Date 17-11-2021

Expt. No. 6

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Expt. - Determination of molecular weight of a polymer by viscosity Average method

Aim

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

Apparatus Required

Ostwald's viscometer, volumetric flasks stop watch, standard flasks.

Reagent required

Polymer, suitable solvents.

Principle

If a polymer is soluble in a suitable solvent, measurement of solution viscosity provides a simple and convenient method. For a particular molecular weight determination. In a capillary viscometer (ostwald / Ubbelhode) the viscosity of a liquid is proportional to the time taken by a known volume of a liquid to flow through a capillary under a specified hydrostatic pressure at a fixed

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temperature. The condition for the flow should ensure that the flow is laminar. Using Poiseuille's equation it is possible to show that if t, η & ρ are the flow time, viscosity and density of a solution respectively; and t_0, η_0, ρ_0 are those of the pure solvent, then

$$\eta/\eta_0 = \rho/\rho_0 \cdot t/t_0$$

The value of η/η_0, is known as the relative viscosity, η_{rel}. In dilute solutions, which are often employed. For molecular weight determination, ρ is not much different from ρ_0 and hence

$$\eta_{rel} = \eta/\eta_0 = t/t_0$$

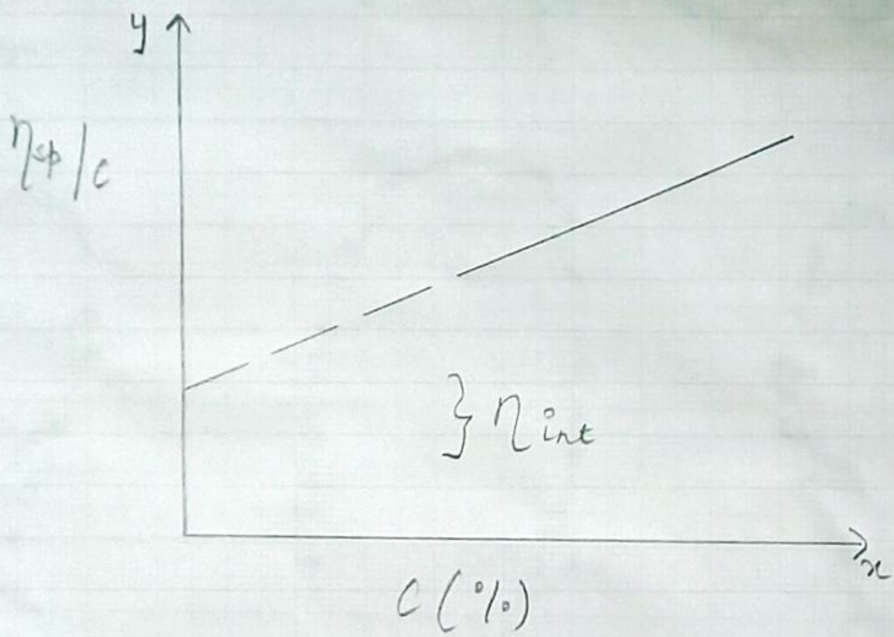
The specific viscosity is defined as

$$\eta_{sp} = \eta_{rel} - 1$$

A plot of η_{sp}/c vs c is a straight line for dilute solutions, the intercept

$$\lim_{c \to 0} \left(\frac{\eta_{sp}}{c} \right) = \eta_{int}$$

Aim → To determine the molecular weight of a polymer in solution by using a Viscometer



· Plot of (η_{sp}/C) vs Concentration of Polymer solution to find out intrinsic viscosity.

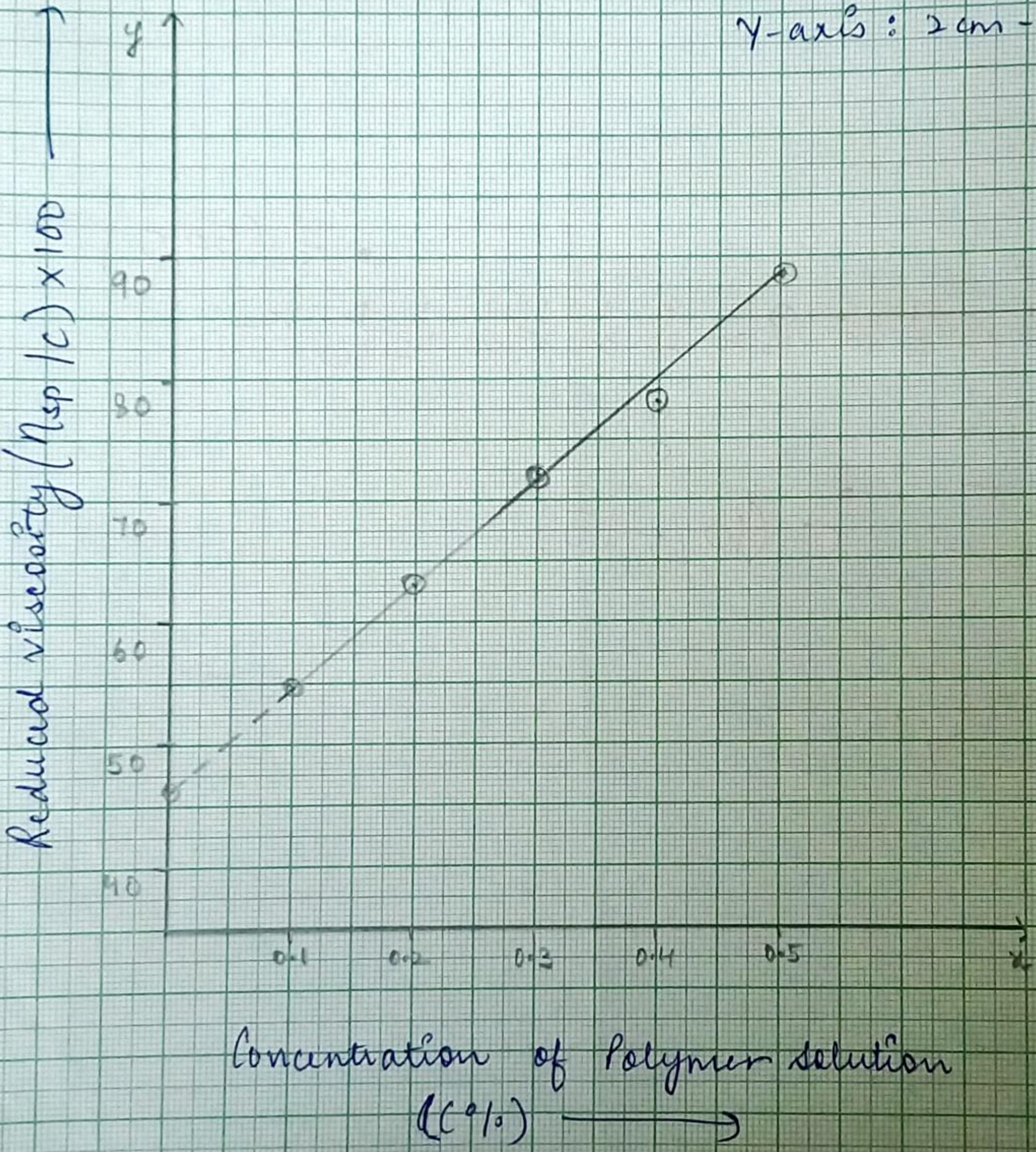
* Calculate η_{rel} and η_{sp}. Plot η_{sp}/c vs c, extrapolate to $c=0$ to obtain η_{int}. From the given values of K and α, calculate the molecular weight.

Sr. No.	Concentration of the polymer solution	Time of flow in sec (average)	Relative viscosity $\eta_{rel} = \frac{\eta}{\eta_0} = t_s/t_0$	Specific viscosity $\eta_{sp} = \eta_{rel} - 1$	Reduced viscosity η_{sp}/c
1.	Pure solvent	$t_0 = 55$	—	—	—
2.	0.1 %	$t_s = 58$	1.0545	0.0545	54.5
3.	0.2 %	$t_s = 62$	1.1273	0.1273	63.6
4.	0.3 %	$t_s = 67$	1.2181	0.2181	72.7
5.	0.4 %	$t_s = 72$	1.3090	0.3090	77.2
6.	0.5 %	$t_s = 79$	1.4363	0.4363	87.2

$[K = 45.3 \times 10^{-3}, \alpha = 0.64]$

Charvi Jain
RA2111047010113

Scale
X-axis : 2 cm - 0.1 %
Y-axis : 2 cm - 10 units



* Calculation

Solvent used = water

Now, $\eta_{int} = k \times M^{\alpha}$

Taking log on both sides

$\log \eta_{int} = \log k + \log M^{\alpha}$

$\Rightarrow \log \eta_{int} = \log k + \alpha \log M$

$\Rightarrow \alpha \log M = \log \eta_{int} - \log k$

From, $\eta_{int} = 46.5$, given $k = 45.3 \times 10^{-3}$, $\alpha = 0.64$

$\Rightarrow \log M = \dfrac{\log 46.5 - \log 45.3 \times 10^{-9}}{\alpha}$

$= \dfrac{\log 46.5 - \log 45.3 + 3 \log 10}{0.64}$

$= \dfrac{1.66 - 1.65 + 3}{0.64} = \dfrac{3.01}{0.64} = 4.703$

$\therefore M = \text{antilog}(4.703) = 50,466.13\,g$

* Result

The molecular weight of given polymer = 50,466.13 g which is known as the intrinsic viscosity η_{int}.

The staudiger - Mark - Houwink 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 'a' is a 'shape' parameter, ~~characteristic~~ which can vary from about 0.5 for well coiled polymers in poor solvents to about 2. For ridgidity extended 'rod' like polymers. From known values of K and a, Molecular weight can be determined.

Procedure

Preparation of variation concentration of polymer in water (solvent)

1% solution of polymer in water will be supplied. We need to prepare at least '5' dilution viz. 0.1%, 0.2%, 0.3%, 0.4% and 0.5% polymer in water before carring out the experiment.

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Dilutions can be done by using volumetric solution from a 1% solution, volume is

$$V_1 = \frac{V_2 \times N_2}{N_1} = \frac{100\,ml \times 0.2\,\%}{1\,\%} = 20\,ml$$

Similarly, any other dilution can be prepared by the above method.

Setup the Ostwald (or Ubbelhode) viscometer and measure the flow time (t_0) of a fixed volume of the pure solvent. Take an average of three readings. Rinse the viscometer throughly with the most dilute solution, measure the flow time (t_1) keeping the flow-volume the same. Repeat the procedure for other solutions.

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