# Quadrant II – Transcript and Related Materials

**Programme: Bachelor of Science (Third Year)**

**Subject: Chemistry**

**Paper Code: CHD 105**

**Paper Title: Properties and processes of Molecular Chemistry**

**Unit:5**

**Module Name: Osmotic Pressure Method and Light Scattering**

**Module No:20**

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## 1)Osmotic pressure method

This method has been used in calculating the molecular weight of lyophilic colloids such as gelatin and other macromolecules or high polymers even at low molar concentration.

The Van't Hoff equation can be directly applied to solutions of polymers having diluted solution. The osmotic pressure is given by relation.

$$\Pi = \frac{nRT}{V} = \frac{CRT}{M}$$

where **$\pi$** – osmotic pressure of a solution of concentration **C** in g/L

**M** – Molecular weight of solute in gram

V – Volume of solution in liters for n moles of macromolecules

This equation is applicable to concentration upto 1% . It fails for high polymer or even at low concentration due to the presence of long chains macromolecules.

# Derivation of osmotic pressure for very dilute solution

If $\pi$ is the osmotic pressure of a solution in which $x_1$ is the mole fraction of the solvent molecule .At equilibrium chemical potential of the solvent on both sides of the Osmometer membrane is given by:

$$RT \ln \gamma_1 x_1 + \pi V_1 = 0 \qquad 1)$$

$\gamma_1$ = 1 activity coefficient of the solvent and.

In case of dilute solution $x_1 \rightarrow 1$and $V_1 \rightarrow V_1^0$

$V_1^0$ – molar volume of the pure solvent. If $x_2$ mole fraction of the solute, then $x_1$ written as $1 - x_2$.

Substituting value of $x_1$ and $V_1$

$RT \ln(1 - x_2) + \pi V_1^0 = 0$ 2)

Taking $\pi V_1^0$ on other side we get

$\pi V_1^0 = -RTln ¿$ 3)

Using taylor series for equation 3) and Taking negative sign common

we get

$\pi V_1^0 = RT ¿$ +… ) 4)

For the polymer solution of concentration $c, x_2 \, is \, given \, by:$

$x_2 = \frac{c/M}{\frac{1}{V_1^0} + \frac{c}{M}} \approx \frac{V_1^0 c}{M}$ dilute solution 5)

M- Molar mass of polymer

Substituting value of $x_2$ in equation 5) and taking $\frac{V_1^0 c}{M}$ common we get

we get

$\pi V_1^0 = RT \frac{V_1^0 c}{M} ¿$ 6)

Cancelling $V_1^0$ from both sides in equation 10 and taking c in the denominator on LHS we get

$\frac{\pi}{c} = RT \frac{1}{M} ¿$ 7)

Consider $\frac{1}{2}\left(\frac{V_1^0}{M}\right) = A_1, \frac{1}{3} ¿$ in equation 7 we get

$\frac{\pi}{C} = \frac{RT}{M} ¿$ 8)

where $A1, A2 \ldots.$Are known as first triad….etc virial coefficients.

Dividing M inside the bracket in equation 8 we get

$\frac{\pi}{C} = RT ¿$ 9)

Consider $\frac{A}{M} = B1, \frac{A_1}{M} = B_2$ in equation 10 we get

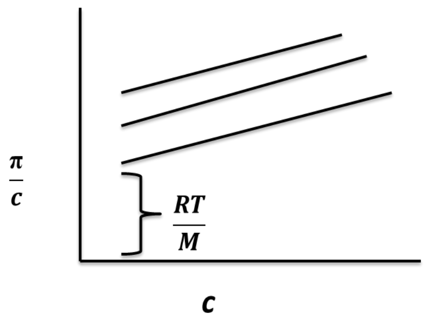
$\frac{\pi}{C} = RT$ ¿ 11)

where $B, B1 \ldots$.Are known as second triad….etc virial coefficients. All these terms are neglected. $\frac{\pi}{C}$ is reduced osmotic pressure.

$\frac{\pi}{C} = \frac{RT}{M}$ 12) This is known as van't Hoff Equation

As the concentration c tends to zero all these terms are neglected. The equation becomes

$$\lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M}$$




Number of solutions of different concentration of the same polymer is prepared and for each concentration osmotic pressure is determined by same standard method. A graph of π/c against concentration c is plotted which gives a straight line plot with positive slope. On extrapolating the graph to zero concentration the intercept of Y axis gives the value of RT/M. Hence the molecular weight is given as:

M¿ $\frac{RT}{intercept}$

This method is limited upto the molecular weight ranging from $10^4$ to $10^6$.

## Light Scattering Method

In case of colloidal dispersion , the colloidal particles being larger in size scatter light to greater extent. This scattering of light is one of the properties of colloidal solution. It was first observed by Tyndall and is known as Tyndall effect. As a result of scattered light colloidal solution appears turbid.The fraction of the incident light scattered per cm length of light path through a sol column is called sol turbidity. This is denoted by T and is evaluated from the expression.

$I_t = I_0 e^{-Tl}$ 1

$I_0$- Intensity of incident light

$I_t$- intensity of transmitted light

l - length of light path

$$\frac{I_t}{I_0} = e^{-Tl}$$

Taking ln on both sides

$$\ln \frac{I_t}{I_0} = -Tl$$

$$T = \frac{1}{l} \ln \frac{I_0}{I_t}$$ Equation for turbidity

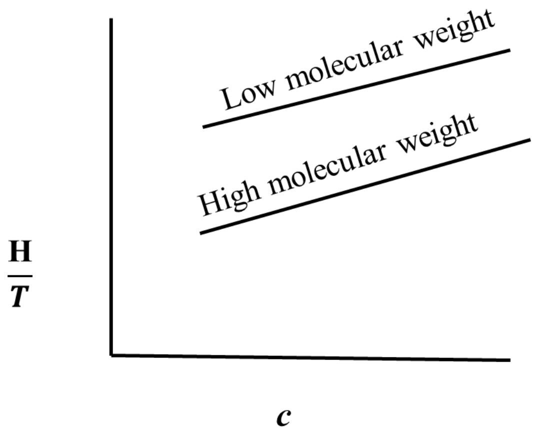
In case of protein and high polymers, turbidity is very small and is determined by measuring the intensity of the light scattered at $90^0$ to the beam. This can be done by using simple type photometer. So turbidity T is related to molecular weight M of macromolecules by following equation

developed by Debye:

$$\lim_{c \to 0} \frac{H_c}{T} = 1/M$$

H – Constant for substance medium combination depends on wavelength of light, refractive index

C- Concentration of solution of macromolecules in g/ml




A graph of Hc /T against concentration c for number of solution of different concentration of same polymer prepared and turbidity of each sol is determined.

It gives a straight line plot with positive slope.

Molecular weight is basically the intercept obtained by extrapolating the graph.

$$M = \frac{1}{Intercept}$$

The turbidity of solution of given concentration increases with increase in molecular weight. This method is useful for solute with molecular weight more than $10^6$

**Limitation**

1. As the amount of light scattered by solutions of macromolecules is very small, it becomes essential to free from impurities such as dust particles which would themselves scatter light considerably .
2. It is valid for macromolecules whose molecular weight is above $10^6$ **.**