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Sample Lab Report  
Due Date  
Partner's Name  
TA

## **Determination of the Molecular Weight of a Polymer via Oswald Viscometry**

### **Abstract**

The flow rates of a series of dilutions of polymer solutions (Cellulose Acetate in acetone and Polyvinyl alcohol in water) were measured using an Oswald viscometer. The intrinsic viscosity solution was found and the average molecular weight of these polymers was determined. A molecular weight of cellulose acetate was determined to be  $13500 \pm 21500$  g/mol, compared to the literature value of 30,000 g/mol, and the molecular weight of polyvinyl alcohol was determined to be  $660 \pm 136000$  g/mol, compared to the literature value of 10,000 g/mol.

### **Introduction**

Viscosity is a measure of the resistance of a fluid to deformation under shear stress. It describes a fluid's internal resistance to flow and is a measure of fluid friction. Liquid viscosities can be accurately measured using a device known as the Oswald viscometer, which is a device for measuring flow times of liquids. The flow rate,  $R$ , of a liquid through the viscometer can be expressed by Poiseuille's Law.

$$R = \frac{V}{t} = \left( \frac{\pi Pr^4}{8\eta\ell} \right) \quad \text{eq. 1}$$

Here  $V$  is the volume of liquid, with a viscosity of,  $\eta$  that passes through the viscometer of radius  $r$  and length  $\ell$  in time  $t$ . The pressure,  $P$ , is constant over the time interval and is the difference in pressure between the inlet and outlet of the viscometer. (3) Equation 1 can be rewritten as:

$$\eta = \left( \frac{\pi Pr^4}{8V\ell} \right) \quad \text{eq. 2}$$

Solving this equation proves difficult. So, it is often easier to consider two different liquids, one with a known viscosity,  $\eta_1$ , and one with an unknown viscosity,  $\eta_2$ . We can take the ratio,  $\eta_1/\eta_2$ , and if we use the same viscometer, under identical conditions, the dependence on the pressure, volume, length and radius of the viscometer cancels (1):

$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2} \quad \text{eq. 3}$$

Recognizing that pressure is due to the force of gravity acting on the liquid, and is function of density, gravitational constant, and the height the equation 3 reduces to

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \quad \text{eq. 4}$$

To determine the viscosity of a polymer requires a similar manipulation. Polymers increase the viscosity of a liquid that they are dissolved in. This increase is due to entanglements of the large macromolecules as they flow along with the solvent. The magnitude of the increase in viscosity is dependant on the size and shape of the polymer. In solution, polymers or bio-molecules exist as pseudo-ordered particles, allowing them to move through the solution and yet remain approximately spherical. How spherical a molecule is depends on the molecule itself as well as the solvent in which it is dissolved. It is possible to determine the molecular weight of a polymer B,  $m_B$ , by studying its viscosity. Einstein derived a relation to explain the viscosity of spherical macromolecules (2)

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = \frac{5}{2} \left( \frac{V_B}{V} \right)$$

Here,  $\eta$  is the viscosity of the solution of macromolecules and solvent and  $\eta_0$  is the viscosity of the pure solvent.  $V$  is the total volume and  $V_B$  is the total volume of the spheres of B present. The specific viscosity,  $\eta_{sp}$ , approaches one in the limit of infinite dilution. In the limit of zero concentration, one can determine an intrinsic viscosity,  $[\eta]$ ,

$$[\eta] = \lim_{c_B \rightarrow 0} \frac{\eta_{sp} - 1}{c_B}$$

where  $c_B$  is the concentration of B in grams per unit volume and should approach 0 after a series of dilutions. Plotting  $(\ln \eta_{sp})/c_B$  vs  $c_B$  should give a straight line, and when extrapolated to  $c_B = 0$  gives a value for  $[\eta]$  (1).

Polymers have a distribution of molecular weights centered around an average mass. To calculate the average molecular weight, one uses the Mark-Houwink formula

$$[\eta] = K(M_B)^a$$

where K and a are known constants depending on the polymer, solvent and temperature (2).

To carry out this experiment, an Oswald viscometer was immersed in a warm water bath set at 25 °C. Flow rate measurements were made for a solution of cellulose acetate in acetone, a solution of polyvinyl alcohol in water, acetone and water. A series of dilutions of the polymer solution were made and the flow rates measured, until the viscometric time measurements for the solution were identical to that of the original solvent.

### Data

Cellulose acetate: 55% pure from Aldrich

Polyvinyl alcohol: 99.9% pure from Aldrich

Standard Oswald Viscometer, manufactured by Ace Glass Company.

Lauda Immersion Circulator #E-100

Grams of cellulose acetate in original solution = 0.9617 g

Grams of polyvinyl alcohol in original solution = 1.2286 g

Acetone				Water	
Trial	Time (s)	Trial	Time (s)	Trial	Time (s)
1	5.91	6	5.74	1	9.36
2	5.73	7	5.93	2	9.25
3	5.95	8	5.93	3	9.37
4	5.87	9	5.97	4	9.36
5	5.86	10	5.92	5	9.34
<b>Average</b>			<b>5.88</b>	<b>Average</b>	
				<b>9.336</b>	

Table 1. Time measurements for pure solvent

Cellulose Acetate					Polyvinyl Alcohol				
Solution	Trail	Time (s)	Mass	Density	Solution	Trial	Time (s)	Mass	Density
			Soln (g)	(g/mL)				Soln (g)	(g/mL)
Original	1	274	0.9992	0.4996	Original	1	13.3	1.989	0.9687
	2	261				2	12.9		
	3	262				3	12.8		

	4	263				4	12.8		
	5	264				5	13		
	<b>Average</b>	<b>264.80</b>				<b>Average</b>	<b>12.96</b>		
<b>A</b>	1	28.33	1.2616	0.6308	<b>A</b>	1	10.6	1.9374	0.9687
	2	27.01				2	10.6		
	3	30.01				3	10.6		
	4	26.92				4	10.6		
	5	26.98				5	10.6		
	6	27.00				<b>Average</b>	<b>10.6</b>		
	<b>Average</b>	<b>27.71</b>			<b>B</b>	1	9.5	1.966	0.983
<b>B</b>	1	11.15	1.3100	0.6550		2	9.5		
	2	11.18				3	9.5		
	3	11.17				4	9.4		
	4	11.25				5	9.6		
	<b>Average</b>	<b>11.19</b>				<b>Average</b>	<b>9.5</b>		
<b>C</b>	1	7.88	1.2575	0.6288					
	2	7.56							
	3	7.71							
	4	7.79							
	5	7.62							
	6	7.66							
	<b>Average</b>	<b>7.70</b>							
<b>D</b>	1	6.21	1.2920	0.6460					
	2	6.60							
	3	6.43							
	4	6.43							
	5	6.55							
	6	6.32							
	<b>Average</b>	<b>6.42</b>							
<b>E</b>	1	5.77	1.2878	0.6439					
	2	5.92							
	3	6.04							
	4	5.80							
	5	5.88							
	6	5.93							
	<b>Average</b>	<b>5.89</b>							

Table 2. Time Measurements for various dilutions

## Calculations

### Sample Calculation

For Cellulose Acetate:

$$\eta_1 = \frac{\rho_1 t_1}{\dots}$$

$$\eta_2 = \frac{\rho_2 t_2}{\dots}$$

$$\eta_{\text{orig}} = 8.54 \times 10^{-3} \text{ Pa sec}$$

$$\eta/\eta_0 = 28.48$$

$$\eta_{sp} = \eta/\eta_0 - 1 = 27.48$$

$c_B$  = g of solvent/100 mL of solution

When calculating  $c_B$  for cellulose acetate, the polymer used was only 55% pure. Therefore all concentrations were multiplied by 0.55 to determine the actual concentration of the polymer.

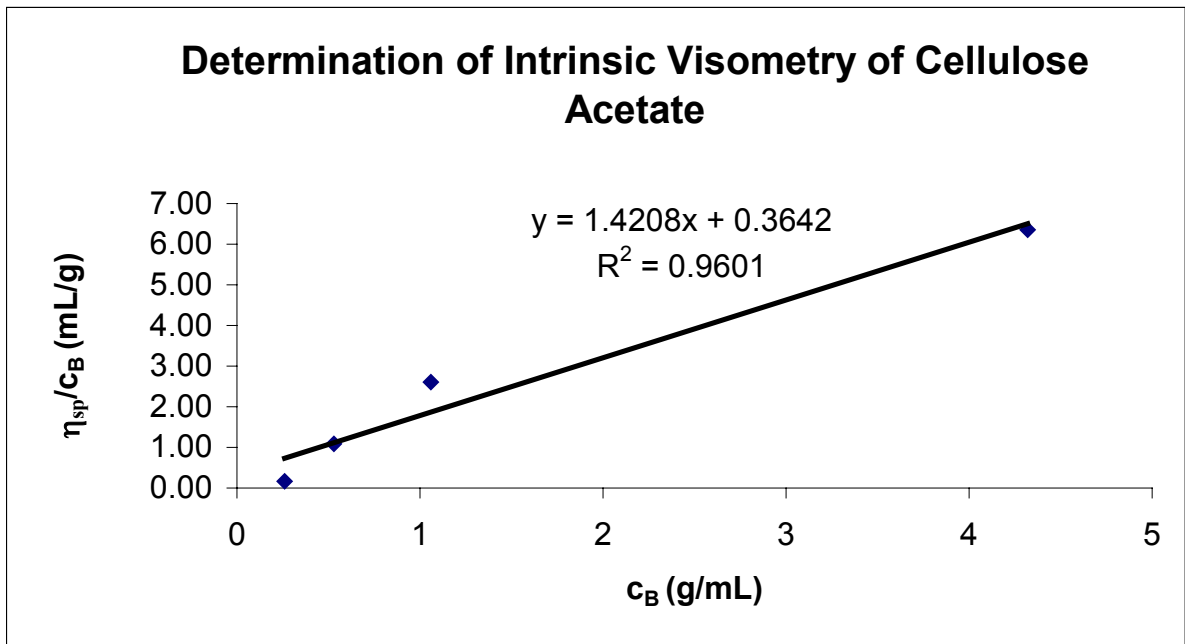


Figure 1. Determination of Intrinsic Viscometry of Cellulose Acetate. The error in slope and intercept given by Excel to be  $\pm 0.2048$  mL/g and  $\pm 0.4594$  respectively.

$$[\eta] = K(M_B)^a$$

$$0.3642 \text{ mL} = (1.49 \times 10^{-4} \text{ cm}^3/\text{g}) M_B^{0.82}$$

$$M_{\text{cellulose acetate}} = 13500 \text{ g/mol}$$

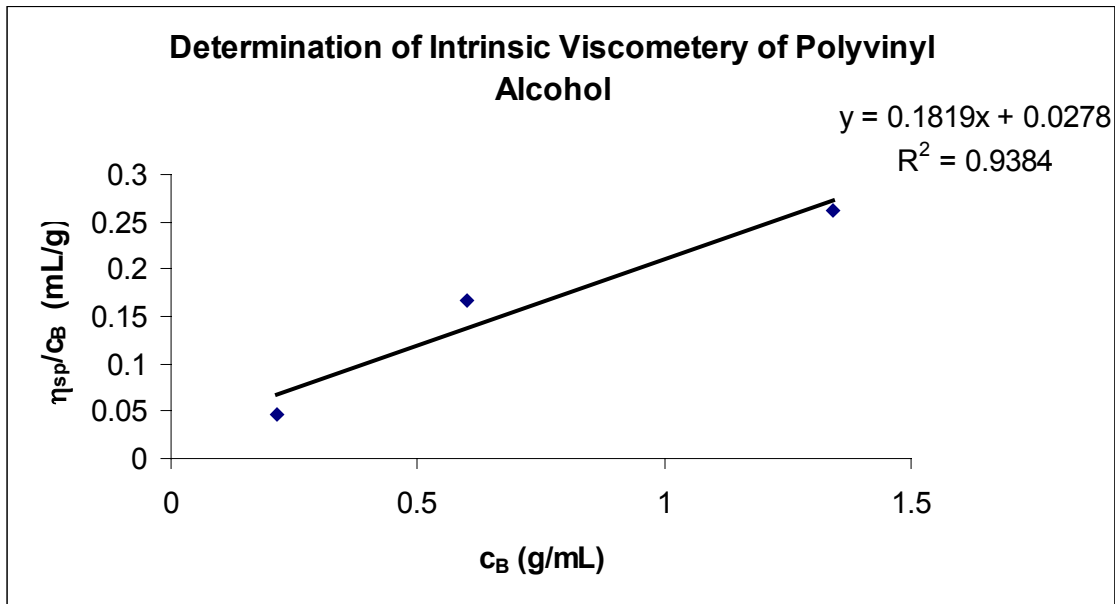


Figure 2. Determination of Intrinsic Viscometry of Polyvinyl Alcohol. The error in slope and intercept given by Excel to be  $\pm 0.03991$  mL/g and  $\pm 0.04661$  respectively.  $M_{\text{polyvinyl alcohol}} = 660 \text{ g/mol}$

For Excel Spreadsheet showing all Calculations, refer to Appendix 1.

$$\text{Percent Error (Cellulose Acetate)} = 55.0\%$$

$$\text{Percent Error (Polyvinyl Alcohol)} = 93.4\%$$

Propagation of Error

For Cellulose Acetate:

The error in the intrinsic viscosity is the error in the intercept of the lines. This can be propagated through to the molecular mass.

$$M_B = ([\eta]/K)^{(1/a)} \text{ where } K \text{ and } a \text{ are literature values for the system.}$$

$$\begin{aligned} dM_B &= (d[\eta])^2 / [\eta]^2 * M_B \\ &= [(0.4594)^2 / 0.3642^2] * 13500 \\ &= 21500 \text{ g/mol} \end{aligned}$$

For Polyvinyl Alcohol:

$$\begin{aligned} dM_B &= (d[\eta])^2 / [\eta]^2 * M_B \\ &= [(0.0399)^2 / 0.0278^2] * 660 \\ &= 136000 \text{ g/mol} \end{aligned}$$

## Results

Compound	Calculated Molecular Weight	Literature Value	Percent Error
Cellulose Acetate	$13500 \pm 21500$ g/mol	30000 g/mol (4)	55.0%
Polyvinyl Alcohol	$660 \pm 136000$ g/mol	10,000 g/mol (4)	93.4%

## Discussion

The determination of a polymer's molecular weight via Oswald viscometry did not provide accurate results. Error was minimized by allowing one partner to do all of the timing, in an attempt to eliminate this systematic error.

One possible problem could have been that the experiment was run in a constant temperature bath at 25 °C, but needed to be removed for the bath to be massed. Once on the balance, the solutions' mass was not constant, but kept increasing. This was due to the fact that the solution was warming after its removal from the water bath. In an attempt to minimize error, all measurements were taken as soon as the solution was put on the scale. However, varying the time it took to get to the scale from the time the solution was removed from the water, even by a few seconds could have drastically affected the mass of the solution. If the mass was actually less than was measured, the concentrations calculated would be too high. Lowering the concentrations would result in an intercept greater than the one calculated, thus giving a higher molecular weight.

Another problem could have been the dilutions. If they were not accurately done, this also could've affected the calculated concentrations. If calculated concentrations were too high, the end result would again be a molecular weight that would be too low. If the calculated concentrations were too low, this would have resulted in a molecular weight that would be too high.

The timing required to determine the viscosity could have been another problem. The viscosity is proportional to the ratio of the time for the polymer solution to the time for the pure solvent. If this ratio is too large, either because the time of the polymer is too

larger or the solvent's time is too low, the viscosity calculated would be too high. If the ratio is too small, the calculated viscosity would be too small.

### **Conclusion**

The determination of molecular weights of polymers using Oswald viscometry was, in this case, an inaccurate technique. Molecular weights of  $13500 \pm 21500$  g/mol and  $660 \pm 136000$  g/mol were found for cellulose acetate and polyvinyl alcohol respectively.

### **References**

- (1) Lab Handout
- (2) Shoemaker, Garland and Nibler. Experiments in Physical Chemistry, 7<sup>th</sup> edition.
- (3) Levine. Physical Chemistry, 5<sup>th</sup> edition.
- (4) [www.chemfinder.com](http://www.chemfinder.com)