Intrinsic Viscosity of Polyvinyl Alcohol

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Abstract

Using a size 150 Oswald Viscometer, the intrinsic viscosities of uncleaved and cleaved (KIO₄ treated) Polyvinyl Alcohol were determined. The intrinsic viscosity for the uncleaved polymer was calculated to be \(0.182 \pm 0.054\) cm\(^3\)/g, while the intrinsic viscosity for the cleaved polymer was \(0.06868 \pm 0.00834\) cm\(^3\)/g. Additionally, the average molar mass of the uncleaved sample was found to be \(4243 \pm 853\) g/mol and the average molar mass of the cleaved polymer was found to be \(1172 \pm 72\) g/mol. The values calculated for the uncleaved polymer were quite low, as the data collected was found to be erroneous.
I. Introduction

The goal of this experiment was to use an Oswald viscometer to calculate the viscosities of various solutions of cleaved and uncleaved Polyvinyl Alcohol (PVOH) and water. To do this, we begin with Poiseuille’s equation for flow in a cylindrical tube:

\[
\frac{dV}{dt} = \frac{\pi r^4 (p_1 - p_2)}{8\eta L} \quad (Eq. 1)
\]

To reduce this, we note that \( r \) and \( L \) are constant for the system. Additionally, the volume that flows will not change, so we can regard \( V \) as constant. We can use the following relationship for pressure:

\[
\Delta P = \rho g \Delta h \quad (Eq. 2)
\]

We can substitute this relationship into equation 1 and take \( g \) and \( \Delta h \) as constants for our viscometer. We need to leave the density variable because it is specific to the fluid in question. If we lump all our constants together into a single apparatus parameter and integrate with respect to \( t \) (from 0 to \( t \)):

\[
\frac{\eta}{\rho} = Bt \quad (Eq. 3)
\]

In this formula, \( \eta \) is the viscosity of a dilute solution, \( \rho \) is the density of the solution, \( t \) is time, and \( B \) is the apparatus constant calculated through calibration of the viscometer with a known fluid (water). This can be used to experimentally determine the viscosities of our solutions. We can also make use of the specific viscosity of the solutions:

\[
\eta_s = \frac{\eta}{\eta_0} - 1 \quad (Eq. 4)
\]

Above, \( \eta_0 \) is the viscosity of the pure solvent. By definition, intrinsic viscosity is defined as the ratio of specific viscosity to the weight concentration of the solute as concentration goes to zero. Physically, this value describes the contribution of the solute to the total viscosity of the solution and can be given mathematically by:

\[
[\eta] = \lim_{c \to 0} \frac{\eta_s}{c} = \lim_{c \to 0} \frac{\ln \left( \frac{\eta}{\eta_0} \right)}{c} \quad (Eq. 5)
\]

Plotting these against concentration and extrapolating to \( c=0 \) will give the intrinsic viscosities for the polymer samples.

Flory and Leutner also showed that the intrinsic viscosity of a polymer in solution can be related to the viscosity-average molar mass by the following empirical relationship:

\[
M_v = 76000 \times [\eta]^{1.32} \quad (Eq. 6)
\]

To calculate the average molar mass of the polymer, the gamma function is employed:

\[
\Gamma(t) = \int_0^\infty x^{t-1} e^{-x} dx \quad (Eq. 7)
\]
Flory showed that the ratio of the average-viscosity molar mass and that average molar mass ($M_n$) can be described as:

$$\frac{M_v}{M_n} = \left[\left(1 + a\right) \Gamma(1 + a)\right]^{\frac{1}{a}} \quad (Eq. 8)$$

For PVOH, the value of $a$ is .76. Therefore, the above equation reduced to:

$$\frac{M_v}{M_n} = 1.89 \quad (Eq. 9)$$

Additionally, from molar mass data from the cleaved and uncleaved polymers, the frequency of “backward” linkages can be calculated for the polymer in question. Consider a sample PVOH molecule:

![Sample PVOH molecule](image)

Figure 1. Sample PVOH molecule.

The premise of this calculation is that cleavage only occurs between 1,2-glycol structures, marked by the red bond above. Therefore, because occurrences of molecules are inversely proportional to molar mass, we can subtract the inverse molar mass of the cleaved polymer by the inverse molar mass. Then, we can divide by the total occurrences, which can be represented by the inverse molar mass of the monomer (Vinyl Alcohol, MW=44.0 g/mol), and rearrange to get the following formula:

$$\Delta = 83 \left(\frac{1}{M'_v} - \frac{1}{M_v}\right) \quad (Eq. 10)$$

II. Experimental Method

The experimental method used to collect viscosity measurements was very similar to that given by Garland et. Al in *Experiments in Physical Chemistry*\(^1\). However, slight modifications were made. Instead of preparing fresh PVOH solutions from a solid, dilutions were made using a premade 24% solution of PVOH (DuPont Elvanol 51-04). From this solution, approximately 1, 2, 3, 4, and 5 volume percent solutions were tested for the uncleaved polymer and approximately 2, 3, 4, 5, and 6 percent volume percent solutions were tested for the cleaved polymer. We conducted three trials for each solution. Additionally, the bath for the viscometer was not maintained at 25°C. Instead, the bath was assumed to have equilibrated with the room temperature. Also, a vacuum tube was used in place of a pipette bulb to draw the solution up through the viscometer. Finally, due to lack of equipment, a
Westphal balance was not used to measure the density of each solution. Instead, the densities were taken to be that of the pure solvent (water).

III. Results

After collecting the time data for all the trials, equation 3 was used to compute the viscosities for all the solutions using the averages time values. The mass concentrations for each of the solutions were computed using the density of PVOH (1.19 g/cm$^3$) as follows:

$$\frac{g}{100ml} = \frac{x \text{ ml PVOH}}{100ml} * \frac{1.19g}{1ml} \quad (Eq. 11)$$

Additionally, the specific viscosities for each solution were calculated using equation 4. The intrinsic viscosities for both solutions were then calculated by plotting both the limit quantities in equation 5 for each polymer against concentration, extrapolating to zero for each plot, and then averaging the two quantities for each polymer.

The data for this experiment were plotted and then linear regression was performed for each set of data:

![Cleaved Polymer Intrinsic Viscosity Plots](image)

Figure 2. Cleaved Polymer Plots to Determine Intrinsic Viscosity.

- Standard Error $\ln(\eta/\eta_0)/c$ versus $c$: .00541
- Standard Error $\eta_{sp}/c$ versus $c$: .01128
Figure 2. Uncleaved Polymer Plots to Determine Intrinsic Viscosity.

- Standard Error $\ln(\eta/\eta_0)/c$ versus $c$: .0288
- Standard Error $\eta_{sp}/c$ versus $c$: .0795

Extrapolating to zero for all these plots gives us the intrinsic velocity. Upon averaging the values of these for each of the polymers:

**Cleaved Polymer:** $[\eta] = .06868 \pm .00834 \text{ cm}^3/g$

**Uncleaved Polymer:** $[\eta] = .1820 \pm .0541 \text{ cm}^3/g$

We can further calculate the average molar mass for both polymers using equations 6 and 8:

**Cleaved Polymer:** $[\eta] = 4243 \pm 853 \text{ g/mol}$

**Uncleaved Polymer:** $[\eta] = 1172 \pm 72 \text{ g/mol}$

From this information, we can calculate the delta value for this sample of PVOH:

$\Delta = .05126$
IV. Discussion

From an email exchange between a DuPont chemical employee\textsuperscript{2}, the average molar mass of PVOH was determined to be 31600 g/mol. Compared to our value, we receive an 86.57% error, which is extremely high.

To propagate the error for this experiment, we notice that the average of the intercepts for the regression lines was the intrinsic viscosity. To estimate the error expected, we can use a form of the following equation:

\[
(dF)^2 = \left(\frac{dF}{dx_1}\right)^2 (dx_1)^2 + \left(\frac{dF}{dx_2}\right)^2 (dx_2)^2 + \ldots + \left(\frac{dF}{dx_n}\right)^2 (dx_n)^2 \quad (Eq.12)
\]

For this experiment, the only measurement taken was time. Therefore, the above equation becomes:

\[
(d\eta)^2 = \left(\frac{d\eta}{dt}\right)^2 (dt)^2 \quad (Eq.13)
\]

To estimate the error expected, we can create an equation to estimate the slope along each line and propagate error from that, as we can expect it to be close to the error for that of the intercept. For each polymer, we can average the errors for both to obtain the expected propagated error.

\[
\text{Cleaved Polymer: } d[\eta] = \pm 0.001007 \frac{\text{cm}^3}{g}
\]

\[
\text{Uncleaved Polymer: } d[\eta] = \pm 0.002159 \frac{\text{cm}^3}{g}
\]

In comparison with the uncertainties calculated for the intrinsic viscosities, these propagated errors are much lower than those experimentally calculated. Viscosity is a very difficult quantity to measure accurately, as the slightest change in a number of variables can affect it.

The operation of an Oswald viscometer involves measuring the time required for a fluid to flow from the upper to lower fiducial mark. Because the viscometer used in this experiment was not automated, this measurement needed to be completed by stopwatch. This introduces operator error into the experimental measurements. In order to minimize this, the size of the viscometer must be larger to require longer flow times. By lengthening time, operator error would be minimized because human reflexes required are not as important as with a smaller viscometer (shorter flow time).

Additionally, the densities of the solutions were not determined accurately. A Westphal balance could have been used to accurately determine the specific gravities of the solutions in question. From Scudiero et al\textsuperscript{3}, the density of the 24% Elvanol solution was measured to be 1.05683 g/cm\textsuperscript{3}. Therefore, assuming our solutions were equivalent to the density of water (1.00005 g/cm\textsuperscript{3} at 23.5°C) won’t give results to a high degree of accuracy.

The solutions prepared in this experiment were not created to an appreciable degree of accuracy. Instead of starting from solid PVOH and measuring out precise masses and volumes for highly accurate concentrations, the solutions made were simply estimated for the percentages PVOH required. These measurements were taken with graduated cylinders, which is far from the best piece of
equipment to use if highly accurate results were desired. A burette, if available, would have been a much better choice.

In collecting data for this experiment, the initial experiment showed less than stellar results. The cleaved data did not show a proper correlation, as the time required did not increase with increasing percentage PVOH. After retrial, this data appeared to follow the correct trend. Initially, the uncleaved data followed a correct trend, but calculations showed significant error. In an attempt to fix this, the 3, 4, and 5 percent solutions for the uncleaved polymer were redone along with the cleaved polymer solutions. Following this, analysis of the uncleaved data indicated that the 1 and 2 percent PVOH solutions may have been low, as the average molar mass was significant less than expected. This meant that the viscosities calculated were too low.

In order to more accurately determine the viscosity of PVOH, further experimentation should be done that includes more accurate solution and density determination. If this was done, the results of said experiment would be expected to be significantly improved.

V. References


Appendix I: Raw Data

Appendix II: Sample Calculations