

Experiment (3)

Molecular weight of a polymer from viscosity measurements

Introduction:

The ratio of the viscosity η of a solution of non-spherical high polymer molecules to the viscosity η_0 of the solvent is related to the molecular weight M of the polymer by the expression :

$$\frac{(\eta/\eta_0 - 1)}{C} = KM^\alpha \quad (1)$$

Where, K is a constant for any given type of polymer, solvent and temperature, α is a function of the geometry of the molecule, and C is the number of grams of polymer in 100 ml of solution .

The term $\{ (\eta / \eta_0) - 1 \}$ is known as the specific viscosity in the form :

$$\eta_{sp}/C = K M^\alpha \quad (2)$$

This equation is only valid for very dilute solution (less than 1 percent) and hence the graph which is drawn of (η_{sp}/c) vs. C is extrapolated to zero concentration. The extrapolated value is known as the intrinsic viscosity $[\eta]$.

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp}/C \quad (3)$$

If the logarithmic function $\ln (\eta / \eta_0)$ is expanded as an infinite series, since the second and higher terms can be neglected as the concentration approaches zero, it will be seen that :

$$\lim_{c \rightarrow 0} (\eta_{sp}/C) = \lim_{c \rightarrow 0} 1/c \ln(\eta / \eta_0) \quad \text{equation (4)}$$

hence,

$$[\eta] = \lim_{c \rightarrow 0} 1/C \ln (\eta / \eta_0) \quad \text{equation (5)}$$

The intrinsic viscosity is therefore the intercept on the graph of either η/c or $1/c \ln(\eta/\eta_0)$ vs. C . A more reliable value of the intercept is obtained by drawing both graphs.

The $[\eta]$ value obtained by this method may then be used to determine the molecular weight of the polymer by applying the equation:

$$[\eta] = K M^\alpha$$

Apparatus and Chemicals:

Bohlin viscometer (see experiment 1), polystyrene and toluene.

Procedure:

1. Prepare the stock solution of the polystyrene in toluene by weighting 5 g of the polystyrene dissolved in 200 ml toluene.
2. Make 5 different concentrations by diluting the stock solution to 2, 4, 8, and 16 times.
3. Measure the average time of flow (t) for each of the above five concentrations using Oswald viscometer at 25°C as explained in experiment number 2.
4. Measure the average flow time of pour toluene (t) at 25°C using Bohlin Viscometer.
5. Calculate η_{sp} for each concentration from: $\eta_{sp} = \{ (\eta / \eta_0) - 1 \}$
6. Record the results in a tabular form as follows:

c	η / η_0	$(\eta / \eta_0) - 1 = \eta_{sp}$	η_{sp}/C	η_{sp}/c

7. Plot η_{sp}/C vs. C and $\{ 1/C \ln(\eta / \eta_0) \}$ vs. C .

8. Extrapolate the graphs to $C \rightarrow 0$ and obtain the intrinsic viscosity $[\eta]$.
9. Calculate the molecular weight of polystyrene M from the equation: $[\eta] = K M^\alpha$, where $K = 1.05 \times 10^{-4}$ and $\alpha = 0.72$.

Experiment (4)
SURFACE CHEMISTRY
Adsorption by Solids from Solution

Introduction:

At the surface of a solid or liquid, molecular forces are usually unbalanced or unsaturated. As a result of this instauration, exposed surface tend to satisfy their residual forces by attracting and retaining onto them other substances with which they come in contact. The phenomenon is known as adsorption.

Solids may adsorb dissolved substances from solutions as well as gases. In sugar refining, for example, colored materials and impurities may be removed by filtering through adsorbents such as charcoal. Adsorption of solutes from solution involves the establishment of equilibrium between the amount adsorbed and the concentration of substance in solution. The variation of the amount adsorbed with concentration may be represented by an isotherm of the Freundliche type:

$$\frac{x}{m} = KC^n \quad (1)$$

where x is the amount of solute adsorbed per m grams adsorbent, C the equilibrium concentration of solute in solution, K and n are constants. The relation may be written in the form:

$$\log \frac{x}{m} = n \log C + \log K \quad (2)$$

A plot of $\log x/m$ against $\log C$ should therefore be straight line of slope n and intercept $\log K$.

Experiment:

Determination of the Adsorption Isotherm of Oxalic Acid on Charcoal

Procedure:

- 1- Prepare exactly 0.1 N NaOH, and 0.5N oxalic acid.

- 2- Into 5 small flasks (bottles) introduce the following solutions:
 - a- 100 ml 0.5 N oxalic acid.
 - b- 75 ml 0.5 N oxalic acid + 25ml distilled H₂O.
 - c- 50 ml 0.5 N oxalic acid + 50ml distilled H₂O.
 - d- 25 ml 0.5 N oxalic acid + 75 ml distilled H₂O.

- 3- Take 10ml of each bottle and titrate against NaOH
- 4- To each bottle, a known weight of charcoal (about 1 gm) is added, leave the solutions for about 30 mins. with occasional shaking.

- 5- Filter each solution through a dry small filter paper into a dry receiver, rejecting the first few mls of filtrate.

- 6- Titrate 10 ml of each filtrate with NaOH

Calculations:

1. Tabulate the results as follows:

V₁ ml of NaOH= 10 ml acid before adsorption.

V₂ ml of NaOH= 10 ml acid after adsorption.

Wt of oxalic acid before adsorption $w_1 = N \cdot V_1 \cdot \text{eq.wt} = \text{mg}/10\text{ml}$

Wt of oxalic acid after adsorption $w_2 = N \cdot V_2 \cdot \text{eq.wt} = \text{mg}/10\text{ml}$

$w_1 - w_2 = \text{wt of oxalic acid adsorbed} = x \text{ mg}/10\text{ml}$

Amount of oxalic adsorbed in 1L = $x \cdot 1000/10 \text{ mg}/\text{L}$

Amount of oxalic adsorbed in 1g = $x \cdot 1000/(10 \times 1000) = x/10 \text{ g}/\text{L}$

$m = \text{weight of charcoal} = 1 \text{ gm.}$

$C = \text{equilibrium concentration in gm}/\text{L}$

$C = w_2 \times 100/1000$

2. Plot $\log x/m$ against $\log C$.

3. From the curve find out the value each of the constants n and K .

Homework

- 1- What is the normality of the resulting solution when 2g of oxalic acid (Mwt=126.03 g/mol) is added to 500 ml of water?
- 2- For a solution of polystyrene in toluene ,the $k= 0.00037$, $\alpha= 0.62$ and Viscosity $[\eta]=3.7$ calculate the Mwt of polystyrene?