CHEMISTRY

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Dr. K. Ananthanarayanan
Associate Professor (Research)
Department of Chemistry
Room No 319, 3rd Floor, Raman Research Park

Email : ananthak@srmist.edu.in
Phone : +91-9840154665

In this class...

Determination of molecular weight of a polymer by viscosity average method

Expt. No. : 8

Experiment

- **Aim :**

  To determine the molecular weight of a polymer in solution by using a Ostwald viscometer.

- **Materials required:**

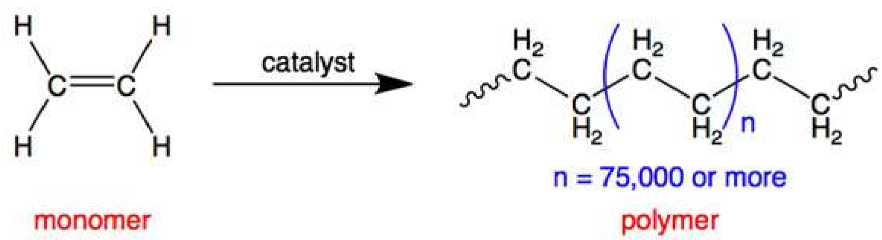
  Ostwald viscometer, beaker, stop watch, standard flasks, pipette, suction bulb

- **Chemicals required :**

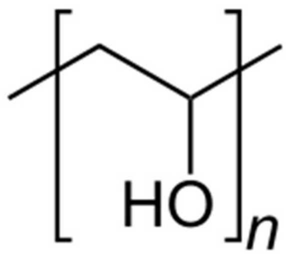
  Given polymer solution, suitable solvents

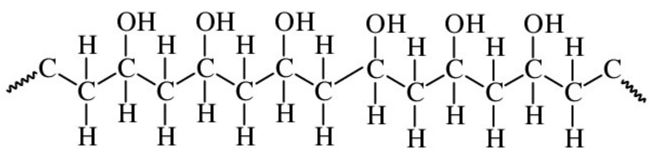
Polymer

- A polymer is a substance or material consisting of very large molecules, or macromolecules, composed of many repeating subunits.
- Polymerization is the process by which monomers (smaller chemical units) are combined to form a polymer.



Polymer used – polyvinyl alcohol





Molecular weight

- The molecular weight of a synthetic polymer **does not have a single value, since different chains will have different lengths and different numbers of side branches**.
- There will **therefore be a distribution of molecular weights, so it is common to calculate the average molecular weight** of the polymer.
- Several different ways to define the average molecular weight - the **two most common being the number average molecular weight and the weight average molecular weight**.
- Other averages exist, such as the **viscosity average molecular weight.**

Number average molecular weight

The number average molecular weight **is defined as the total weight of polymer divided by the total number of molecules.**

$$\text{Total weight} = \sum_{i=1}^{\infty} N_i M_i$$

where N_i is the number of molecules with weight M_i

$$\text{Total number} = \sum_{i=1}^{\infty} N_i$$

The number average molecular weight is therefore given by:

$$\overline{M_N} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$$

Weight average molecular weight

The weight average molecular weight **depends not only on the number of molecules present, but also on the weight of each molecule**. To calculate this, N_i is replaced with $N_i M_i$.

$$\overline{M_W} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

This can also be written as:

$$\overline{M_W} = \sum_{i=1}^{\infty} w_i M_i$$

where w_i is the weight fraction of polymer with molecular weight M_i.

Molecular weight

Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 50.000 g/mol and 9 moles of polymer molecules having molecular weight of 30.000 g/mol.

$$\overline{M}_n = \frac{(9 \text{ mol x } 30{,}000 \text{ g/mol}) + (5 \text{ mol x } 50{,}000 \text{ g/mol})}{9 \text{ mol} + 5 \text{ mol}} = 37{,}000 \text{ g/mol}$$

$$\overline{M}_w = \frac{9 \text{ mol}(30{,}000 \text{ g/mol})^2 + 5 \text{ mol}(50{,}000 \text{ g/mol})^2}{9 \text{ mol}(30{,}000 \text{ g/mol}) + 5 \text{ mol}(50{,}000 \text{ g/mol})} = 40{,}000 \text{ g/mol}$$

Viscosity average molecular weight

$$\overline{M}_V = \left[\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i}\right]^{1/a}$$

where a is the exponent in Staudinger-Mark-Houwinks equation: [η] = k*M^a ([η] = intrinsic viscosity). For a flexible polymer in a good solvent, a ≈ 0.7.

M_V is determined by viscosity measurements.

Determination of molecular weight

a. Absolute method :

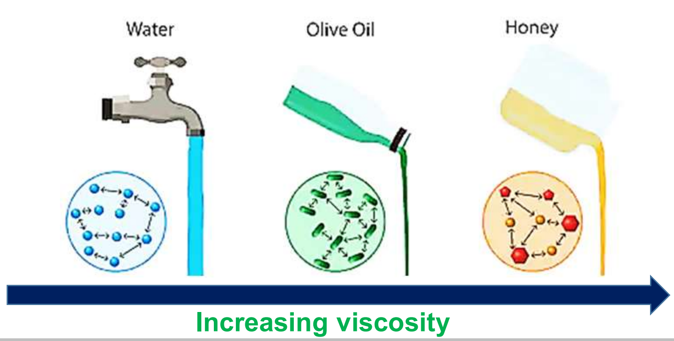
Mass spectrometry
Colligative property
End group analysis
Light scattering
Ultracentrifugation.

b. Relative method : **Solution viscosity**

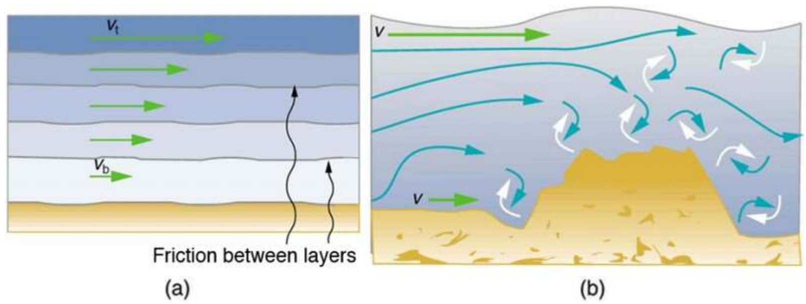
c. Fractionation method : GPC (Gel Permeation Chromatography)

Viscosity

- Viscosity is a measure of a fluid's resistance to flow.
- It describes the internal friction of a moving fluid caused due to intermolecular forces between particles within the fluid.
- A fluid with large viscosity resists motion because its molecular makeup gives it a lot of internal friction.



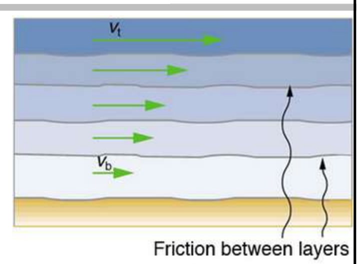
Laminar flow



- Laminar flow occurs in layers without mixing. Notice that viscosity causes drag between layers as well as with the fixed surface.
- An obstruction in the vessel produces turbulence. Turbulent flow mixes the fluid. There is more interaction, greater heating, and more resistance than in laminar flow.

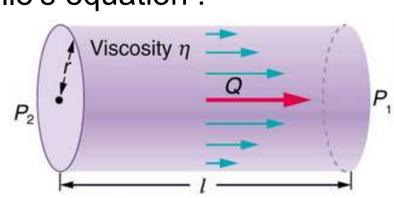
Poiseuille's equation

- The precise definition of viscosity is based on **laminar**, or non turbulent, flow characterized by the smooth flow of the fluid in layers that do not mix.



- The **flow rate Q** *of* the laminar flow of an incompressible fluid having **viscosity η** through a horizontal tube of **uniform radius r and length l** is given by the Poiseuille's equation :

$$Q = \frac{(P_2 - P_1)\pi r^4}{8\eta l}$$



Principle

- In a capillary viscometer, the **viscosity of a liquid is proportional to the time taken by a known volume of liquid to flow through the capillary under a specified hydrostatic pressure at a fixed temperature.**

- Provided the flow is laminar, using the **Poiseuille's equation it is possible to show that if t, η and ρ are the flow time, viscosity and density of solution :**

$$\frac{\eta}{\eta_o} = \frac{\rho}{\rho_o}\frac{t}{t_o}$$

$\frac{\eta}{\eta_o}$ = Relative viscosity η_{rel}

The specific viscosity is defined as $\eta_{sp.} = \eta_{rel} - 1$

Relative viscosity : $\eta_{rel} = \frac{\eta}{\eta_o} = \frac{t}{t_o}$

η : solution viscosity
η_o: solvent viscosity
t : flow time of solution
t_o: flow time of solvent

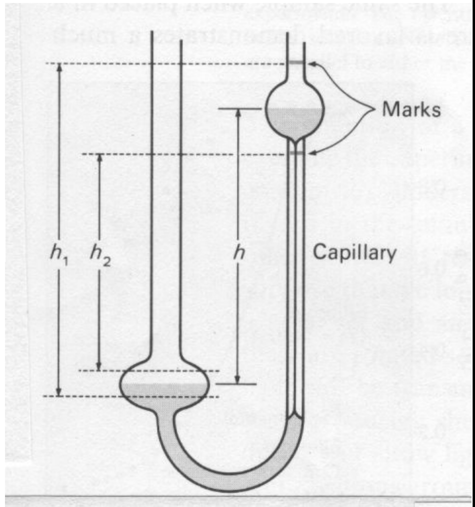
Specific viscosity : $\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{t - t_o}{t_o} = \eta_{rel} - 1$

Reduced viscosity : $\eta_{rel} = \frac{\eta_{sp}}{c}$

Intrinsic viscosity : $[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$

- The ratio of a solution's specific viscosity to the concentration of the solute, extrapolated to zero concentration.
- Intrinsic viscosity reflects the capability of a polymer in solution to enhance the viscosity of the solution

Ostwald Viscometer

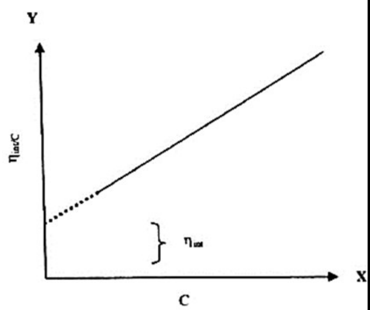


Principle contd..

- The Staudinger – Mark – Houwink's equation which relates η_{int} with molecular weight

$$\eta_{int} = K(M)^{\alpha}$$

- Where 'K' is an empirical parameter characteristic of a particular solute – solvent pair and 'α' is a shape parameter. (both are constants). a = Mark-Houwink constant relating to structure (0 to 0.1 – sphere, 0.35 to 0.80 – random coil, 1.5 to 2 – rigid rod).
- Plot of η_{sp} /C Vs C , extrapolated to C= 0 gives η_{int}
- From known values of K and α , molecular weight can be determined.



Procedure

- 1% solution of polymer (PVA) in water will be supplied. Prepare at least 5 dilutions i.e 0.1%, 0.2% , 0.3% , 0.4% and 0.5% polymer in water.
- Dilutions can be done by using the volumetric expression $N_1V_1 = N_2V_2$.
- Set up the Ostwald viscometer and measure the flow time (t_0) of a fixed volume of pure solvent (12.5 ml). Take the average reading (at least three iterations).
- Rinse the viscometer thoroughly with the most dilute solution, measure the flow time (t_1) keeping the flow volume the same.
- Repeat the procedure for other solutions.
- Calculate η_{rel} and η_{sp}. Plot η_{sp} /C Vs C , extrapolate to C= 0 to obtain η_{int}. From the given values of K and α , calculate the molecular weight.

Tabular column

S.No.	Concentration of the polymer solution	Time of flow in sec (average)	Relative viscosity $\eta/\eta_0 = t_s/t_0$	Specific viscosity $\eta_{sp}=\eta/\eta_0-1$	Reduced viscosity η_{sp} /C
1.	Pure Solvent	t_0			
2.	0.1%	t_s			
3.	0.2%	t_s			
4.	0.3%	t_s			
5.	0.4%	t_s			
6.	0.5%	t_s			

Calculation

Solvent used Water

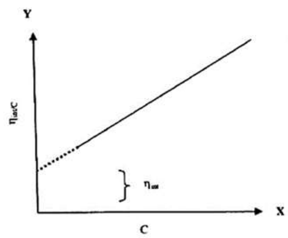
$\eta_{int} = K \times M^{\alpha}$

$\log\eta_{int} = \log K + \alpha \log M$

$\alpha \log M = \log \eta_{int} - \log K$

$\log M = \dfrac{\log \eta_{int} - \log K}{\alpha}$

$M = Anti \log \dfrac{[\log \eta_{int} - \log K]}{\alpha}$



Plot η_{sp}/C Vs C.

Extrapolate the straight line to Y axis

The intercept is η_{int}.

From the relationship, $\eta_{int} = KM^{\alpha}$ where K and α are constants,

(For PVA solution $K = 45.3 \times 10^{-3}$, $\alpha = 0.64$)

Result

- The molecular weight of the given polymer is =

Tabular column, values

Sl. No	Concentration of the polymer solution (c) (%)	Time of flow in sec (average) sec	Relative viscosity $\frac{n}{n_0} = \frac{t}{t_0}$	Specific viscosity n_{sp}= (relative viscosity -1)	Reduced viscosity $\frac{n_{sp}}{c}$
1	**Pure solvent**	**38 (t_o)**	**------**	**-------**	**-------**
2	**0.1**	**43**	**1.131**	**0.131**	**1.31**
3	**0.2**	**46**			
4	**0.3**	**50**			
5	**0.4**	**55**			
6	**0.5**	**62**			