ENAS 606 : Polymer Physics

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Size and Mass Characterization - Non Scattering

1 Viscosity Measurements

1.1 Viscosity Definitions

There are several different "types" of viscosities that one may encounter in fluid dynamics. First, we differentiate between the *kinematic* and *dynamic* viscosities, referred to by symbols ν and μ or η . They are related via the density of the medium, with $\nu = \eta/\rho$. The units of dynamic viscosity are Poise or Pa.s and the dimensions are $[ML^{-1}T^{-1}]$. Kinematic viscosity has dimensions of $[L^2T^{-1}]$ and is thus sometimes referred to as a momentum diffusivity. For a complex fluid in which a solvent viscosity η_s is modified to the a concentration c of a second phase species resulting in an overall viscosity η , the following viscosities are defined in Table 1.

 Table 1: Definition of Viscosities

Name	Expression
Relative Viscosity	$\eta_r = \eta/\eta_s$
Specific Viscosity	$\eta_{sp} = \eta_r - 1$
Reduced Viscosity	$\eta_{red} = \eta_{sp}/c$
Inherent Viscosity	$\lim_{c\to 0} (\eta_r/c)$
Intrinsic Viscosity	$[\eta] = \lim_{c \to 0} (\eta_{sp}/c)$

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

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

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:

$$\eta = \eta_2 \left(1 + (5/2)\phi + \dots \right) \tag{1}$$

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

$$\phi = (c/M)N_A V_h \tag{2}$$

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

$$\eta_{sp} = (5/2)(c/M)N_A V_h [\eta] = (5/2)N_A V_h/M$$
(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 $3.67 \times 10^2 4$ /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

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

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

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

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.

1.3 Intrinsic Viscosity Determination

We can either use the *Huggins equation*, which is derived from a virial expansion of the specific viscosity in powers of the intrinsic viscosity, or the *Kraemer equation*, which results from an expansion of the inherent viscosity, to determine the intrinsic viscosity.

1.3.1 Huggins Equation

The specific viscosity is related to the intrinsic viscosity by a power series of the form

$$\eta_{sp} = k_0 [\eta] c + k_1 [\eta]^2 c^2 + k_2 [\eta]^3 c^3 + \dots$$

where $k_0, k_1, k_2...$ are dimensionless constants, and $k_0 = 1$.

Dividing by concentration, and truncating to only the second term, we form the Huggins equation as

$$\eta_{sp}/c = \left[\eta\right] + k_H \left[\eta\right]^2 c \tag{6}$$

The constant k_H is termed the Huggins constant and has values ranging from 0.3 in good solvents to 0.5 in poor solvents. It contains information about hydrodynamic and thermodynamic interactions between coils in solution. A plot of the reduced viscosity, extrapolated to zero concentration yields the intrinsic viscosity.

1.3.2 Kraemer Equation

We may construct another expansion based on the relative viscosity, in dilute solutions where the specific viscosity is much less than 1.

$$\ln(\eta_r) = \ln(1 + \eta_{sp}) \approx \eta_{sp} - (1/2)\eta_{sp}^2$$

Using the expression for the specific viscosity in the Huggins equation above, Eq. 6, provides Equation 7, the Kraemer equation.

$$\ln(\eta_{r}) = [\eta] c + (k_{H} - 1/2) [\eta]^{2} c^{2}$$

$$\ln(\eta_{r})/c = [\eta] c + k_{K} [\eta]^{2} c$$
(7)

A plot of the inherent viscosity, extrapolated to zero concentration, yields the intrinsic viscosity. Viscometry yield a viscosity average molecular weight, \bar{M}_{ν} where

$$\bar{M}_{\nu} = \left(\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}\right)^{1/a}$$

where n_i is the number density of chains of molar mass M_i .

2 Osmotic Pressure

Osmometry provides absolute measurements of molecular weight. It relies on Flory-Huggins lattice theory for a connection between the chemical potential of a solution and the polymer-solvent interaction along with the size of the polymer.

From thermodynamics, we know that the difference between the chemical potential of the solvent in the solution and that in the pure state is given as

$$\mu_1 - \mu_1^\circ = -\Pi \bar{V}_1$$

where the molar volume of the solvent, \bar{V}_1 is presumed to be independent of pressure. From F-H theory,

$$\mu - \mu^{\circ} = -RT\phi/N + RT(\chi - 1/2)\phi^2$$

where N is the degree of polymerization, or the number of lattice sites occupied by the polymer and χ is related to the Gibbs free energy difference for the formation of a solvent-monomer contact, $\Delta g_{12} = g_{12} - (1/2)(g_{11} + g_{22})$ on a lattice of coordination z

$$\chi = (z-2)\Delta g_{12}/k_B T$$

This provides

$$\Pi = RT(n_2/V) + RT(1/2 - \chi)N^2V_1(n_2/V)^2$$

where n_1 and n_2 are he number of solvent and polymer molecules respectively. The number density of polymer molecules is related to the mass concentration and molecular weight as $n_2/V = (m/V)(n_2/m) = c/\overline{M}_n$ since the number average molecular weight is given as

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = m/n_2$$

We can now write:

$$\Pi/c = (RT/\bar{M}_n) + (RT/V_1) (1/2 - \chi) (NV_1/\bar{m}_n)^2 dx^2$$

From the lattice theory, $N = V_2/V_1$ and so $NV_1/\bar{M}_n = V_2/\bar{M}_n = 1/\rho_2$ so we arrive at Equation 8.

$$\Pi/c = \left(RT/\bar{M}_n\right) + \left(RT/V_1\rho_2^2\right)\left(1/2 - \chi\right)c\tag{8}$$

Under theta conditions, $\chi = 1/2$ and so

$$(\Pi/c)_{\theta} = RT/\bar{M}_n$$

In general, we can evaluate RT/\bar{M}_n as the value of the reduced osmotic pressure in the zero concentration limit, so

$$(\Pi/c)_{c\to 0} = RT/\bar{M}_n$$

The remaining term yields the second virial coefficient, providing information about the thermodynamics of the system. The theta temperature can be evaluated by plotting the value of the second virial coefficient and finding where it is equal to zero.

$$A_2 = (1/2 - \chi) / V_1 \rho_2^2 \tag{9}$$

References

- [1] P. de Gennes, Scaling Concepts in Polymer Physics, Cornell University Press, 1979.
- [2] M. Rubinstein and R. Colby, *Polymer physics*, Oxford University Press, 2003.
- [3] G. Strobl, The Physics of Polymers: Concepts for Understanding Their Structures and Behavior, Springer, 1997.
- [4] P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.
- [5] P. Lovell and R. Young, Introduction to Polymers, Chapmen & Hall, UK, 1991.