.
7. To begin the run, switch the injector from “Load” to “Inject”. Hold the switch in the “Inject” position for approximately 10 seconds and then return it back to the “Load” position.
8. Wait for the GPC to finish the run. This should take about 20-30 minutes.
9. Clean the injection syringe with a small amount of fresh mobile phase solution.
10. After the run has finished, hit “INJ A” and a report should be printed.

**For your report:**

### Observations and Calculations:

- 1) Record the calculations for the dilutions in the lab notebook.
- 2) Tabulate the data for each run with the Ubbelohde viscometer. Use the equations in the section "Brief Background" to perform calculations.
- 3) Plot  $\frac{\eta_{sp}}{c}$  vs.  $c$  and  $\frac{1}{c} \ln \left[ \frac{\eta_c}{\eta_s} \right]$  vs.  $c$  plots to calculate the intrinsic viscosity. Indicate on each plot your synthesis conditions (% acrylamide, TEMED conc., AMPS conc.). Also calculate the Huggins constants.
- 4) Use equation 4 to calculate the molecular weight.
- 5) Tabulate the data for each run with the Couette viscometer.
- 6) Plot shear stress vs. shear rate over the range studied for each concentration. Indicate not only the concentration but also the synthesis conditions.
- 7) Then plot  $\log(\text{shear stress})$  vs.  $\log(\text{shear rate})$  and see if it can be fitted with a single slope. Does equation (9) work? If yes, what is the value of  $n$ ?
- 8) Determine viscosity for each concentration solution studied at the lowest shear rate observed and plot  $\log(\text{viscosity})$  vs.  $\log(\text{concentration})$ . Determine if there is a single slope.
- 9) (If optional GPC analysis is performed:) Compare the GPC elution time (volume) with the universal calibration plot provided to calibrate your results. Calculate the weight average molecular weight and the number average molecular weight for your PAM sample. From these, calculate the polydispersity index.

### Discussion:

- 1) Examine each of the equations in the section "Brief Background" and equation (2) of experiment 1 in light of your observations.
- 2) Are the Huggins constants reasonable?
- 3) Examine the equations and your data to suggest methods to improve the accuracy of measurement.
- 4) (For your own benefit; not needed in the report) Borrow the molecular weight (from Mark Houwink equation) and lowest shear rate viscosity data of one other group that synthesized PAM such that the expected molecular weight was different from the PAM you used. Compare viscosity results and the synthesis conditions in both cases. Does it make sense?