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Experiment 4: Determination of Viscosity Average Molecular Weight of Polymer

Objectives:

Determine the viscosity average molecular weight of a polymer.

Theory:

Viscosity is an internal property of a fluid that offers resistance to flow. It is due to the internal friction of molecules and mainly depends on the nature & temperature of the liquid.

Many methods are available for measuring viscosity of polymer solution. The Ostwald method is a simple method for the measurement of viscosity, in which viscosity of liquid is measured by comparing the viscosity of an unknown liquid with that of liquid whose viscosity is known. In this method viscosity of liquid is measured by comparing the flow times of two liquids of equal volumes using same viscometer.

Consider two liquids are passing through a capillary of same viscometer. Then the coefficient of viscosity of liquid (η_2) is given by equation

$$\eta_2 = \frac{\eta_1 \rho_2 t_2}{\rho_1 t_1}$$

Here t_1 and t_2 are the time of flow of the liquids and ρ_1 and ρ_2 are the respective densities. And η_1 is the coefficient of viscosity of water.

For a given liquid η has a specific value at the same temperature.

Various mixtures of two non-interacting liquids viscosities will lie among the viscosities of those pure components.

The time of flow of liquid depends on the viscosity and composition. In this method the flow times are measured for different known compositions and a graph is plot for time of flow and compositions. The unknown composition can be determined by plotting a graph for the time of flow and compositions.

The molecular weight of the polymer is measured by using viscometer and the molecular weight obtained by this technique is called viscosity average molecular weight. The molecular weight of the polymer solution is very high so the viscosity of polymer solution is very high compared to that of pure solvent.

From the Mark-Houwink equation the relationship among the molecular weight and viscosity are given below

$$[\eta] = KM^\alpha$$

Where $[\eta]$ is the intrinsic viscosity, M is Molecular weight, K and α are constants for a particular polymer solvent system.

If we know the K and α values for a given polymer solution the intrinsic viscosity and molecular weight can be calculate using the above equation.

Polymer-solvent system	$K \times 10^{-3} \text{mL/g}$	α
PMMA-Acetone	7.70	0.70
PMMA-Benzene	5.20	0.76
PMMA-Toluene	7.0	0.71
Poly vinyl acetate-Acetone	10.2	0.72
Poly vinyl acetate-Benzene	56.3	0.62
Poly vinyl acetate-Acetonitrile	41.5	0.62
Poly vinyl alcohol-Water	45.3	0.64
Poly styrene-Benzene	10.6	0.735
Poly styrene-Toluene	11.0	0.725

Terms Related to Viscosity Measurements:-

$$\text{Relative Viscosity} = \frac{\eta}{\eta_0} = \frac{t}{t_0} = \eta_r$$

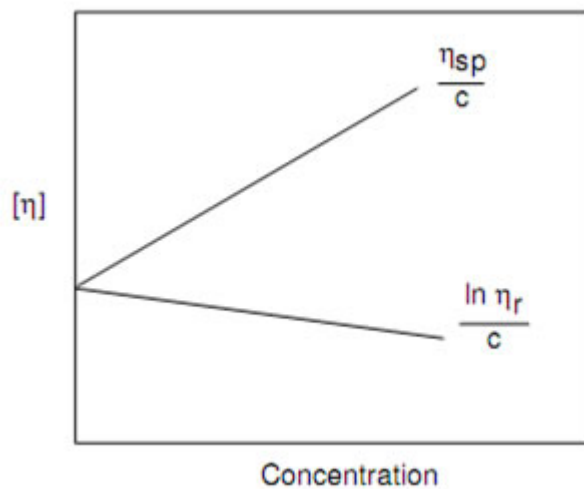
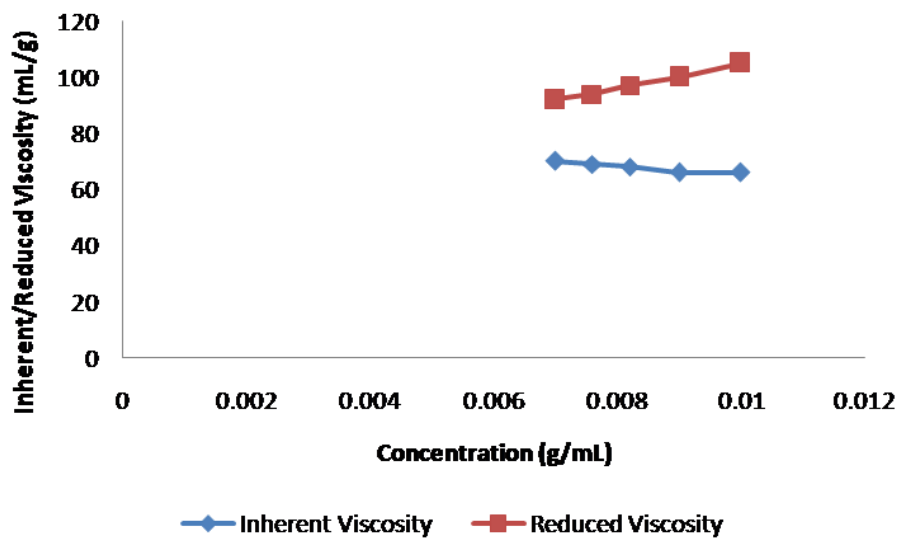
$$\text{Specific Viscosity} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_r - 1 = \eta_{sp}$$

$$\text{Reduced Viscosity} = \frac{\eta_{sp}}{C} = \eta_{red}$$

$$\text{Inherent Viscosity} = \frac{\ln \eta_r}{C} = \eta_{inh}$$

$$\text{Intrinsic Viscosity} = \left(\frac{\eta_{sp}}{C} \right)_{C \rightarrow 0} = \left(\frac{\ln \eta_r}{C} \right)_{C \rightarrow 0} = [\eta]$$

For measuring intrinsic viscosity of polymer sample, solutions of known concentrations are prepared, the flow times of solvent (t_0) and the solutions (t) are measured using viscometer. Double extrapolation plots of reduced viscosity against concentration and inherent viscosity against concentration is plotted by calculating the corresponding reduced viscosity and inherent viscosity. The intrinsic viscosity is given by the common ordinate intercept of these graphs.



Procedure:

Determining the Intrinsic Viscosity of the Polymer- solvent system:

1. Select the Polymer.
2. Select the Solvent.
3. Determine the Time of flow of the solvent (t_0).
4. Determine the time of flow of polymer-solvent system at different concentrations.
5. From the concentration and time of flow, the inherent viscosity and reduced viscosity are calculated using the equations;

$$\frac{\ln \eta_r}{C} = \eta_{inh} \qquad \frac{\eta_{sp}}{C} = \eta_{red}$$

6. Inherent Viscosity = , Reduced Viscosity =
7. A graph is drawn by plotting reduced viscosity against concentration and inherent viscosity against concentration.
8. Intrinsic viscosity can be obtained by extrapolating the graph to zero concentration.
9. From the value of intrinsic viscosity, the viscosity average molecular weight of the polymer can be calculated by using the equation.

$$[\eta] = KM^\alpha$$

Observations and Calculations:

Conc: (g/dl)	Flow Time of Polymer-Solvent system (t) sec	Flow Time of Solvent (t_0) sec	$\eta_r = \frac{t}{t_0}$	$\eta_{sp} = \eta_r - 1$	Reduced Viscosity, $\eta_{red} = \frac{\eta_{sp}}{C}$ (dl / g)	$\ln \eta_r$	Inherent Viscosity, $\frac{\ln \eta_r}{C} = \eta_{inh}$
0.02	87	69	1.26	0.26	13	0.23	11.5
0.04	111	69	1.60	0.60	15	0.47	11.75
0.06	135	69	1.95	0.95	15.83	0.66	11
0.08	165	69	2.39	1.39	17.37	0.87	10.8
0.1	196	69	2.84	1.84	18.4	1.04	10.4

Calculation :

$$[\eta] = 119$$
$$K = 10.6 \times 10^{-3}$$

$$\alpha = 0.735$$
$$[\eta] = KM^\alpha$$

$$119 = 10.6 \times 10^{-3} \times M^{0.735}$$
$$M = 7.4 \times 10^6$$

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Result: The viscosity average molecular weight of the polymer is $= 7.4 \times 10^6$ g/mol