Determination of the Intrinsic Viscosity, Average Molecular Weight, and Fraction of Unit Linkages of Poly(vinyl alcohol) via the Mark-Houwink Equation

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Running Title: *Viscosity of Polymers*

## INTRODUCTION

Polymers are commonly characterized by the molecular weight of their overall structure and the monomeric units that are combined to form them. One relatively simple method of characterizing a polymer through its molecular weight is achieved through the measurement of viscosity (detailed in the *Viscosity of Binary Solutions*). Specifically, the measurement of the viscosity of the polymer dissolved in a solution allows for the extrapolation of the Huggins constant and the intrinsic viscosity $[\eta]$, from the specific viscosity, $\eta_{sp}$ of solutions containing a varying concentration of the dissolved polymer. The specific viscosities are colligative, linearly dependent on the concentration of the polymer, allowing for the use of linear regression analysis to find the intrinsic viscosity, which is independent of the concentration of polymer.

The intrinsic viscosity of the polymer's cleaved and uncleaved forms are used in conjunction with previous experimentally determined Mark-Houwink parameters to determine the viscosity-average molecular weight of the polymer. The viscosity-average molecular weight of both the pre-cleaved and cleaved polymer is then used with the monomeric unit's molecular weight and the derived gamma functions ratio to find the numeric molecular weight.

In this experiment, we used an Ostwald viscometer to measure the viscosities of solutions of poly-(vinyl alcohol) dissolved in distilled water for varying concentrations of both the cleaved and uncleaved forms. By using a known liquid, specifically, pure distilled water, we were able to find the calibration constant of the viscometer, as the flow of the liquid follows Poiseuille's law (eq. 1). This was then used with the solutions density to find the viscosities (eq. 2). These solution viscosities were used with the solvent viscosity to find the specific viscosities that depend on the concentration of the polymer. The intrinsic viscosity of the polymer's cleaved and uncleaved form, along with the viscosity-average molecular weight, numeric molecular weight, and monomeric linkage fraction ratio were found in the data analysis, detailed in the discussion section.

## METHODOLOGY

A stock solution of 0.016 g/mL poly (vinyl-alcohol) was diluted with distilled water to prepare a 100 mL 50% (by volume) solution, which was used as the source of the uncleaved polymer. For the cleaved polymer, the same stock solution was diluted with distilled water to prepare a 100 mL 50% (by volume) solution, with the addition of 0.25 g of $KIO_4$ and heated in a temperature bath of ~70℃.

Both the cleaved and uncleaved solutions were then diluted to prepare varying concentrations, specifically 40%, 60%, and 80% (by volume) of PVOH in distilled water.

The viscometer was calibrated at 20℃ to find the calibration constant from eq. 2 by running 10 mL of pure distilled water and taking several time measurements that agreed within 0.5 seconds. 10 mL of each solution concentration for both the cleaved and uncleaved solutions were

then measured several times each for their flow times. The same video recording method from the "*Viscosity of Binary Solutions*" was employed to provide time measurements with precision to the hundredth of a second. Similarly, we also employed solution washes after each concentration was measured.

## RESULTS AND DISCUSSION

Several flow time trials were performed with distilled water at $20℃$ (denoted by 0% polymer solution). It is also worth noting that the uncleaved data was obtained from group 2, and thus they have their own respective calibration measurements and thus calibration constant. Several flow time trials were performed until the measurements agreed within 0.5 seconds (or at most 5 trials) for each concentration amounts of both the cleaved and uncleaved polymer, tabulated as follows.

| Uncleaved PVOH | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Trial 5 | Avg. |
|---|---|---|---|---|---|---|
| 80% | 20.74 | 20.84 | 20.84 | 21.09 | 21.21 | 20.94 |
| 60% | 18.61 | 18.76 | 18.76 | 18.7 | 18.24 | 18.61 |
| 40% | 15.83 | 15.7 | 15.88 | 15.75 | 15.79 | 15.79 |
| 0% | 12.38 | 12.34 | 12.36 | 12.36 | 12.44 | 12.38 |
| 100% | 23.78 | 24.03 | 24.21 | 24.08 | 24.11 | 24.04 |

TABLE 1. **Flow Time Measurements (seconds) for Varying Concentrations of Uncleaved PVOH**. Note that the 0% solution refers to the pure water calibration. Also, the 100% solution does not indicate pure PVOH, rather 10 mL of the original prepared stock solution after 50:50 dilution. This applies from all tables that follow.

| Cleaved PVOH | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Trial 5 | Avg. |
|---|---|---|---|---|---|---|
| 80% | 12.68 | 12.72 | 13.29 | 12.75 | 13.34 | 12.96 |
| 60% | 12.97 | 12.78 | 12.72 | 12.85 | 13.03 | 12.87 |
| 40% | 12.85 | 12.75 | 12.77 | 12.69 | 12.64 | 12.74 |
| 0% | 12.35 | 12.34 | 12.29 | 12.56 | 12.5 | 12.41 |
| 100% | 13.4 | 13.61 | 13.68 | 13.6 | 13.72 | 13.60 |

TABLE 2. **Flow Time Measurements (seconds) for Varying Concentrations of Cleaved PVOH**.

The measured flow times for the pure water were then used with the known reference values at $20℃$, its density, $0.9882$ $g/mL$, and its viscosity, $0.010016$ $g/cm \cdot s$, along with eq. 2, to find the calibration constants $c$ of each viscometer, both approximately $0.00081$ $cm^2/s^2$. This calibration constant was then used to convert the flow times for each concentration into the corresponding viscosities of the solutions. These solution viscosities were then used to calculate the dimensionless specific viscosities, $\eta_{sp}$ along via eq. 3.

| Uncleaved PVOH | Viscosity $\eta$ $(g/cm \cdot s)$ | Specific Viscosity $\eta_{sp}$ |
|---|---|---|
| 80% | 0.0170 | 0.6923 |
| 60% | 0.0150 | 0.5040 |
| 40% | 0.0128 | 0.2759 |
| 0% | 0.0100 | 0.0000 |
| 100% | 0.0195 | 0.9426 |

TABLE 3. **Calculated Viscosities and Specific Viscosities for Varying Concentrations of Uncleaved PVOH**.

| Cleaved PVOH | Viscosity $\eta$ $(g/cm \cdot s)$ | Specific Viscosity $\eta_{sp}$ |
|---|---|---|
| 80% | 0.0105 | 0.0441 |
| 60% | 0.0104 | 0.0372 |
| 40% | 0.0103 | 0.0268 |
| 0% | 0.0100 | 0.0000 |
| 100% | 0.0110 | 0.0962 |

TABLE 4. **Calculated Viscosities and Specific Viscosities for Varying Concentrations of Cleaved PVOH**.

The ratio of specific viscosities to the mass concentration of the PVOH in solution were then calculated and graphed vs. the mass concentrations – figure 1 and 2. By defining the intrinsic viscosity, independent of concentration, by eq. 4, we can find the intrinsic viscosities through this graph and the Huggins constant.

| Uncleaved PVOH | Mass Concentration $c_m$ $(g/mL)$ | $\eta_{sp}/c_m$ |
|---|---|---|
| 80% | 0.0064 | 108.17 |
| 60% | 0.0048 | 105.01 |
| 40% | 0.0032 | 86.205 |
| 100% | 0.0080 | 117.83 |

TABLE 5. **Calculated Specific Viscosity/Mass Concentration Ratios for Varying Concentrations of Uncleaved PVOH**.

| Cleaved PVOH | Mass Concentration $c_m$ (g/mL) | $\eta_{sp}/c_m$ |
|:---:|:---:|:---:|
| 80% | 0.0064 | 6.9008 |
| 60% | 0.0048 | 7.7571 |
| 40% | 0.0032 | 8.3615 |
| 100% | 0.0080 | 12.029 |

TABLE 6. **Calculated Specific Viscosity/Mass Concentration Ratios for Varying Concentrations of Cleaved PVOH**.
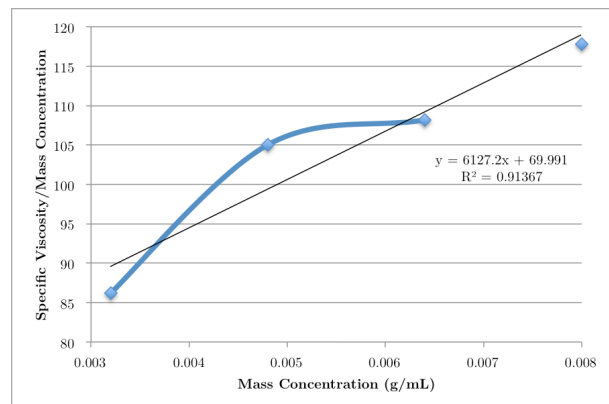


FIGURE 1. **Graph of the ratio of specific viscosities to the mass concentration vs. the mass concentration for the Uncleaved Polymer.**
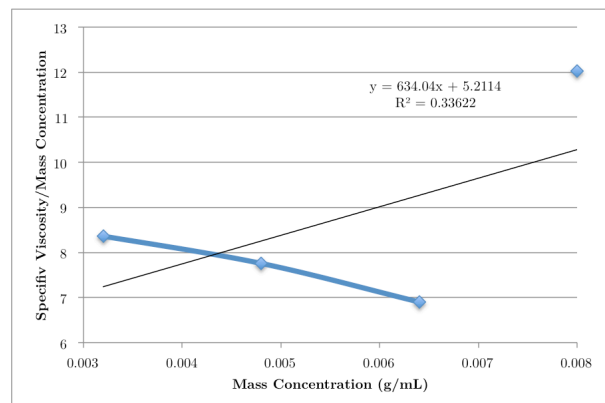


FIGURE 2. **Graph of the ratio of specific viscosities to the mass concentration vs. the mass concentration for the Cleaved Polymer.**

The graphs of figures 1 and 2 are based on equation 5 in the $y$-intercept form, $y = mx + b$, with the higher-order term neglected. We see that the slope of these curves are $k[\eta]^2$, where $k$ is the Huggins constant, and the $y$-intercepts are the intrinsic viscosities. Using a linear fit trend line and linear regression analysis, we were able to extrapolate the $y$-intercept, which is the intrinsic viscosity, or the specific viscosity at which the

concentration of the polymer approaches zero. This analysis led to the determined values of 69.99 $cm^3/g$ and 5.211 $cm^3/g$ for the intrinsic viscosities of uncleaved and cleaved PVOH respectively. In addition, we were able to find the Huggins constants for the uncleaved and cleaved solutions as 1.034 and 36.25 respectively. Compared to the standard of ~0.35 for flexible polymers in a good solvent, we can conclude either that the PVOH is not a flexible polymer (unlikely as it is a straight chain polymer with single bond linkages), or that the solvent of distilled water was not very effective at dissolving the polymer (also unlikely, as we qualitatively observed the opposite). What most likely is the cause for these large differences is experimental error. There is evidence for this, as the uncleaved PVOH measurement shows a linear decrease in specific viscosity as the concentration is increased, contrary to what we would logically expect, in which increase the concentration of the high viscosity polymer would increase the specific viscosity of the solution. The cause of the experimental error that led to this unexpected trend could be attributed to improper washes of the Ostwald viscometer, as the polymer tends to aggregate on the glassware. Another possible source of error could be improper timing, albeit unlikely, as several trials showed similar time measurements.

Using the intrinsic viscosities of the uncleaved and cleaved PVOH solutions with previously determined Markovnikov-Houwink parameters, we were able to use eq. 6 to find viscosity-average molecular weights of the polymer in both the uncleaved and cleaved form.

| $K$ $(cm^3\ g^{-1})$ | $a$ Values | Molecular Weight Ranges | $M_v$ Uncleaved | $M_v$ Cleaved |
|:---:|:---:|:---:|:---:|:---:|
| 0.020 | 0.76 | $(0.6 - 2.1) \times 10^4$ | 46044 | 1509.6 |
| 0.30 | 0.50 | $(0.9 - 17) \times 10^4$ | 54430 | 301.76 |
| 0.14 | 0.60 | $(1.0 - 7) \times 10^4$ | 31491 | 415.00 |

TABLE 7. **Viscosity-Average Molecular Weights of the Uncleaved and Uncleaved Polymers with their Corresponding Mark-Houwink Parameters.**

It should be noted that these parameters were experimentally obtained at $25℃$ , while the ambient temperature our laboratory was limited

to was $20℃$, so these calculated viscosity-average molecular weights are not as accurate as desired. However, the magnitudes match with expected values. The literature reference shows an average molecular weight of 31600 g/mol for the uncleaved PVOH, indicating that the third set of parameters gave the most accurate determination for the molecular weight. The numeric average molecular mass of the uncleaved and cleaved polymer were found to be (using the third parameter's S value) 16662 g/mol and 219.58 g/mol respectively. The magnitudes of the cleaved PVOH solutions also make sense logically, indicating that the $KIO_4$ was able to cleave the polymer into approximately 75+ separate parts, on the order of $10^2$, in contrast with the uncleaved PVOH, with magnitudes on the order of $10^4$ g/mol.

The ratio $f$ of cleaved units to the total units in the system were determined for each set of Markovnikov-Houwink parameters using eq. 7. The first set of parameters yielded an $f$ value of 0.05, while in contrast, the other two parameters yielded $f$ values of 0.26 and 0.19 respectively. Seeing as how the molecular weight is within the ranges of only the second and third parameter, the first $f$ value would not be accurate. The other two have at least the same magnitude with a percent difference of 36.8%.

**QUESTIONS & FURTHER THOUGHTS**

1.  Verification of the cited $S$ values in the appendix table using the following equation and the listed $a$ values:

$$\frac{M_v}{M_n} = S = [(1+a)\Gamma(1+a)]^{1/a}$$

    where the gamma function is given as

$$\Gamma(a) = \int_0^\infty x^{a-1}e^{-x}\,dx$$

    For the given Mark-Houwink $a$ parameters, we have the gamma function computing to the following values.

$$
\begin{array}{ccc}
a = 0.76 & a = 0.50 & a = 0.60 \\
\Gamma(1+a) \approx 0.92 & \Gamma(1+a) \approx 0.87 & \Gamma(1+a) \approx 0.89
\end{array}
$$

    Which when substituted back into the original equation along with their respective values of $a$, yield 1.89, 1.77, and 1.81 respectively, matching the values given in the text.

2.  The definition of $f$ gives us

$$f = \frac{\frac{1}{M_n^1} - \frac{1}{M_n^0}}{\frac{1}{M^0}}$$

    We can substitute in the definition of $S$ from the previous question:

$$\frac{M_v}{M_n} = S \Rightarrow M_n = \frac{M_v}{S}$$

$$f = \frac{\frac{1}{M_n^1} - \frac{1}{M_n^0}}{\frac{1}{M^0}} \Rightarrow f = \frac{\frac{S}{M_v^1} - \frac{S}{M_v^0}}{\frac{1}{M^0}} = M^0\left(\frac{S}{M_v^1} - \frac{S}{M_V^0}\right) = SM^0\left(\frac{1}{M_v^1} - \frac{1}{M_V^0}\right)$$

3.  Similar experiments to this one could be used to determine the viscosities of biopolymers, where instead of $KIO_4$ being used to cleave, varying parameters from physiological conditions such as pH or temperature. Differences in viscosities for the same given mass concentration of a biopolymer under different pH conditions, for example, would indicate cleavage and denaturation. This could further be expanded by varying the pH of the solutions in a serial method in order to quantify the exact amount of cleavage of the biopolymer using the same calculations that were performed in this experiment – finding the $f$ values will quantify this.

4.  The assumption that PVOH polymers act as spherical molecules when determining the specific and intrinsic viscosities is a relatively good one. The polar hydroxyl moiety of the monomeric units of PVOH, along with the flexibility granted by the polymeric linkages being single bonds, the PVOH should conform to a spherical-like glob in a polar solvent – water, with a clathrate structure forming around due to polar interactions. A macromolecule that does not conform to a spherical shape would be $\beta$ proteins, which would form their secondary structures as $\beta$ sheets, providing difficulty conforming to a tertiary globular structure.

5.  In the vapor phase, the structure of a polymer such as PVOH would not be spherical as described in the previous question in which it was in an aqueous solution. Rather, the vapor phase PVOH molecules would most likely be extended out in random directions, with constant rotation around the polymeric linkages due to the high-energy state.

6. Given a measured intrinsic viscosity of $86 \, \text{cm}^3/\text{g}$ at $25°\text{C}$, and using the Mark-Houwink parameters listed in the appendix table, along with the Mark-Houwink equation below, we can report the following range of molecular weights for the polymer.

$$[\eta] = KM^a \Rightarrow M = \sqrt[a]{\frac{[\eta]}{K}}$$

$$\sqrt[0.76]{\frac{86}{0.02}} = 60378.11$$

$$\sqrt[0.50]{\frac{86}{0.30}} = 82177.78$$

$$\sqrt[0.60]{\frac{86}{0.14}} = 44389.89$$

Average Molecular Weight Range: $(4.4 \text{ to } 6.1) \times 10^4$ g/mol.

## REFERENCES

- Atkins, P. and De Paula, J. *Physical Chemistry: Thermodynamics, Structure, and Change*, 9th ed. W. H. Freeman, Oxford University Press, 2010; p 687 – 686.
- Halpern, A. and McBane, G. *Experimental Physical Chemistry: A Laboratory Textbook*, 3rd ed. W. H. Freeman, 2006; p 493 – 504.
- Viscopedia - A free encyclopedia for viscosity. http://www.viscopedia.com/viscosity-tables/substances/, (accessed Apr 04, 2017).

## APPENDIX – EQUATIONS

All calculated values from the discussion and result section were determined using the following equations.

$$\frac{dV}{dt} = \frac{\pi r^4 \Delta P}{8 \eta L}$$

eq. 1

Poiseuille's Law, where $dV/dt$ is the volume flow rate of the liquid emerging from the tube, $r$ and $L$ are, respectively the radius and length of the tube in the Ostwald viscometer, $\Delta P$ is the pressure difference, and $\eta$ is the viscosity coefficient.

$$\eta = \frac{\pi r^4 g}{8V} \rho t = c \rho t$$

eq. 2

The viscosity $\eta$, of a solution based on the calibration constant $c$ of the viscometer, the solutions density $\rho$ and the ambient temperature $t$.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

eq. 3

The specific viscosity, based on the viscosity of the solution and the viscosity of the pure solvent, $\eta_0$.

$$[\eta] = \lim_{c_m \to 0} \left( \frac{\eta_{sp}}{c_m} \right)$$

eq. 4

The intrinsic viscosity $[\eta]$, based on the specific viscosity and the mass concentration $c_m$.

$$\frac{\eta_{sp}}{c_m} = [\eta] + k[\eta]^2 c^m + k' c_m^2$$

eq. 5

The concentration dependence of the specific viscosity, $k$ is the Huggins constant.

$$M_v = \left( \frac{1}{K} \right)^{1/a} [\eta]^{1/a}$$

eq. 6

The viscosity-average molecular weight $M_v$, based on Markovnikov-Houwink parameters $a$ and $K$.

$$f = SM^0 \left( \frac{1}{M_v^1} - \frac{1}{M_v^0} \right)$$

eq. 7

The ratio $f$ of cleaved units to the total units in the system. The $S$ values are based on the Mark-Houwink parameters used to determine the $M_v$ values. $M_v^1$ for the cleaved polymer and $M_v^0$ for the uncleaved polymer.

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**APPENDIX – REFERENCE VALUES**

**Reference Values (at 25℃)**

| $K$ (cm$^3$ g$^{-1}$) | $a$ Values | Molecular Weight Ranges | S Values |
|:---:|:---:|:---:|:---:|
| 0.020 | 0.76 | $(0.6 - 2.1) \times 10^4$ | 1.89 |
| 0.30 | 0.50 | $(0.9 - 17) \times 10^4$ | 1.77 |
| 0.14 | 0.60 | $(1.0 - 7) \times 10^4$ | 1.81 |