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| Experiment 6: Intrinsic Viscosity |
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# Abstract

This experiment aims to use the property of intrinsic viscosity to determine molecular weight of the polystyrene polymer and the affinity of the polymer to the solvents toluene and cyclohexane. Solutions of 0.2, 0.15, 0.1, and 0.05% polystyrene in the two different solvents were created, for a total of eight solutions. Using Ostwald’s viscometer in a heated water bath, flow rates for each solution and the pure solvents were measured with a stopwatch. The specific viscosity was calculated, and a plot of concentration against specific viscosity divided by concentration yielded the intrinsic viscosity by plotting a best-fit line and taking the y-intercept. The subsequent calculations with given constants in the Mark-Houwink equation yielded calculated molecular weights of 338 kg/mol and 287 kg/mol for polystyrene in toluene and cyclohexane solution, respectively, compared to the actual value of 260 kg/mol. Furthermore, Einstein’s formula for spherical rigid particles yielded a hydrodynamic volume of the polymer of 2.52E-17 mL/g and 8.37E-18 mL/g for the toluene and cyclohexane solvents, respectively. The larger volume in toluene suggests that toluene is the better solvent, also supported by a quick analysis of their chemical structures.

# Introduction

Intrinsic viscosity is a method widely used for characterizing macromolecules in solution, more specifically, determining the molecular weight of polymers. This is because intrinsic viscosity, denoted as , follows the Mark-Houwink equation, seen below in Equation 1.

Equation : Mark-Houwink Equation

Where M is the molecular weight, and K and a are specific to a given polymer in a given solvent at a given temperature. They can be defined with standards of molecular weight and are often tabulated in handbooks. Once these constants are known, finding the intrinsic viscosity can help estimate the molecular weight of a polymer.

Furthermore, polymers tend to exist in solution as a coil. The length of this coil is dependent on the affinity of the polymer to the solvent: if the solvent is undesirable, the polymer will tend to stick to itself instead of the solvent, shortening the coil. If the solvent is desirable, the coil will stick to the solvent more, stretching the coil out. Thus, this method of intrinsic viscosity can distinguish between good and poor solvents for a certain polymer.

In this experiment, an Ostwald’s viscometer, shown in figure 1, will be used to determine the amount of time that a liquid takes to flow a fixed distance at a fixed temperature. By measuring the time it takes for a liquid to pass from the starting mark to the ending mark, and using the equation seen in Equation 2, a relationship between viscosity and time can be established.

Diagram, schematic

Description automatically generated

Figure : Ostwald's Viscometer

Equation : Relationship Between Viscosity and Flow Time

Where is the density of the solution and B is the constant specific to the Ostwald’s viscometer. As these two values are effectively constant, a new relationship can be set up, as seen in Equation 3.

Equation : Calculation of Intrinsic Viscosity

Where t is the flow time of the solution and t0 is the flow time of the pure solvent. Finally, subtracting 1 from this ratio yields the specific viscosity, and dividing specific viscosity by concentration and plotting the best fit line will yield the intrinsic viscosity when the concentration is zero, at the y-intercept.

Another application of the intrinsic viscosity is the determination of the hydrodynamic volume by Einstein’s formula for rigid spherical particles, as seen in equation 4.

Equation : Einstein's Formula for Rigid Spherical Particles

Where NA is Avogadro’s number, M is the molecular weight of the polymer, and vH is the hydrodynamic volume.

# Experimental

To begin the experiment, the water in the container was heated to 30°C. Then, solutions of polystyrene with concentrations of 0.2%, 0.15%, 0.10%, 0.05% in toluene and cyclohexane were prepared, for a total of eight solutions. These solutions were created by diluting a stock solution of 0.2% polystyrene in toluene and cyclohexane solvents.

To begin, the viscosity of pure toluene was measured with the Ostwald’s viscometer. To do so, the viscometer was filled with about 20 mL of sample solution until about half of the large cavity was filled. The tube was then placed into the water bath with a clamp to reach equilibrium.

Once equilibrium was reached, the left side of the tube (refer to figure 1) was plugged with a finger while a pipetting ball was used on the right side to draw suction and pull the liquid over the start mark. When the finger was released, the timer was started when the liquid passed the start mark and stopped when the liquid passed the stop mark. This was repeated three times to obtain an average. This was repeated for increasing concentrations of polystyrene in toluene solutions.

Before doing the experiment for cyclohexane and its solutions, the tube was rinsed with pure toluene twice and pure cyclohexane twice. The bath was also heated up to 34°C, and began with pure cyclohexane and increasing concentrations of polystyrene.

# Results

The time was recorded with human input into a stopwatch, started when the fluid level was observed to be crossing the start line in the Ostwald’s viscometer and stopped when the fluid level reached the end line of the viscometer. The three trials for each concentration were averaged out. The table for the toluene solvent is shown in figure 2. One notable trend is the consistent increase of time elapsed as the concentration of polystyrene increases.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| % | Concentration (g/cm^3) | time 1 | time 2 | time 3 | avg. |
| 0.2 | 0.002 | 9.66 | 9.44 | 9.55 | 9.55 |
| 0.15 | 0.0015 | 9.60 | 9.06 | 9.28 | 9.31 |
| 0.1 | 0.001 | 9.03 | 9.02 | 8.95 | 9.00 |
| 0.05 | 0.0005 | 8.39 | 8.49 | 8.44 | 8.44 |
| pure toluene | | 7.98 | 8.08 | 8.06 | 8.04 |

Figure : Flow Times for Different Concentrations of Polystyrene in Toluene

For each trial, the ratio on the right side of equation 3 was calculated, and 1 was subtracted to find the specific viscosity. Finally, that value was divided by the concentration in g/mL and plotted to find the intrinsic viscosity using the y-intercept of a best fit line. The sample calculations for toluene solvent are attached below in figure 3, as well as both plots in figures 4 and 5.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| % | concentration | t/t0 | t/t0 - 1 | nsp / c |
| 0.2 | 0.002 | 1.187810945 | 0.18781095 | 93.9054726 |
| 0.15 | 0.0015 | 1.158374793 | 0.15837479 | 105.583195 |
| 0.1 | 0.001 | 1.119402985 | 0.11940299 | 119.402985 |
| 0.05 | 0.0005 | 1.049751244 | 0.04975124 | 99.5024876 |
| pure toluene | |  |  |  |

Figure : Specific Viscosity Calculations for Polystyrene in Toluene

Figure : Specific Viscosity Plot for Polystyrene in Toluene

Figure : Specific Viscosity Plot for Polystyrene in Cyclohexane

Finally, these intrinsic viscosity values were plugged into equation 1 with constants of 0.011 mL/g and 0.725 for the values of K and a for toluene and 0.082 mL/g and 0.5 for K and a for cyclohexane. This yielded a value of 338 kg/mol for the polymer in toluene and 287 kg/mol for the polymer in cyclohexane. Finally, plugging into Einstein’s equation for hydrodynamic volume, the value of 2.52E-17 mL/g was obtained for the toluene solvent and 8.37E-18 mL/g for the cyclohexane solvent.

# Discussion

The actual value of the molar mass of the polymer, as seen on the manufactured bottle, was 260 kg/mol. Although the overall error is small, the human factor in this experiment is the source for a lot of error. The flow time of the fluids were measured with a human controlling a stopwatch, using naked vision to determine when the fluid passes the start and stop lines in the viscometer. This likely caused the molecular weight to inflate, as a longer measured time would lead to a larger value for t/t0, which would increase the nsp and increase the values found on the plot. However, given all the possible sources for human error, these values are notably close to the actual value stated by the manufacturer.

The hydrodynamic volume of the polymers in solution are noticeably different, as the polystyrene in toluene takes up approximately three times the volume of the polystyrene in cyclohexane. This provides some information regarding the interactions of the polymers in the two different solvents. Referring back to the coil illustration in the introduction, the hydrodynamic volume provides information about the affinity of the solvent for the solute. As poor solvents will not allow the solute polymer to stretch out, and it will tend to interact with itself, it will form a ball shape, taking up little hydrodynamic volume. This is opposed to a good solvent, where the polymer will stretch out and occupy more volume.

Given this notion, we experimentally find that toluene seems to be a better solvent for polystyrene than cyclohexane, as the hydrodynamic volume is so much larger. This is supported by a quick analysis of the structures of each of the molecules and the intramolecular forces they would experience. Each structure is seen below in figure 6.

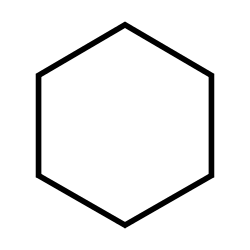
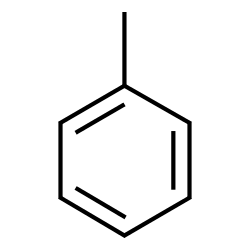
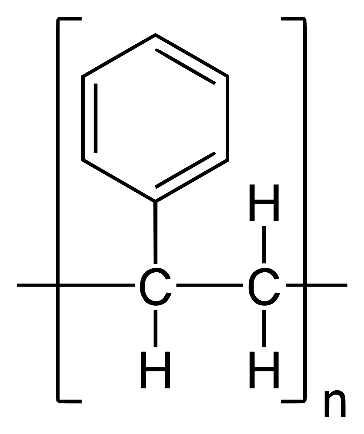


Figure : Structures of Polystyrene, Toluene, and Cyclohexane (left to right)

Given these figures, the ability for the benzene rings in polystyrene and toluene to distribute charge makes these two molecules more polarizable than cyclohexane, which does not allow the distribution of charge through a conjugated pi system. Thus, the London dispersion forces of the polystyrene and toluene are stronger and more similar and are able to interact with each other. Polystyrene in cyclohexane, on the other hand, is more likely to interact with its own benzene rings than the solvent, and thus, tend to not stretch the coils in solution.

# Appendix

1. Datasheet for Experimental Data 