https://www.eng.yale.edu/polymers/docs/classes/polyphys/lecture_notes/5/handout5_wsu2.html

1.2 Viscosity of Polymer Solutions

The viscosity of even dilute polymer solutions is usually far larger than just the viscosity of the background solvent, due to the large differences in size between the polymer and solvent molecules. In the non-free draining limit, we consider the polymer chain to move as an equivalent impermeable particle with an associated hydrodynamic volume that produces the same drag as the polymer chain. The friction coefficient is given by Stokes law as

$$f = 6\pi\eta_s R_h$$

where R_h is the hydrodynamic volume. The hydrodynamic volume is related in some way to the physical size of the chain, given by the mean square radius of gyration as

$$f = K_0 \eta_\eta \langle R_g^2 \rangle_0^{1/2}$$

where α_η is the hydrodynamic coil expansion factor.

1.2.1 Intrinsic viscosity

We will derive the Mark-Houwink equation starting from a basic consideration of the viscosity of a dilute suspension, as described by the Stokes equation for effective viscosity:

$$\eta = \eta_2 \left(1 + (5/2)\phi + ...\right) \qquad (1)$$

where φ is the volume fraction of particles in the system, given by the hydrodynamic volume of the polymer coils as

$$\phi = (c/M) N_A V_h \qquad (2)$$

The specific viscosity and intrinsic viscosities, defined in Table 1 are readily derived from the Einstein equation, 1, as

$$\begin{aligned} \eta_{sp} &= (5/2)(c/M)N_A V_h \\ [\eta] &= (5/2)N_A V_h/M \end{aligned} \qquad (3)$$

The hydrodynamic volume is given by

$$V_h = \left(\alpha_\eta \langle R_g \rangle_0^{1/2}\right)^3$$

so the intrinsic viscosity is

$$[\eta] = \Phi_0 \alpha_\eta^3 \left(\langle R_g^2 \rangle_0^{3/2}/M\right)$$

Φ_0 is a constant which depends on the distribution of segments within the coil. A value of 3.67x10^{2}4 /mol is appropriate for non-draining Gaussian coils [5]. For Gaussian chains, the ratio of the mean square radius of gyration to the molecular weight is a constant, so we have

$$[\eta] = K_\theta \alpha_\eta^3 M^{1/2} \tag{4}$$

where

$$K_\theta = \Phi_0 \left(\langle R_g^2 \rangle_0 / M \right)^{3/2}$$

Equation 4 is called the Flory-Fox equation.

The hydrodynamic coil expansion factor scales roughly with $M^{1/10}$ so we further reduce this to

$$[\eta] = K M^a \tag{5}$$

where a is a constant between 0.5 and 0.8. Equation 5 is the Mark-Houwink equation. Calibration of the constants K and a for a particular polymer in a particular solvent at a given temperature allows determination of the molecular weight by simple measurement of the concentration dependence of the viscosity to yield the intrinsic viscosity. This is discussed in the next section.