

3.8.3 The Mark-Houwink-Sakurada relationship

Empirical relationship between the **viscosity average MW** and **intrinsic viscosity**.

$$[\eta] = KM_v^a \quad (3.97)$$

K, a= Constants for a particular polymer-solvent pair at a particular temperature

(See **Table 3.10** for values of K and a) **<M_w** of sharp fraction of MWD is usually **substituted for M_v** since M_v is difficult to measure directly>

Values of a

0.5 ≤ a ≤ 0.8 for random coil (0.5 @ Flory Θ temperature (α = 1), 0.8 in thermodynamic good solvent (α ∝ M^{0.1}) → α increase from M⁰ to M^{0.1}).

Table 3.10 Selected intrinsic viscosity–molecular weight relationship, $[\eta] = KM_v^a$ (77)

Polymer	Solvent	T(°C)	K × 10 ^{3a}	a ^b
cis-Polybutadiene	Benzene	30	33.7	0.715
i-Polypropylene	1-Chloronaphthalene	139	21.5	0.67
Poly(ethyl acrylate)	Acetone	25	51	0.59
Poly(methyl methacrylate)	Acetone	20	5.5	0.73
Poly(vinyl acetate)	Benzene	30	22	0.65
Polystyrene	Butanone	25	39	0.58
Polystyrene	Cyclohexane (θ-solvent)	34.5	84.6	0.50
Polytetrahydrofuran	Toluene	28	25.1	0.78
Polytetrahydrofuran	Ethyl acetate hexane (θ-solvent)	31.8	206	0.49
Cellulose trinitrate	Acetone	25	6.93	0.91

Source: J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, sec. IV.

^aEuropean units, concentrations in g/ml. Units do not vary with a. Units of K are cm³·mol^{1/2}/g^{3/2}.

^bThe quantity a, last column, is the exponent in equation (3.97).

Table 3.11 Values of the Mark–Houwink–Sakurada exponent a

a	Interpretation
0	Spheres
0.5–0.8	Random coils
1.0	Stiff coils
2.0	Rods

In general $0 \leq \alpha \leq 2$ (See Table 3.11)

K is often given in terms of universal constant, ϕ

$$K = \phi \left(\frac{\overline{r_0^2}}{M} \right)^{3/2} \quad (3.98)$$

$\overline{r_0^2}$ = Mean square of end-to-end distance of the **unperturbed coil**.

Often MHS eq is conveniently expressed in the form of

$$[\eta] = \phi \left(\frac{\overline{r_0^2}}{M} \right)^{3/2} M^{1/2} \alpha^3 = KM^{1/2} \alpha^3 \quad (3.99)$$

If the intrinsic viscosity is measured both in Θ -solvent and good solvent, **the expansion of coil is estimated as** (Note $\alpha=1$ in Θ -solvent)

$$\langle R_e = R_{e0} \alpha \quad (3.95) \rangle$$

$$[\eta]/[\eta]_{\Theta} = \alpha^3 \quad (3.100)$$

Values of α vary from unity in Flory Θ -solvent to about 2 or 3 increasing with M.

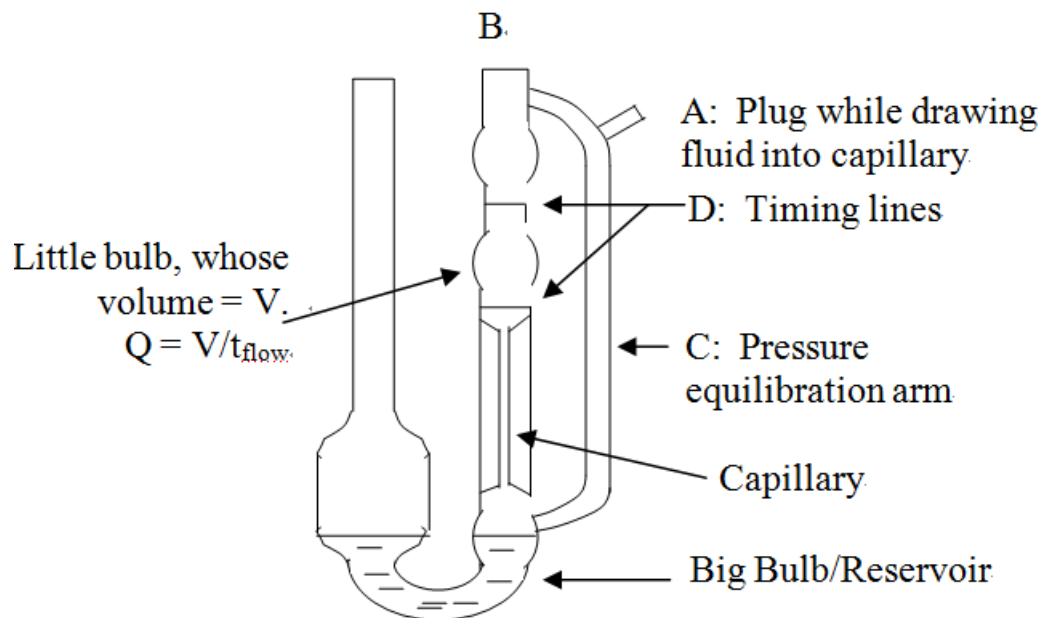
3.8.4 Intrinsic viscosity experiments

Mostly dilute solutions up to 1% polymer are made up. Then

$\eta_{rel} \sim 1.6$ for the highest concentration

Ubbelohde viscometer is used to measure the viscosity.

(See below for the operation principle)



Capillary viscometer is working based on the Hagen-Poiseuille Law:

$$Q = \frac{V}{t} = \frac{\pi R^4 \Delta P}{8 \eta L} \quad (Q = \text{Volumetric flow rate})$$

Rearranging gives ($\Delta P = \rho gh$)

$$\frac{\eta}{\rho} = \frac{\pi R^4 gh}{8LV} t = K t \quad K = \text{Capillary constant}$$

$$\rightarrow \eta = K t \rho$$

Then

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t \rho}{t_0 \rho_0}$$

For dilute solution $\rho \sim \rho_0$, then

$$\eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0}$$

Scan Figure 3.14

$$\left[\frac{\eta_{sp}}{c}\right]_{c=0} = [\eta] \quad (3.86)$$

$$\left[\frac{\ln(\eta_{rel})}{c}\right]_{c=0} = [\eta] \quad (3.88)$$

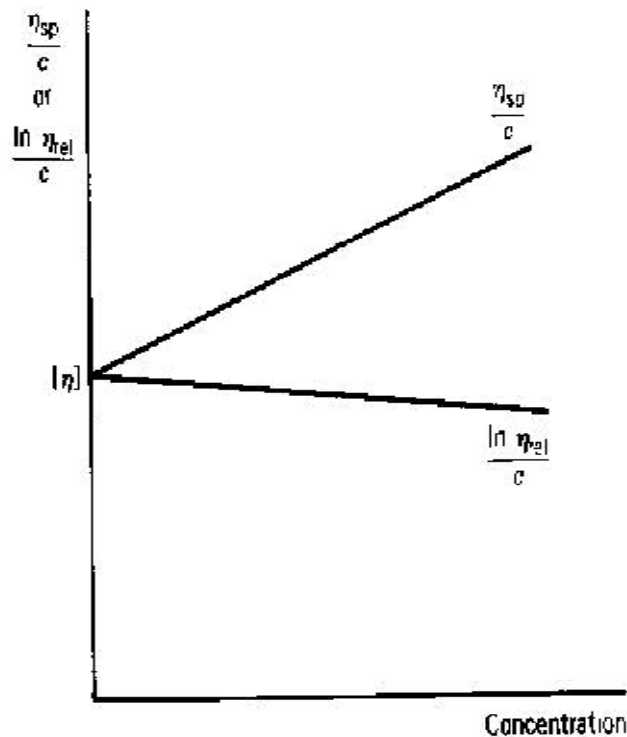


Figure 3.14 Schematic of a plot of η_{sp}/c and $\ln \eta_{rel}/c$ versus c , and extrapolation to zero concentration to determine $[\eta]$.

Two practical points must be noted:

- 1) Both lines must be extrapolated to the same intercept at zero concentration
- 2) Sum of the slopes is related through the Huggins eq

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad (3.101)$$

and through Craemer eq,

$$\frac{\ln(\eta_{rel})}{c} = [\eta] - k''[\eta]^2c \quad (3.102)$$

Subtracting (102) from (101) gives

$$k' + k'' = 0.5 \quad (3.103)$$

If either of these requirements is not met, molecular aggregation, ionic effects, or other problems may be indicated. For many polymer-solvent system $k'=0.35$, $k''=0.15$ (Negative).

In order to determine K and a in MHS eq, a double logarithmic plot of M_w vs intrinsic viscosity is prepared (Figure 3.15)

$$[\eta] = KM_w^a \quad (3.97)$$

For calibration, narrow MWD polymer should be used.

[Scan Figure 3.15 here](#)

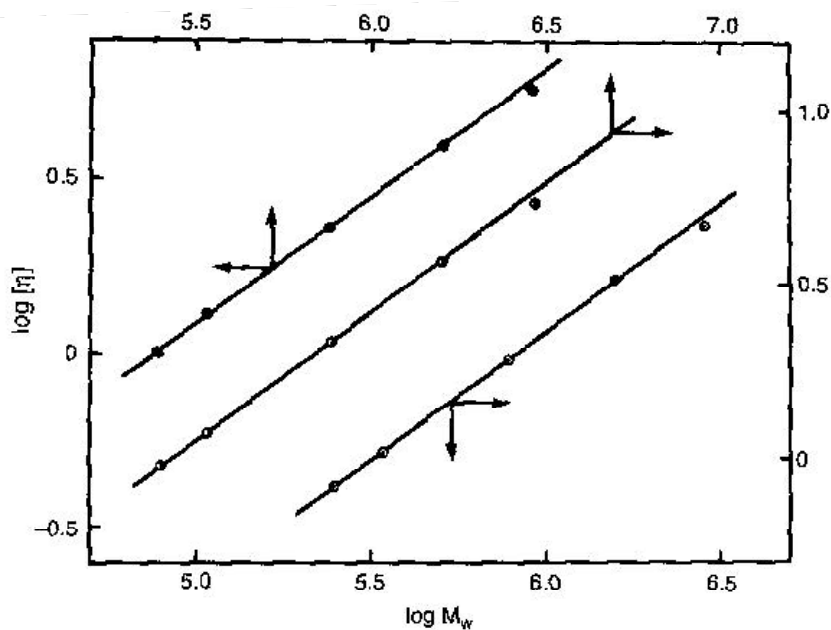


Figure 3.15 Double logarithmic plots of $[\eta]$ versus M_w for anionically synthesized polystyrenes, which were then fractionated leading to values of M_w/M_n of less than 1.06. Filled circles in benzene, half-filled circles in toluene, and open circles in dichloroethylene, all at 30°C (75). The arrows indicate the axes to be used. Units for $[\eta]$ in 100 ml/g.

3.8.5 Example Calculation Involving Intrinsic Viscosity

Say we are interested in a fast, approximate molecular weight of a polystyrene sample. We dissolve 0.10 g of the polymer in 100 ml of butanone and measure the flow times at 25°C in an Ubbelohde capillary viscometer. The results are

Pure butanone	110 s
0.10% Polystyrene solution	140 s

Starting with equation (3.84), and noting that the flow time is proportional to the viscosity,

$$\eta_{\text{rel}} = \frac{\eta}{\eta_0} = \frac{140}{110} = 1.273$$
$$\eta_{\text{sp}} = \eta_{\text{rel}} - 1 = 0.273$$
$$\frac{\eta_{\text{sp}}}{c} = \frac{0.273}{0.001} \text{ ml/g} = 2.73 \times 10^2 \text{ ml/g}$$

As an approximation, assume that the concentration is near zero, and the $[\eta]$ is $2.73 \times 10^2 \text{ ml/g}$, equation (3.86). This obviates the extrapolation in Figure 3.14 that is required for more accurate results. Using the Mark-Houwink-Sakurada relation, equation (3.97) and Table 3.11, we have

$$[\eta] = KM_v^a$$
$$2.73 \times 10^2 = 39 \times 10^{-3} M_v^{0.58}$$
$$M_v = 4.26 \times 10^6 \text{ g/mol}$$

Note that the units of **K** are irregular, depending on the value of *a*. Usually the units of **K** are omitted from tables.

3.9 Gel permeation chromatography

Also called size exclusion chromatography (SEC)

Depending on the hydrodynamic radius, molecule may or may not enter small pores in a bed of cross-linked polymer (Stationary phase). Smaller molecules diffuse in and out of the pores via Brownian motion and are delayed. Large molecules pass by and continue in the mobile phase. (See [Figure 3.16](#))