CHEM 360 L

EXPERIMENT 10

The Viscosity of a Polymer Solution

Introduction

This experiment demonstrates the measurement of molecular weight. The viscosity of solutions of macromolecules arises from the entanglement of large molecules in the flowing solvent. One would expect this effect to depend on the size and shape of the solute molecules. The molecular weight has an obvious effect on the size of the molecule, but the nature of the solvent-solute interaction will affect both the size and the shape. The coefficient of viscosity, η, relates the frictional force resisting flow to the pressure head (P), the tube radius (r), the tube length (l), and the flow rate (R):

$$\eta = \frac{\pi \mathrm{Pr}^4}{8Rl}$$

In this experiment, the viscosity is determined by comparing the flow time with that of a solvent of known viscosity:

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

where ρ_1 and ρ_2 are the densities of the two solutions. The **specific viscosity**, η_{sp}, is defined as:

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

(where η_0 is the viscosity of the pure solvent) and was shown by Einstein to be equal to 2.5 times the fractional volume occupied by the (assumed to be large and spherical) macromolecules. The **intrinsic viscosity**, $[\eta]$, is the property indicative of molecular size and shape:

$$[\eta] = \lim_{(c \to 0)} \frac{\eta_{sp}}{c} = \lim_{(c \to 0)} \frac{1}{c} \ln(\frac{\eta}{\eta_0})$$

where c is the concentration of solute in grams/100 mL. The intrinsic viscosity has been found to be related to the molecular weight by the following empirical formula:

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

where K is a constant and *a* is a measure of the elongation of the molecule (*a*=1/2 for spherical molecules, as high as 1.8 for extended molecules. The solvent-solute interaction will determine whether the molecule is spherical (poor solvent) or elongated (good solvent).

Procedure

All groups will work at the same temperature (25^{o}C). Prepare 50 mL of a solution containing approximately 1 gram of polystyrene in toluene. Take 25 mL of this solution and dilute to 50 mL with toluene. Repeat this until solutions of 1/2, 1/4, and 1/8 of the initial concentration have been made. Place the solutions in the constant temperature bath. Place a reasonable (the water level should be within the large bulb throughout the runs) amount of distilled water in the viscometer (in the bath). Draw the water column up above the top line, and measure the time required to travel from the upper to lower line. Repeat this three times for the water. Do likewise for each of the toluene/polystyrene solutions and for pure toluene.

Calculations

The viscosity of water at 25^{o}C is 0.8937 cP, its density is 0.99777 g cm^{-3}. Determine the viscosities of the toluene and solutions from the flow times and the density of toluene.

Plot both $\frac{\eta_{sp}}{c}$ and $\frac{1}{c}\ln(\frac{\eta}{\eta_0})$ versus c, and extrapolate to c=0 to get

the intrinsic viscosity. Calculate the molecular weight from the intrinsic viscosity values. K for this system is 3.7×10^{-4}, *a* is 0.62.