

Determination of Molecular Mass by OSMOMETRY

osmotic pressure is the only colligative property that is useful for investigating macromolecules.

osmotic pressure measurements are used for studying macromolecules because osmotic changes are larger than the changes in boiling point elevation, freezing point depression and vapour pressure lowering.

If π is the osmotic pressure of a solution in which the mole fraction of the solvent is x_1 , then the condition for equilibrium for the chemical potential of the solvent on both sides of the semipermeable membrane gives

$$RT \ln x_1 + \pi \bar{V}_1 = 0 \quad \text{--- (1)}$$

where γ_1 = Activity coefficient of the solvent
 $\bar{V}_1$ = Partial molar volume of the solvent in the solution

for a dilute soln,

$$x_1 \rightarrow 1 \quad \text{and}$$

$$\bar{V}_1 \rightarrow V_1 \quad \text{the molar volume of the pure solvent.}$$

If we replace x_1 by $(1 - x_2)$ where x_2 is the mole fraction of the solute, then the expansion of the logarithm gives

$$\pi \bar{V}_1^0 = RT \left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \dots \right) \quad \text{--- (2)}$$

For a polymer soln, of concn. C , x_2 is given by

$$x_2 = \frac{C/M}{1/V_1^0 + C/M} \approx \frac{V_1^0 C}{M} \text{ For a dilute soln.} \quad \text{--- (3)}$$

Where M = molar mass of the polymer
 Substituting eqn. (3) in eqn. (2) for an ideal solution. We get

$$\frac{\pi}{C} = \frac{RT}{M} \left[1 + \frac{1}{2} \left(\frac{V_1^0}{M} \right) C + \frac{1}{3} \left(\frac{V_1^0}{M} \right)^2 C^2 + \dots \right] \quad \text{--- (4)}$$

Which is the virial expression of the form,

$$\frac{\pi}{C} = \frac{RT}{M} (1 + A_2 C + A_3 C^2 + \dots) \quad \text{--- (5)}$$

Eqn. (5) is often in the form

$$\frac{\pi}{C} = \frac{RT}{M} \left[\frac{1}{M} + B_2 C + B_3 C^2 + \dots \right] \quad \text{--- (6)}$$

Where B_2, B_3 etc. are the second, third, etc. virial coefficients.

Eqn. (6) is the van't Hoff equation relating the osmotic pressure of a polymer soln. with the molecular mass of the polymer.

The quantity π/C is called reduced osmotic pressure.

If the third term is neglected, a graph of π/C versus C would be a straight line which when extrapolated to $C=0$ gives RT/M as the intercept on the π/C axis.

i.e.

$$\lim_{C \rightarrow 0} (\pi/C) = \frac{RT}{M}$$

from the intercept, the molecular mass M is calculated.

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