

Transport Properties and Chemical Kinetics: Viscosity of Liquids Part 1: Low Viscosities

and

Polymers:

Molecular Weight and Monomer Linkage

Properties of Poly(vinyl alcohol)

CHEM 357 – Section 2

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Introduction and Objective

The objective of this experiment is to measure and analyze the viscosities of ideal (toluene/p-xylene) and non-ideal (methanol/water) binary solutions and their components. In addition, the principles of viscosities will be applied to determine the viscosity-average molecular weight of poly(vinyl alcohol) (PVOH) and the fraction of “head-to-head” monomer linkages in the polymer. Viscosity is a useful property to study because it can be used to define and then later identify highly complex mixtures and fluid systems, to which it may be difficult to assign other properties (i.e. density, melting point). Assigning specific mixtures with desired qualities a standard viscosity allows for quality control measures in the industrial context when manufacturing, oils, resins, and paints for example. Defining the viscosity of a mixture also allows for the determination of the rate of mass transport within the mixture. This in turn allows for the analysis and manipulation of reaction kinetics within fluids of different viscosities. (Chem 357 Manual)

Experimental Procedure

An Ostwald viscometer was used in this experiment. This apparatus is used to track the amount of time it takes for a volume of fluid to flow between the upper and lower fiducial marks on the viscometer body. By calibrating the viscometer to a liquid of known viscosity, like water, the viscosities of other fluids and mixtures can be determined. For the first experiment, several solutions were made with varying ratios of methanol to water (20% methanol by volume, 40%, 60%, 80%, and 100%) and of toluene to p-xylene (100% toluene by volume, 80%, 60%, 40%, 20%, and 0%). First the viscometer was calibrated with water. The viscometer was filled with 10 mL of water and the amount of time it took for the meniscus to pass from the upper fiducial mark to the lower mark was recorded. This measurement was repeated several times. Next, this same procedure was repeated for each mixture created (each time with 10 mL of solution), recording several measurements for each sample and thoroughly cleaning the viscometer between each run with a few mL of the solution from the next trial.

For the polymer experiment, it was necessary to first create a 100 mL stock solution of 50% PVOH. Next another stock solution of cleaved polymer was created by combining half the PVOH stock with KIO_4 and heating to dissolve the solid. From each the uncleaved and cleaved stock solutions, 80, 60, 40, and 20% solutions were created. Next, the viscometer was once again calibrated with water, since this experiment was done on a different day than the first experiment. Then, starting from the most dilute uncleaved sample, the times to move from the upper to lower fiducial marks were recorded; several trials were conducted for each sample. Finally, this procedure was repeated for the cleaved polymer samples. The timed runs were all conducted at room temperature, 25°C.

Results

Viscosity

The repeated runs for each sample were averaged, to give one value for the flow time, t . Knowing the viscosity, η , and density, ρ , of water, as well as the experimental flow time from water (from the calibration), t , it was possible to find the value of the constant, k , which takes into consideration the physical characteristics of the viscometer. Viscosity is related to these variables as represented in the equation below:

$$\eta = k\rho t \text{ (Equation 9, p. 299)}$$

For the specific viscometer used in the experiment, k was determined to be 0.011. Now, knowing the value of k , the densities of each solution (from the appendices in the manual), and the average flow time, t , for each solution, it was possible to determine the viscosity of each solution. In addition to viscosity, the fluidity, F , of each solution was determined by taking the reciprocal of the viscosity. Next, the fluidities of the pure liquids, denoted by the symbol F^* , (pure water and methanol for the water/methanol system and pure toluene and p-xylene for the toluene/p-xylene system) were used, along with the mole fraction of each liquid in each solution (determined from the volume of each liquid) to determine the fluidity of the mixture according to equation 4 in the manual (297) shown below:

$$F \cong x_A F_A^* + x_B F_B^*$$

In addition, the viscosities of the mixtures were calculated from the viscosities of the pure liquids, denoted by the symbol, η^* , and the mole fractions of each pure liquid in the mixture, as proposed by Kendall, and represented by equation 6 in the manual (297) shown below:

$$\ln \eta = x_A \ln \eta_A^* + x_B \ln \eta_B^*$$

The results are summarized in the table below:

	20% MeOH	40% MeOH	60% MeOH	80% MeOH
η, viscosity (P)	0.0126	0.0140	0.0137	0.0105
F, fluidity (P⁻¹)	79.4	71.3	72.9	95.5
F, by Eqn. 4	120	129	141	159
η, by Eqn. 6	0.00846	0.00793	0.00729	0.00647

Table 1: Experimental viscosity and fluidity data for the methanol/water system.

	100% Toluene	80% Toluene	60% Toluene	40% Toluene	20% Toluene	0% Toluene
η, viscosity (P)	0.00676	0.00685	0.00685	0.00688	0.00707	0.00708
F, fluidity (P⁻¹)	147.9	145.9	146.0	145.4	141.4	141.2
F, by Eqn. 4	147.9	146.7	145.4	144.1	142.7	141.2
η, by Eqn. 6	0.00676	0.00682	0.00688	0.00694	0.00701	0.00708

Table 2: Experimental viscosity and fluidity data for the toluene/p-xylene system.

Polymers

The viscometer was calibrated to water (as described in the section above). The density of the polymer was assumed to be the same as that of water. Knowing the characteristics of the viscometer from the water calibration and summarized in the constant c , the density, ρ , of each samples, and the average flow time, t , for each dilution, it was possible to calculate the viscosity of each sample according to the following equation

$$\eta = c \rho t \text{ (Equation 3, pg. 494)}$$

The specific viscosity, η_{sp} , was determined according the following equation, where η_0 is the viscosity of pure water

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \text{ (Equation 4, pg. 494)}$$

The mass concentration, c_m , for each dilution was determined based on the given concentration of the stock solution $c_m = 0.016 \text{ g mL}^{-1}$ and the percentage dilution of each sample. Using the η_{sp} and c_m it was

possible to determine the intrinsic viscosity, $[\eta]$ of the uncleaved and cleaved polymer. The data is summarized in Table 3 and Table 4 below.

UNCLEAVED	40%	30%	20%	10%
η , viscosity (P)	0.0130	0.0117	0.0111	0.00955
η_{sp}	0.461	0.319	0.242	0.0734
c_m (g mL ⁻¹)	0.0064	0.0048	0.0032	0.0016
η_{sp} / c_m	72.0	66.4	75.5	45.8

Table 3: Viscosity, specific viscosity, and mass concentration of uncleaved polymer solutions.

CLEAVED with KIO ₄	40%	30%	20%	10%
η , viscosity (P)	0.00928	0.00897	0.00892	0.0089
η_{sp}	0.0425	0.00772	0.00193	1.95E-16
c_m	0.0064	0.0048	0.0032	0.0016
η_{sp} / c_m	6.64	1.61	0.603	1.22E-13

Table 4: Viscosity, specific viscosity, and mass concentration of cleaved polymer solutions.

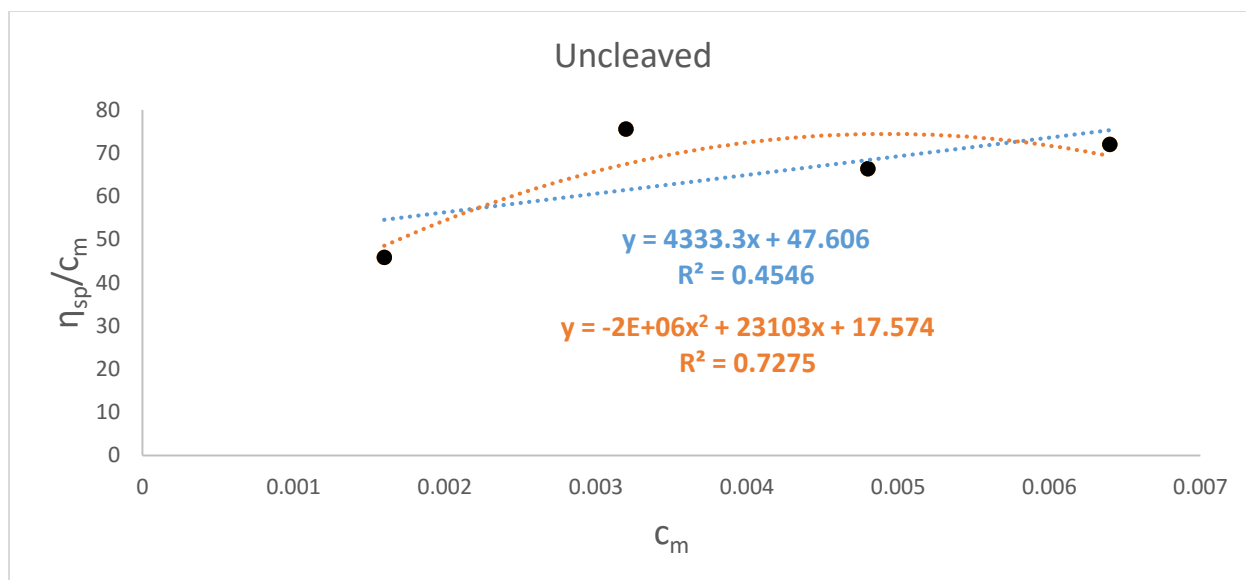
The following equation defines the intrinsic viscosity which is a property that is inherent to a given polymer, independent of the concentration.

$$[\eta] = \lim_{c_m \rightarrow 0} \left(\frac{\eta_{sp}}{c_m} \right) \text{ (Equation 7, pg. 495)}$$

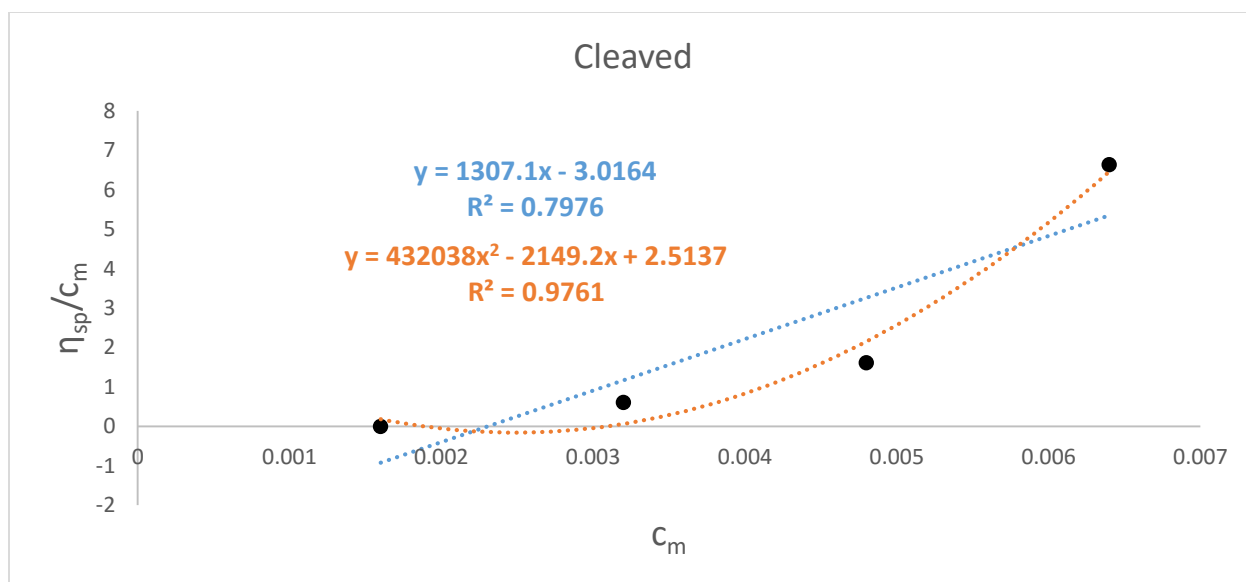
The reduced specific viscosity (η_{sp}/c_m), however, is dependent on the polymer concentration, thus plotting η_{sp}/c_m versus c_m could reveal this dependence. The terms are related by the equation below

$$\frac{\eta_{sp}}{c_m} = [\eta] + k[\eta]^2 c_m + k' c_m^2 \text{ (Equation 8, pg. 495)}$$

The lab manual states that the quadratic term can often be ignored, reducing the equation to a linear relationship. The plots of η_{sp}/c_m vs. c_m were fit with both quadratic (keeping the second order term, $k'c_m^2$) and linear (ignoring it) equations to determine $[\eta]$ and k , which is known as the Huggins constant. Graph 1 and Graph 2 below show these plots along with the best-fit lines. Table 5 below summarizes the values found for the intrinsic viscosity and Huggins constant based on each type of fit, for both the uncleaved and cleaved polymers.



Graph 1: The reduced specific viscosity, η_{sp}/c_m , plotted against mass concentration, c_m , to determine intrinsic viscosity, $[\eta]$ and the Huggins constant, k as shown by Equation 8 in the lab manual. The plot was fit with both linear and polynomial approximations. Since this data is for the cleaved polymer, the intrinsic viscosity is denoted as $[\eta]^0$ and the Huggins constant is denoted k^0 in Table 6 below to denote the values pre-cleavage.



Graph 2: The reduced specific viscosity, η_{sp}/c_m , plotted against mass concentration, c_m , to determine intrinsic viscosity, $[\eta]$ and the Huggins constant, k as shown by Equation 8 in the lab manual. The plot was fit with both linear and polynomial approximations. Since this data is for the cleaved polymer, the intrinsic viscosity is denoted as $[\eta]'$ and the Huggins constant is denoted k' in Table 6 below to denote the values post-cleavage.

Linear Fit		Polynomial Fit	
$[\eta]^0$ ($\text{cm}^3 \text{g}^{-1}$)	47.6	$[\eta]^0$	17.6
Huggins Constant, k^0	1.91	Huggins Constant, k^0	74.8
$[\eta]'$	-3.07	$[\eta]'$	2.51
Huggins Constant, k'	144	Huggins Constant, k'	-340

Table 5: Intrinsic viscosities and Huggins constants determined for both uncleaved and cleaved polymer using both linear and polynomial best-fit lines from Graph 3 and Graph 4 above.

	Linear fit				Polynomial Fit			
K = 0.02, a = 0.76, S = 1.89	M_n^0	14700	M_n'	---	M_n^0	3950	M_n'	306
	M_v^0	27700	M_v'	---	M_v^0	7470	M_v'	578
	f				f			
K = 0.3, a = 0.5, S = 1.77	M_n^0	14200	M_n'	57.1	M_n^0	1940	M_n'	39.7
	M_v^0	25200	M_v'	101	M_v^0	3430	M_v'	70.2
	f				f			
K = 0.14, a = 0.6, S = 1.81	M_n^0	9150	M_n'	---	M_n^0	1740	M_n'	68.0
	M_v^0	16600	M_v'	---	M_v^0	3150	M_v'	123
	f				f			

Table 6: The viscosity-average molecular weights and the number-average molecular weights for uncleaved (M_v^0 and M_n^0) and cleaved (M_v' and M_n') polymer, as well as the head-to-head fraction, f , determined from three sets of Mark-Houwink parameters previously determined for PVOH (given on pg. 498 of the lab manual).

Discussion

Polymers

For all plots, the polynomial best-fit lines had better R^2 values, so the values determined from those equations will be discussed. The intrinsic viscosity data in Table 5 looks like it makes sense, at least in relative numbers, if not absolute values. The viscosity pre-cleavage is $17.6 \text{ cm}^3 \text{ g}^{-1}$ and the viscosity post-cleavage is $2.51 \text{ cm}^3 \text{ g}^{-1}$, indicating that as the polymer was cleaved, the viscosity of the solution was decreasing and approaching that of the solvent, as was expected. The lab manual states that the intrinsic viscosity of polydisperse PVOH was determined to be $86 \text{ cm}^3 \text{ g}^{-1}$ (pg. 503) they do not give a source for this data or indicate this was a theoretical value, but assuming this is reliable data, then the intrinsic viscosities determined in this experiment are at least in the same order of magnitude as this value. The Huggins constants determined do not match the typical values reported in the manual of 0.35 to ~ 2 (pg. 495), although the viscosities determined and shown in Table 3 and Table 4 do fall into the typical range of 0.002 to 0.04 P reported in the manual (pg. 296), meaning that perhaps it is not the collected data causing the discrepancy in k values, but maybe the chosen best-fit curves or the need for a broader set of data to create more distinct trends.

The viscosity average molecular weights of the polymer were determined pre- and post-cleavage to have a range of values depending on which pair of Mark-Houwink parameters for K and a were used. Variation was also found in the fraction of head-to-head linkages in the polymer depending on which constants were used. For $K = 0.02$ and $a = 0.76$, $M_v^0 = 7470 \text{ u}$ and $M_v' = 578 \text{ u}$, and $f = 0.133$. For $K = 0.3$ and $a = 0.5$, $M_v^0 = 3430 \text{ u}$ and $M_v' = 70.2 \text{ u}$, $f = 1.09$. For $K = 0.14$ and $a = 0.6$, $M_v^0 = 3150 \text{ u}$ and $M_v' = 123 \text{ u}$, $f = 0.622$. The first set of parameters produces values that are significantly different from the second and third set. Thus comparing the second and third set, the molecular weight of the uncleaved polymer is around 3290 u and the cleaved polymer is about 97 u . Given that the molecular weight of one monomer unit is 44 u , the results show that the KIO_4 cleaves the polymer into short sections, two to three monomer units long. Thus the 1,2-diol structures are found every two to three units along the polymer. This ratio is reflected best by the last set of parameters which produces a head-to-head fraction of 0.622.

Questions and Further Thoughts

- Is it possible to have a homogenous binary liquid solutions whose viscosity is higher (or lower) than that of either of the two component liquids?

Theoretically it should be possible for a solution of two liquids to have a higher or lower viscosity than either of the component liquids. Since viscosity is a quantitative measure of how difficult it is for molecules to move past each other in a fluid, it is a measure of the intermolecular forces between the particles that make up that fluid. Thus if the intermolecular forces between the two component liquids in a mixture are stronger than those between the molecules in each individual mixture, the mixture will be more viscous than either of the components. Similarly, if the two component liquids are miscible but do not interact as strongly with each other as they do with themselves, the resulting mixture will be less viscous.

- *Using the definition of f , derive equation (18) and use the result in (17) to obtain (19).*

The ratio f is defined as the increase in the number of solute molecules in solution after treatment with KIO_4 divided by the total number of monomer units represented in a polymer sample; this equal to the ratio of 1,2-diol structures to the total 1,2-diol and 1,3-diol arrangements in the system

- *What experiments could be carried out on proteins and other biopolymers to examine the effect of solution conditions on the extent of denaturation?*

It is expected that the more a protein is denatured, the more viscous the solution becomes. This is because the protein structure becomes more linear and loosely packed as the tertiary and quaternary protein structures are lost. The denaturation may cause individual protein molecules to aggregate with each other leading to the increase in viscosity. The paper cited in the references section below has found that the denaturation of a protein is accompanied with an increase in viscosity even in solutions in which the proteins do not aggregate (although the aggregation of these proteins causes an even greater increase in viscosity). The authors of the paper suggest that the increase in viscosity is due to the increase in “hydration” of each protein molecule as the molecule is denatured. Thus, the extent of denaturation of a protein could be determined using a viscometer to track the change in viscosity in different samples of protein that are denatured to different extents.

- *If the intrinsic viscosity of PVOH in water was determined to be $86 \text{ cm}^3 \text{ g}^{-1}$ at 298 K, what range of molecular weights can be reported for the polymer?*

The Mark-Houwink equation tell us that

$$[\eta] = KM^a$$

This equation can be rearranged as follows

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

allowing us to solve for the molecular weight from the intrinsic viscosity if the values for K and a are known. With $K = 0.02$ and $a = 0.76$, $M_v = 60378 \text{ g/mol}$; with $K = 0.30$ and $a = 0.50$, $M_v = 82178 \text{ g/mol}$; with $K = 0.14$ and $a = 0.60$, $M_v = 44390 \text{ g/mol}$. Thus, the range of molecular weights for this polymer is approximately 44400 – 82200 g/mol.

Conclusion

It was shown that it is possible to use viscosity measurements to determine the molecular weight of a polymer in solution. Pairs of Mark-Houwink parameters determined in previous studies were used to accomplish the transformation of data from run-time viscometer results of uncleaved versus cleaved polymer into the molecular weight of the polymer. Some results were consistent with the expected

values, while others were not. In order to get more conclusive results, it is suggested that the experiment be performed with a greater number of dilutions to reveal more distinct trends, allowing for the more accurate determination of intrinsic viscosity and therefore the molecular weight of PVOH.

References

Chemistry 357 Laboratory Manual

<http://www.viscopedia.com/viscosity-tables/substances/methanol/>

<http://www.viscopedia.com/viscosity-tables/substances/water/>

<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2141169/pdf/341.pdf>