Vapour Pressure Osmometry & Light scattering Technique

Vapor-Phase Osmometry

Based on vapour pressure lowering: Colligative property $\overline{M_n}$

P_1 is vapour Pressure of solvent:

$$P = P_1 + P_2 = x_1 P_1^0 + x_2 P_2^0$$

If solute is non volatile:

$$P = x_1 P_1^0 = (1 - x_2) P_1^0$$

After rearranging:

$$x_2 = 1 - \frac{P}{P_1^0} = \frac{P_1^0 - P}{P_1^0} = \frac{-\Delta P}{P_1^0}$$

ΔP: lowering in vapour Pr

$$\frac{\Delta P}{P_1^0} = -x_2 = \frac{W_2/M_2}{(W_1/M_1) + (W_2/M_2)}$$

$$\lim\left(\frac{\Delta P}{P_1^0}\right)_{c_2 \to 0} = -\frac{(W_2/M_2)}{(W_1/M_1)} = -\frac{W_2 M_1}{W_1 M_2} = -c_2 \frac{V_1^o}{M_2}$$

Writing in virial form:

$$\frac{\Delta P}{P_1^0} = -V_1^0 c_2 \left[\frac{1}{M} + Bc_2 + Cc_2^2 + \cdots\right]$$

We can relate ΔP with ΔT using Clausius Clapeyron equation:

$$\Delta T = \frac{\Delta P}{P_1^0} \cdot \frac{RT^2}{\Delta H_v}$$

Latent heat of vaporization of solvent

$$\boxed{\frac{\Delta T}{c_2} = -\frac{RT^2}{\Delta H_v} V_1^0 \left[\frac{1}{M} + Bc_2 + Cc_2^2 + \cdots\right]}$$

M_n of solute can now estimate by measuring $\frac{\Delta T}{c_2}$ while extrapolating it to c_2=0

Practical Aspects

- NO need of membrane in VPO.
- k_s is an instrument constant
- Depend on T, solvent, thermistor pair

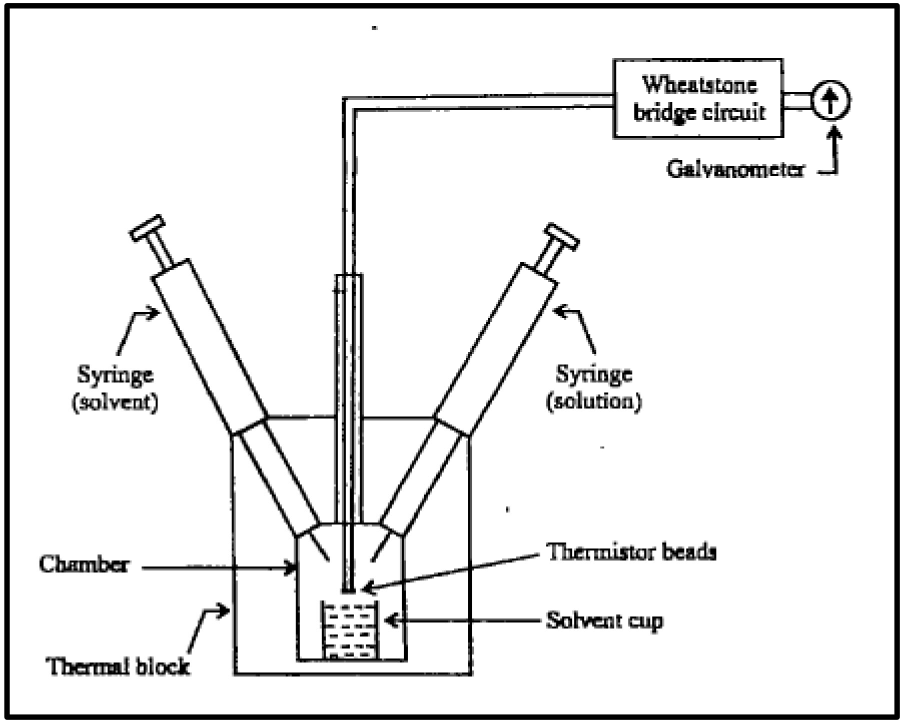
$$\frac{\Delta T}{c_2} = k_s\left[\frac{1}{\overline{M}_n} + Bc_2 + Cc_2^2 + \cdots\right]$$

- ΔT can be measured very accurately as a fn of the bridge imbalance output voltage

$$\frac{\Delta V}{c} = \frac{K}{M} + KBc$$

$$K = M(\Delta V/c)_{c\to 0}$$

Calibration constant



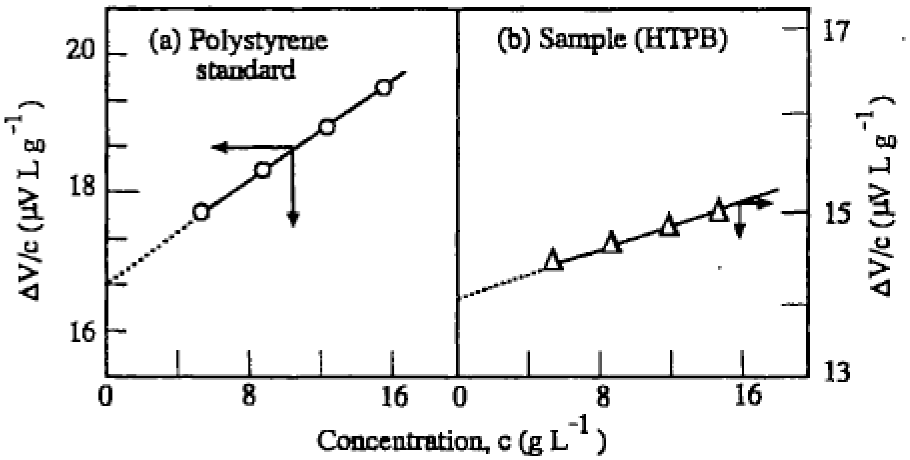
Schematic diagram of a vapour phase osmometer

VPO data for PS of known MW & HTPB in Toluene (70^0C). MW of HTPB…???

Polymer	Concentration, c (g/L)	Bridge output, ΔV (μV)
Standard polystyrene of $\overline{M}_n = 1800$	6	107
	9	164
	12	224
	15	287
HTPB of unknown molecular weight	6	85
	9	129
	12	176
	15	225

$$\frac{\Delta V}{c} = \frac{K}{M} + KBc$$

$$K = M(\Delta V/c)_{c\to 0}$$



Light-Scattering Method

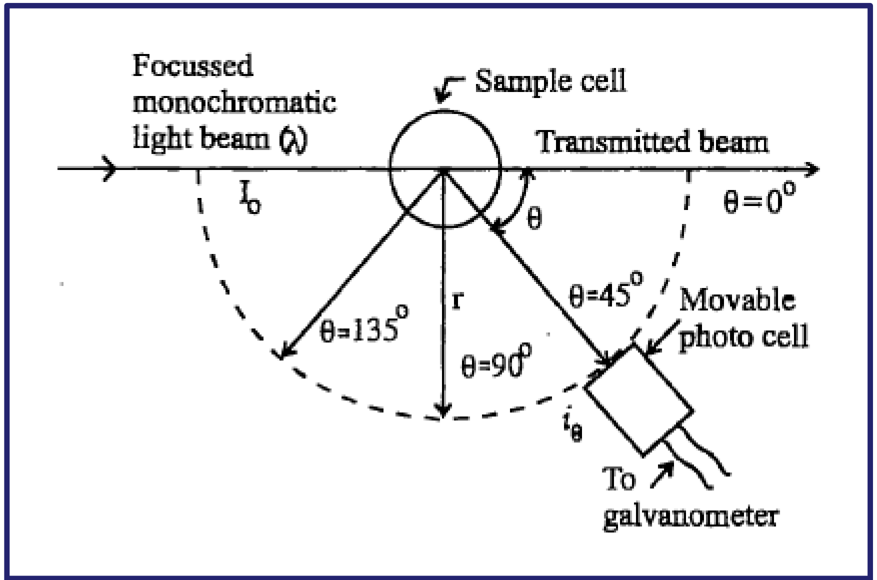
- ❖ Important technique for determination of Mw.
- ❖ Provide information about size and shape of polymer molecules in solution
- ❖ Also characterize the interaction between solvent and polymer molecules
- ❖ Large difference in intensity of incident beam and light scattered beam from polymer solution.

Rayleigh Ratio (R_θ):

Equation for gaseous molecules:

$$\frac{i_\theta r^2}{I_0(1+\cos^2\theta)} = R_\theta = \frac{2\pi^2}{\lambda^4 N_{Av}} \frac{(\bar{n}-1)^2 M}{c}$$

c: conc. of gas (mass/vol)



Arrangement of apparatus to measure light scattered from solution

Can not applicable to the liquids due to strong intermolecular forces are present in Liquids

Light-Scattering Method contd..

❖Einstein developed approach for liquids:

- **Based on local fluctuations in the density, so in refractive index and hence in scattering of incident light.**

$$R_\theta = \frac{i_\theta r^2}{I_0(1 + \cos^2\theta)} = \frac{2\pi^2}{\lambda^4 N_{Av}} \frac{RT}{\beta}\left(\tilde{n}\frac{d\tilde{n}}{dp}\right)^2$$

$$R_\theta(\text{solution}) - R_\theta(\text{solvent})$$

- **Presence of solute in solution causes additional scattering of light**

(Debye model incorporate local fluctuation due to solute concentration:

Random thermal motion are opposed by the osmotic pressure of the solution:

Excess scattering from liquid due to the solute

$$R'_\theta = \frac{i'_\theta r^2}{I_0(1 + \cos^2\theta)} = \frac{2\pi^2}{\lambda^4 N_{Av}}\left(\tilde{n}_0\frac{d\tilde{n}}{dc}\right)^2 \frac{RTc}{(\partial\Pi/\partial c)_T}$$

$$R_\theta(\text{solution}) - R_\theta(\text{solvent})$$

Specific RI increment with c

Light-Scattering Method contd..

❖ **Osmotic pressure for monodisperse solute**

$$\left(\frac{\partial \Pi}{\partial c}\right)_T = RT\left(\frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots\right)$$

❖ **Can be estimate by galvanometer readings (*I*) directly**

$$R'_\theta = \frac{k(I_g - I_{gs})\sin\theta}{1 + \cos^2\theta}$$

$$\frac{volume\ viewed\ at\ \theta = 90^0}{volume\ viewed\ at\ \theta}$$

$$R_\theta = \frac{k I_{gs} \sin\theta}{1 + \cos^2\theta}$$

I_{gs} measured at angle θ and known value of R_θ for the solvent

Relation b/w Turbidity and Rayleigh Ratio

❖ **Turbidity: is measure of decrease of the incident beam Intensity (I_0) scattered I_s per unit length, after passing through of solution.**

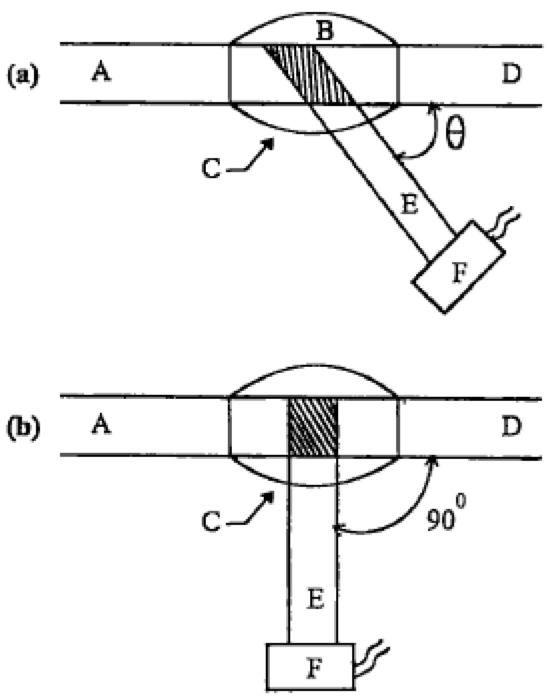
- Can be related as bear's law: $$I/I_0 = e^{-\tau \ell}$$

$$e^{-\tau \ell} = \frac{I_0 - I_s}{I_0} = \frac{I_0 - I_s' \ell}{I_0} = 1 - \frac{I_s' \ell}{I_0}$$

After expanding this series:

$$\tau = I_s'/I_o$$

$$e^{-\tau \ell} = 1 - \tau \ell + \tfrac{1}{2}(\tau \ell)^2 - \tfrac{1}{6}(\tau \ell)^3 + \cdots \simeq 1 - \tau \ell$$



The variation of effective scattering volume (shaded) with angle: (a) $\theta < 90°$; (b) $\theta = 90°$. A: incident beam; B: polymer solution in solvent; C: scattering cell; D: light trap; E: scattered light beam; F: movable photocell connected to galvanometer.

Relation b/w Turbidity and Rayleigh Ratio

Total light intensity scattered per unit length through all angles polar coordinates

$$I_s' = \int_0^{\pi}\int_0^{2\pi} r^2 i_\theta' \sin\theta \, d\theta \, d\phi \qquad R_\theta' = \frac{i_\theta' r^2}{I_0(1 + \cos^2\theta)}$$

$$\frac{I_s'}{I_0} = \tau = \int_0^{\pi}\int_0^{2\pi} R_\theta'(1+\cos^2\theta)\sin\theta \, d\theta \, d\phi \qquad R_\theta' = \frac{2\pi^2}{\lambda^4 N_{Av}}\left(\tilde{n}_0 \frac{d\tilde{n}}{dc}\right)^2 \frac{RTc}{(\partial\Pi/\partial c)_T}$$

$$\tau = \frac{2\pi^2}{\lambda^4 N_{Av}}\left(\tilde{n}_o \frac{d\tilde{n}}{dc}\right)^2 \frac{RTc}{(\partial\Pi/\partial c)_T} \underbrace{\int_0^{\pi}(1+\cos^2\theta)\sin\theta \, d\theta \int_0^{2\pi} d\phi}_{16\pi/3}$$

$$\boxed{\tau = \frac{I_s'}{I_0} = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)\frac{\left(\tilde{n}_o \frac{d\tilde{n}}{dc}\right)^2 RTc}{(\partial\Pi/\partial c)_T}} \qquad \boxed{\tau = \frac{16\pi}{3}R_\theta' = \left(\frac{16\pi}{3}\right)\frac{i_\theta' r^2}{I_0(1+\cos^2\theta)}}$$

❖ **Light scattering of solution may now be related to the solute molecular weight**

$$\frac{\Pi}{c} = RT\left(\frac{1}{M} + A_2c + A_3c^2 + \cdots\right)$$

$$\left(\frac{\partial \Pi}{\partial c}\right)_T = RT\left(\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right)$$

$$\boxed{\tau = \frac{I_s'}{I_0} = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)\frac{\left(\tilde{n}_0\frac{d\tilde{n}}{dc}\right)^2 RTc}{(\partial\Pi/\partial c)_T}}$$

$$\tau = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)c\left(\tilde{n}_0\frac{d\tilde{n}}{dc}\right)^2 \Big/ \left(\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right)$$

$$\boxed{H = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)\left(\tilde{n}_0\frac{d\tilde{n}}{dc}\right)^2}$$

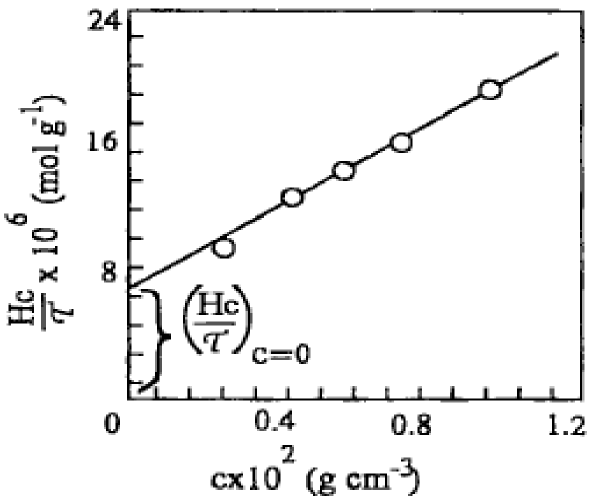
$$\boxed{\frac{Hc}{\tau} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots}$$

$$K = \frac{3H}{16\pi} = \left(\frac{2\pi^2}{\lambda^4 N_{Av}}\right)\left(\tilde{n}_0\frac{d\tilde{n}}{dc}\right)^2$$

$$\frac{Kc}{R_\theta'} = \frac{3Hc}{16\pi R_\theta'} = \frac{Hc}{\tau} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots$$

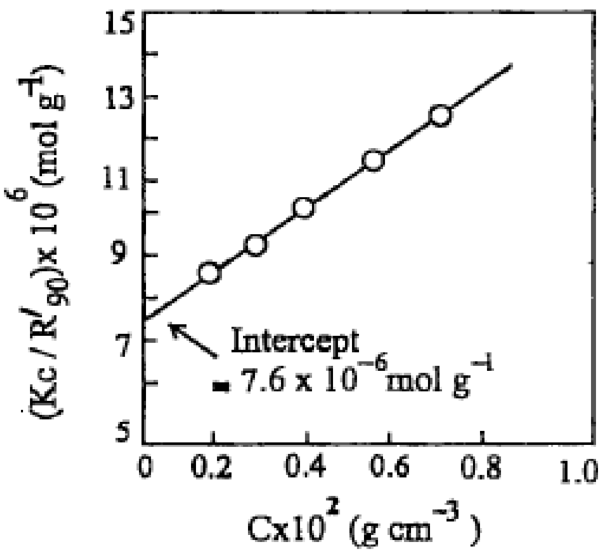
Light scattering determination of the molecular weight of polystyrene

$$\frac{Hc}{\tau} = \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots$$



$$\frac{Kc}{R'_\theta} = \frac{3Hc}{16\pi R'_\theta} = \frac{Hc}{\tau} = \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots$$

Plot of K_c/R'_{90} versus c in the absence of interference effect



Example:

- ❖ Typical light scattering data for solutions of polystyrene in benzene (n_0=1.5010) with λ=4358Å at 20^{o}C

- ❖ Determine the molecular weight of the polymer?

$$\boxed{H = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)\left(\tilde{n}_0 \frac{d\tilde{n}}{dc}\right)^2}$$

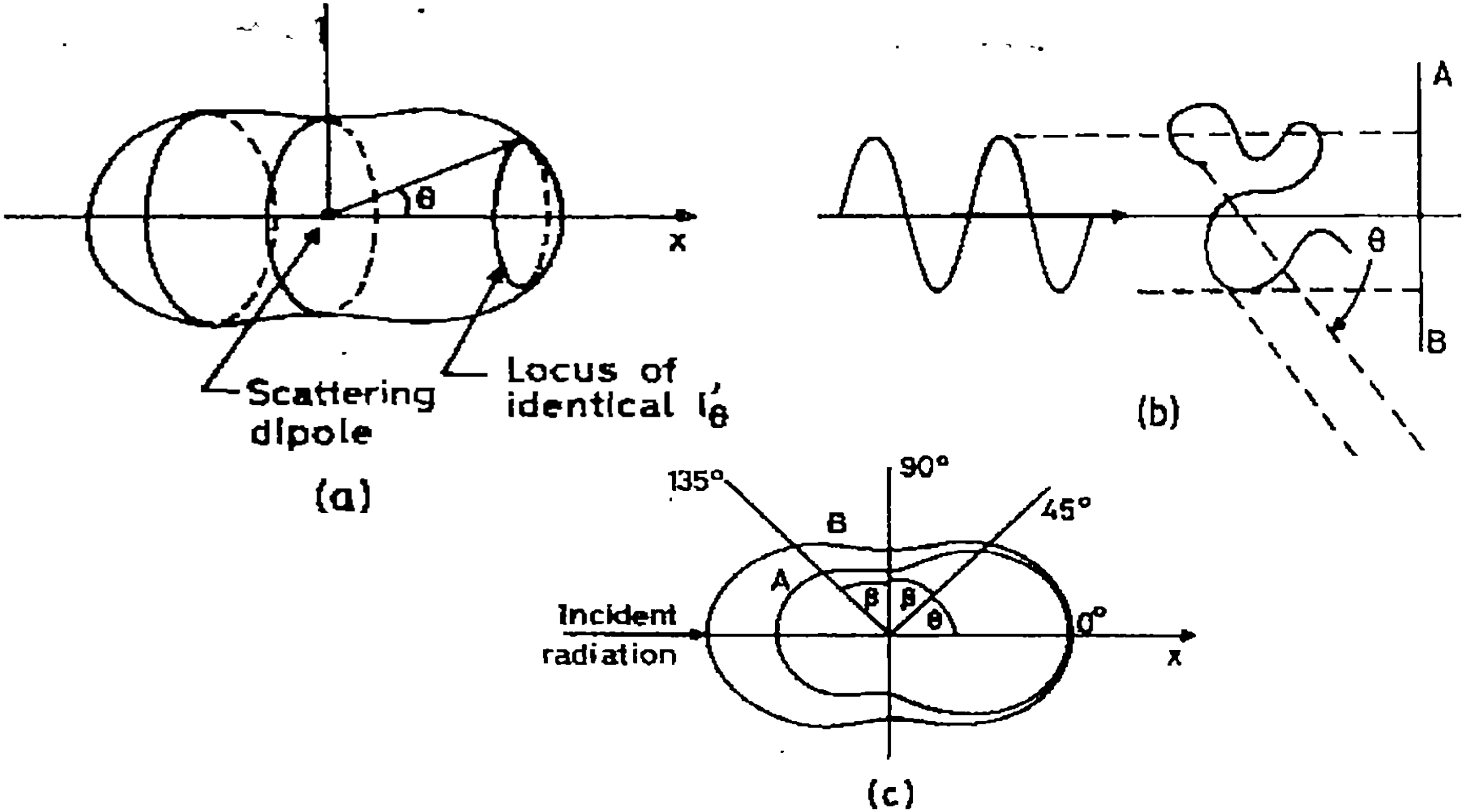
$$H = \left(\frac{32\pi^3}{3\lambda^4 N_{Av}}\right)\tilde{n}_0^2 \left(\frac{\tilde{n} - \tilde{n}_0}{c}\right)^2$$

$$\left(\frac{Hc}{\tau}\right)_{c=0}$$

$$\boxed{\frac{Hc}{\tau} = \frac{1}{M} + 2A_2 c + 3A_3 c^2 + \cdots}$$

Conc. (g/100 cm^3)	$(\tilde{n}-\tilde{n}_o)\times10^2$	$\tau\times10^2$ (cm^{-1})
0.175	0.021	0.093
0.385	0.043	0.144
0.594	0.066	0.182
0.730	0.082	0.198
1.000	0.110	0.226

Dissymmetry of Scattering



$$z_\beta = \frac{i'_{90^\circ - \beta}}{i'_{90^\circ + \beta}} = \frac{i'_\theta}{i'_{\pi-\theta}} = \frac{R'_\theta}{R'_{\pi-\theta}}$$

$$P(\theta) = \frac{(R'_\theta)_{\text{observed}}}{(R'_\theta)_{\text{no interference}}} = \frac{(i'_\theta)_{\text{observed}}}{(i'_\theta)_{\text{no interference}}}$$

$$\frac{Kc}{(R'_\theta)_{\text{observed}}} = \frac{Kc}{P(\theta)\,(R'_\theta)_{\text{no interference}}}$$

$$= \frac{1}{P_\theta}\left[\frac{1}{M} + 2A_2c + 3A_3c^2 + \cdots\right]$$

$$\frac{Kc}{R'_\theta} = \frac{Hc}{\tau} = \frac{1}{M.P(\theta)} + 2A_2c$$

$$\left(\frac{Kc}{R'_\theta}\right)_{c\to 0,\ \theta\to 0} = \left(\frac{Hc}{\tau}\right)_{c\to 0,\ \theta\to 0} = \frac{1}{M}$$

Scattering Factor

$$P(\theta) = \frac{2}{u^2}\left[e^{-u} - (1-u)\right]$$

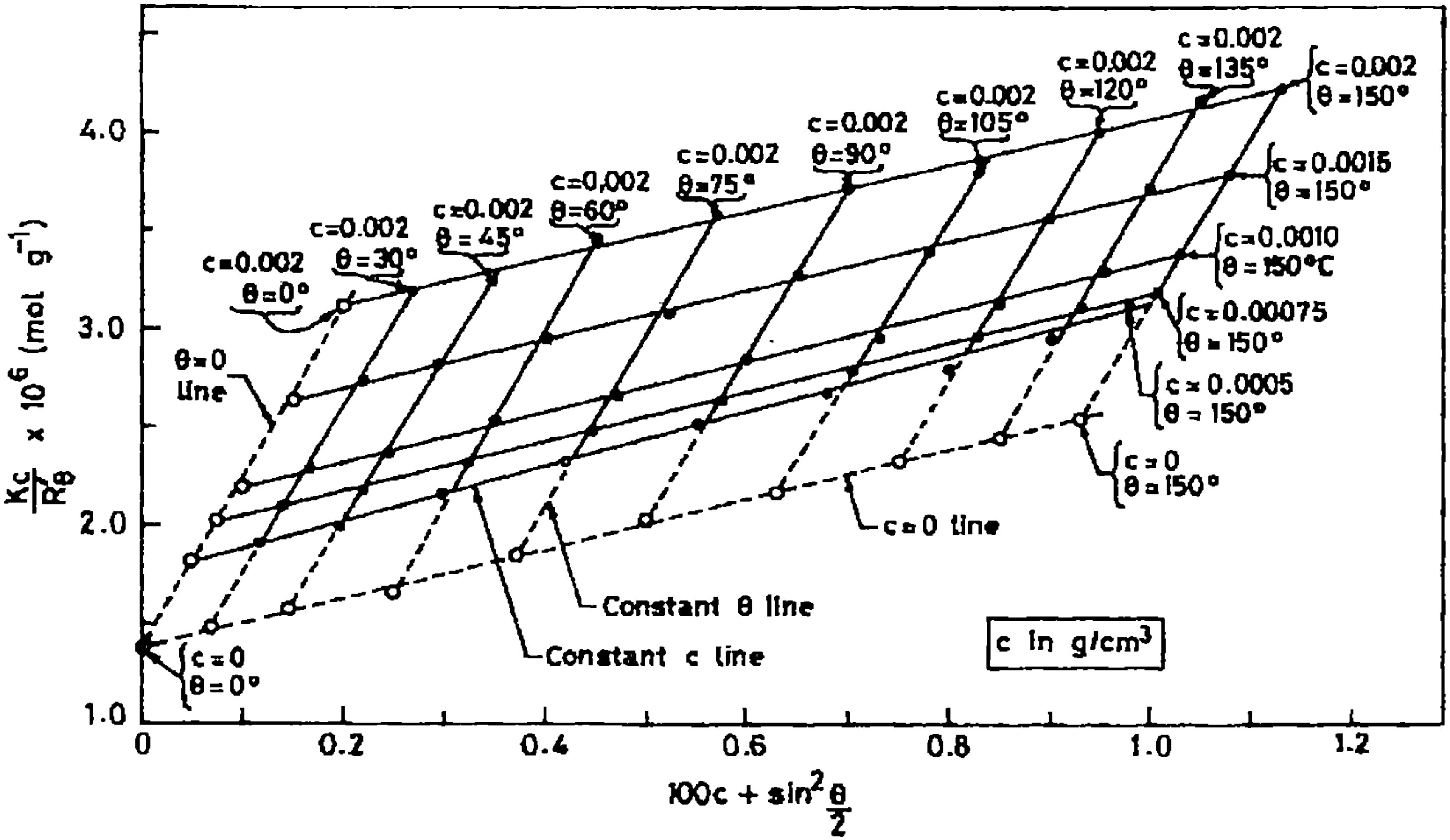
$$u = \left(\frac{2}{3}\right)\left(\frac{\langle r^2\rangle}{\lambda'^2}\right)\left(2\pi \sin\frac{\theta}{2}\right)^2$$

$$P(\theta) = 1 - u/3$$

$$1/P(\theta) = 1 + \left(\frac{8\pi^2}{9\lambda'^2}\right)\langle r^2\rangle \sin^2\frac{\theta}{2}$$

$$\frac{Kc}{R'_\theta} = \frac{Hc}{\tau} = \frac{1}{M} + \left(\frac{1}{M}\right)\left(\frac{8\pi^2}{9\lambda'^2}\right)\langle r^2\rangle \sin^2(\theta/2) + 2A_2c$$

Zimm Plots



Zimm plot for the polystyrene sample