Membrane Osmometry

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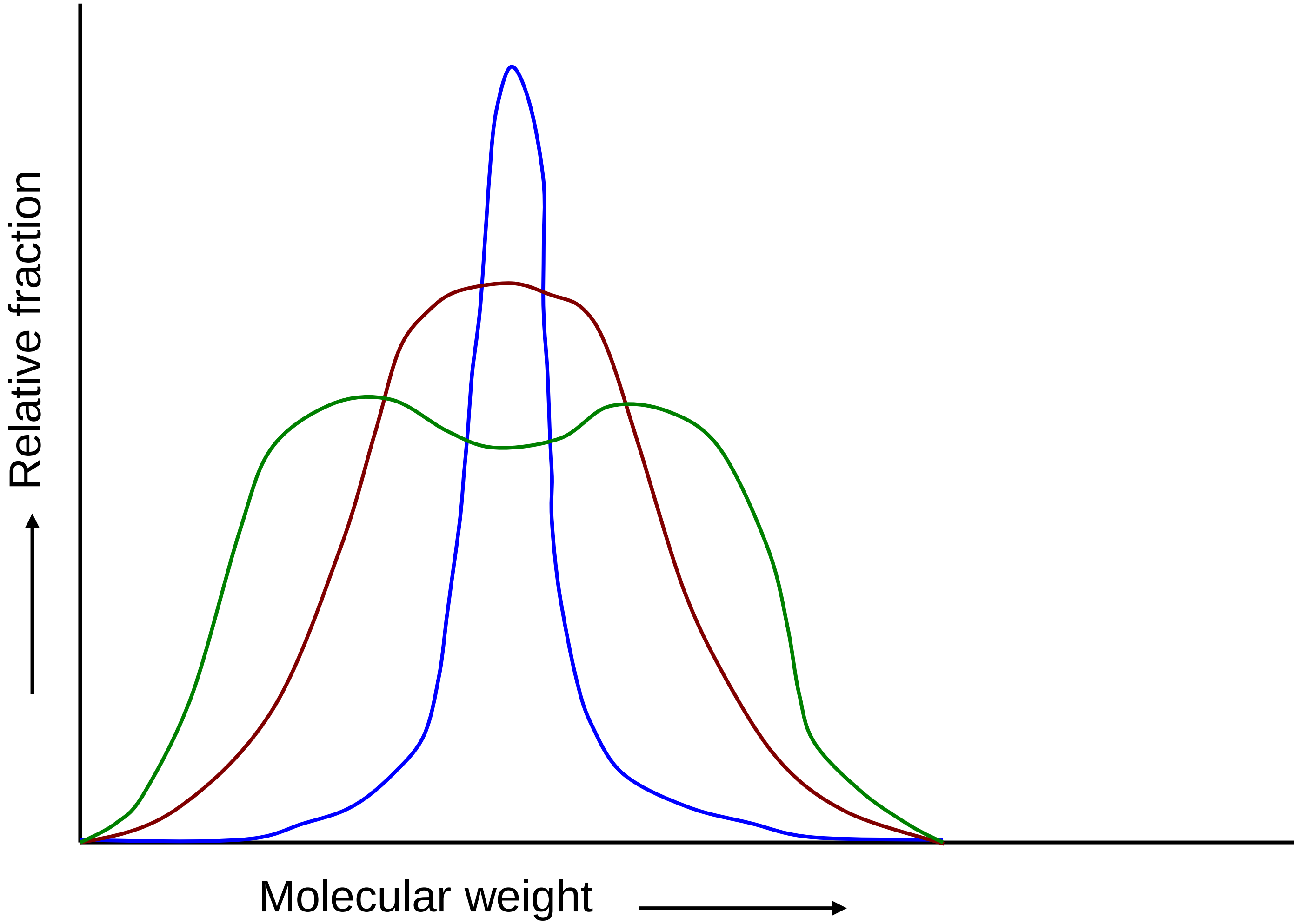
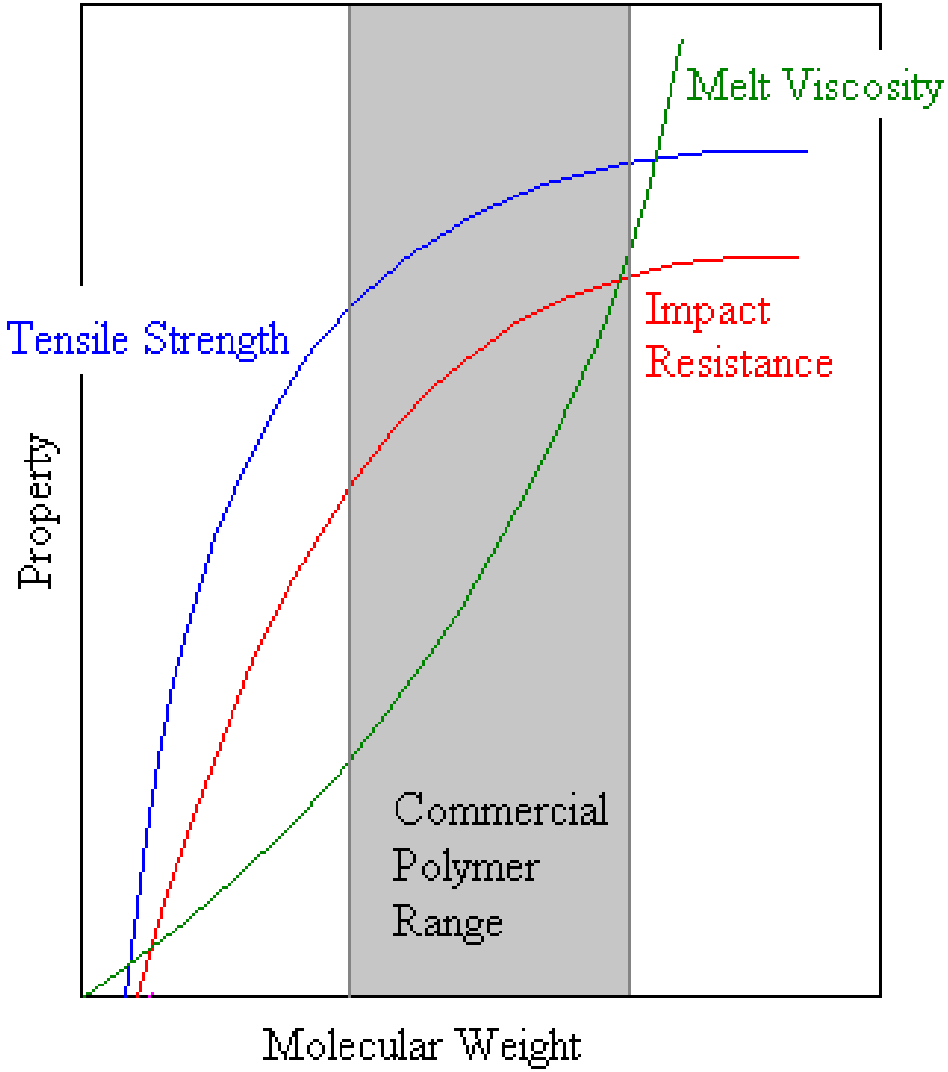
Membrane Osmometry

- Molecular Weight and polymer properties
- Methods Used to determine Mn, Mw
- Membrane Osmometry
  - Introduction and Theory
  - Measuring Mn by osmotic pressure
- Conclusions: Advantages and disadvantages
- Questions

Representative differential weight distribution curves[1]



Relationship of polymer properties to molecular weight.[1]



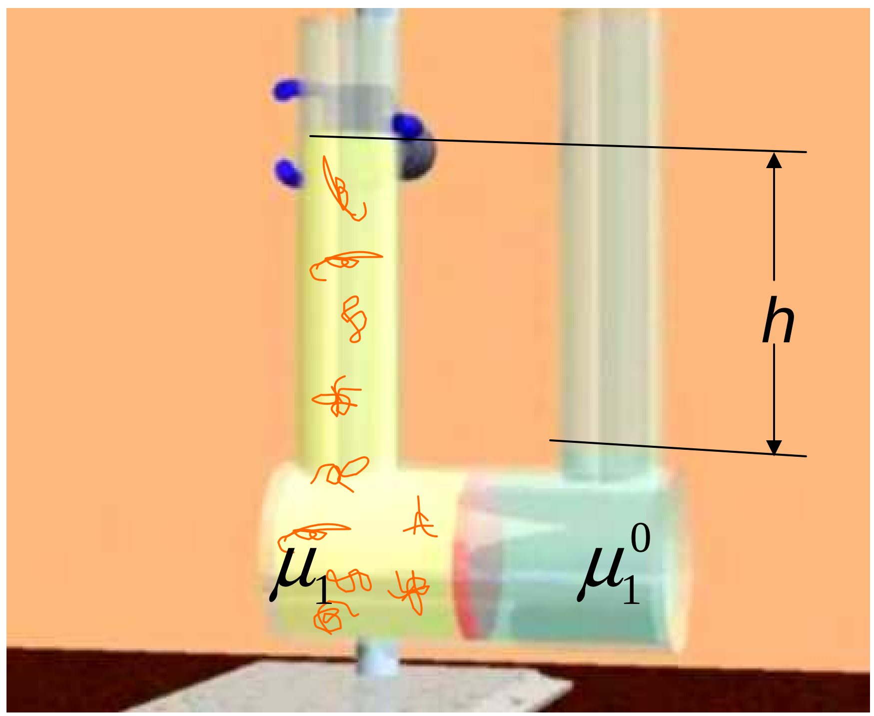
Typical Molecular Weight Determination Methods[1]

Method	Type of mol. wt. avg.	Range	Info.
Light scattering (LS)	$\overline{M}_w$	To ∞	Shape
Membrane osmometry	$\overline{M}_n$	$2x10^4$ to $2x10^6$	
Vapor phase osmometry	$\overline{M}_n$	To $4x10^4$	
Electron and X-ray microscopy	$\overline{M}_{n,w,z}$	10^2 to ∞	Shape, dist
Ebulliometry	$\overline{M}_n$	To $4x10^4$	
Cryoscopy	$\overline{M}_n$	To $5x10^4$	
End Group Analysis	$\overline{M}_n$	To $2x10^4$	
Osmodialysis	$\overline{M}_n$	500-2500	
Centrifugation	$\overline{M}_{z,w}$	To ∞	
SEC, with *c* detector	Relative	To ∞	Mol w Dist
SEC, with *c* and LS detectors	$\overline{M}_{n,w}$	To ∞	Mol w Dist
Viscometry	Relative	To ∞	

Membrane Osmometry
Introduction and Theory

Osmosis and Osmotic Pressure

Osmosis and Chemical Potential



Equilibrium of Chemical Potential[2]

$$\mu_1^0 = \mu_1 + \int_{P_0}^{P} \left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} dP \qquad (I)$$

$$From\ \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}\ it\ follows\ that \qquad (II)$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} = \frac{\partial}{\partial n_1}\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2}$$

$$Since \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} = V\ (i.e.\ the\ solution\ volume)\ then \qquad (III)$$

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,n_1,n_2} = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} = \overline{V}_1 \qquad (IV)$$

$$\mu_1^0 = \mu_1 + (P - P_0)\overline{V}_1 \qquad (V)$$

$$\mu_1 - \mu_1^0 = -\pi\overline{V}_1 \qquad (VI)$$

Osmotic Pressure

Floury – Huggins expression for $\mu_1 - \mu_1^0$

$$\mu_1 - \mu_1^0 = -\mathrm{R}T\phi_2 / x + \mathrm{R}T\left(\chi - \frac{1}{2}\right)\phi_2^2 \qquad (VII)$$

$$\pi = \mathrm{R}T\phi_2 / x\overline{V}_1 + \mathrm{R}T\left(\frac{1}{2} - \chi\right)\phi_2^2 / \overline{V}_1 \qquad (VIII)$$

$$\overline{V}_1 = V_1 \qquad (IX)$$

$$\phi_2 = \frac{xn_2}{(n_1 + xn_2)} \approx \frac{xn_2}{n_1} \qquad (X)$$

$$V \approx n_1 V_1 \qquad (XI)$$

$$\phi_2 / x\overline{V} = n_2 / V \qquad (XII)$$

$$\pi = \mathrm{R}T(n_2 / V) + \mathrm{R}T\left(\frac{1}{2} - \chi\right)x^2 V_1 (n_2 / V)^2 \qquad (XIII)$$

Osmotic Pressure and $\overline{M}_n$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{m}{n_2} \qquad (XIV)$$

$$\frac{n_2}{V} = \left(\frac{m}{V}\right)\left(\frac{n_2}{m}\right) = \frac{c}{\overline{M}_n} \qquad (XV)$$

$$\frac{\pi}{c} = \frac{\mathrm{R}T}{\overline{M}_n} + \left(\frac{\mathrm{R}T}{V_1}\right)\left(\frac{1}{2} - \chi\right)\left(\frac{xV_1}{\overline{M}_n}\right)^2 c \qquad (XVI)$$

$$x = V_2 / V_1 \qquad (XVII)$$

$$\frac{xV_1}{\overline{M}_n} = \frac{V_2}{\overline{M}_n} = \frac{1}{\rho_2} \qquad (XIX)$$

$$\frac{\pi}{c} = \frac{\mathrm{R}T}{\overline{M}_n} + \left(\frac{\mathrm{R}T}{V_1 \rho_2^2}\right)\left(\frac{1}{2} - \chi\right)c \qquad (XX)$$

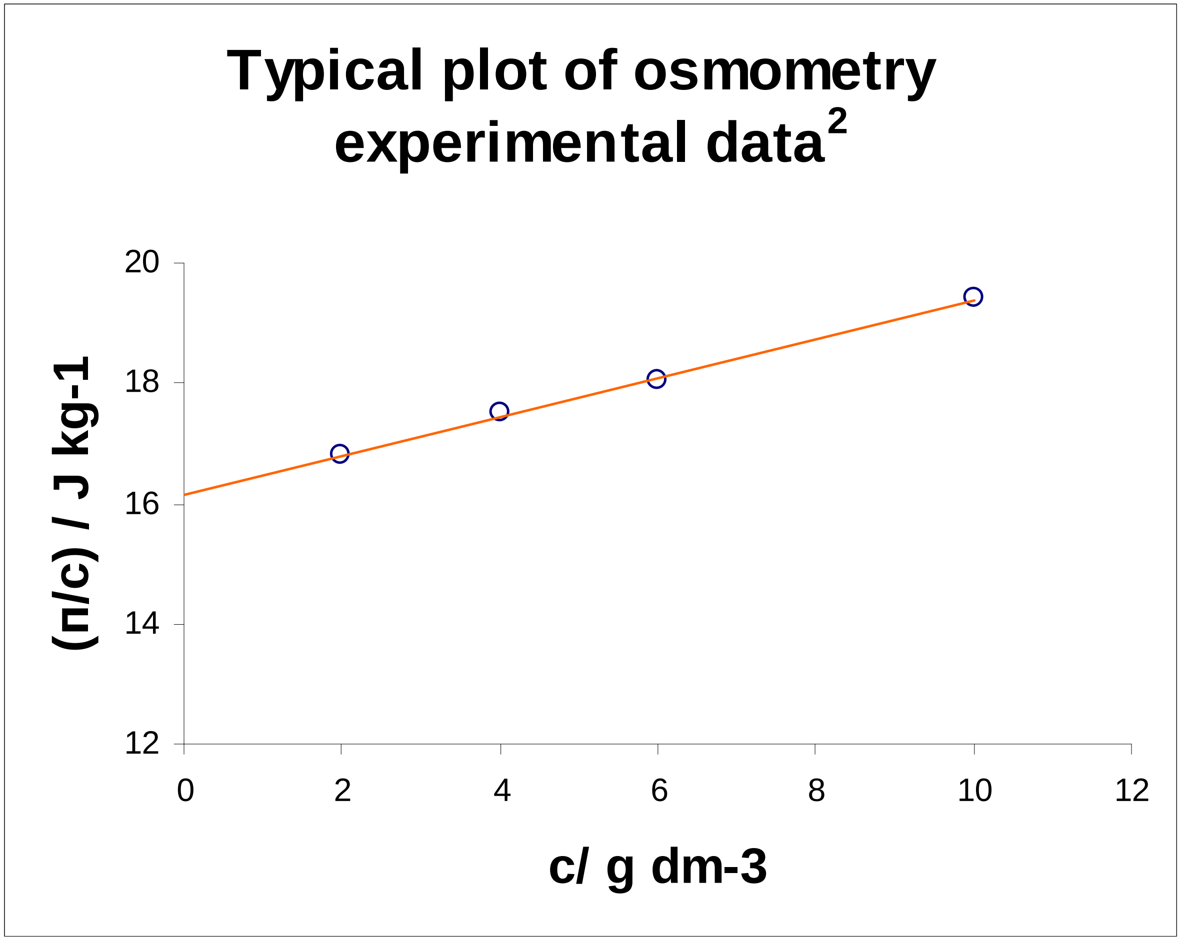
Osmotic Pressure and $\overline{M}_n$

$$\left(\frac{\pi}{c}\right)_{\theta} = \frac{\mathrm{R}T}{\overline{M}_n} \qquad (XXI)$$

$$\left(\frac{\pi}{c}\right)_{c\to 0} = \frac{\mathrm{R}T}{\overline{M}_n} \qquad (XXII)$$

$$\frac{\pi}{c} = \mathrm{R}T\left(\frac{1}{\overline{M}_n} + A_2 c + A_3 c^2 + \ldots\right) \qquad (XXIII)$$

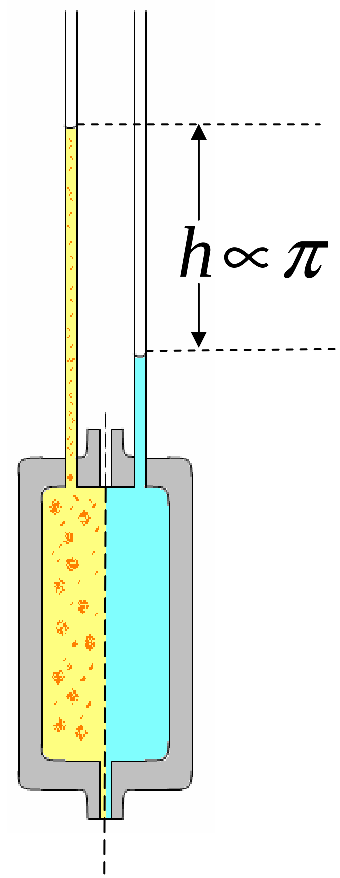
Osmotic Pressure and $\overline{M}_n$



Measuring $\overline{M}_n$ by osmotic pressure

Membrane osmometers used:

- Static osmometer[2]
  - Equilibrium by natural diffusion
  - Large cell volumes
  - Long equilibrium times

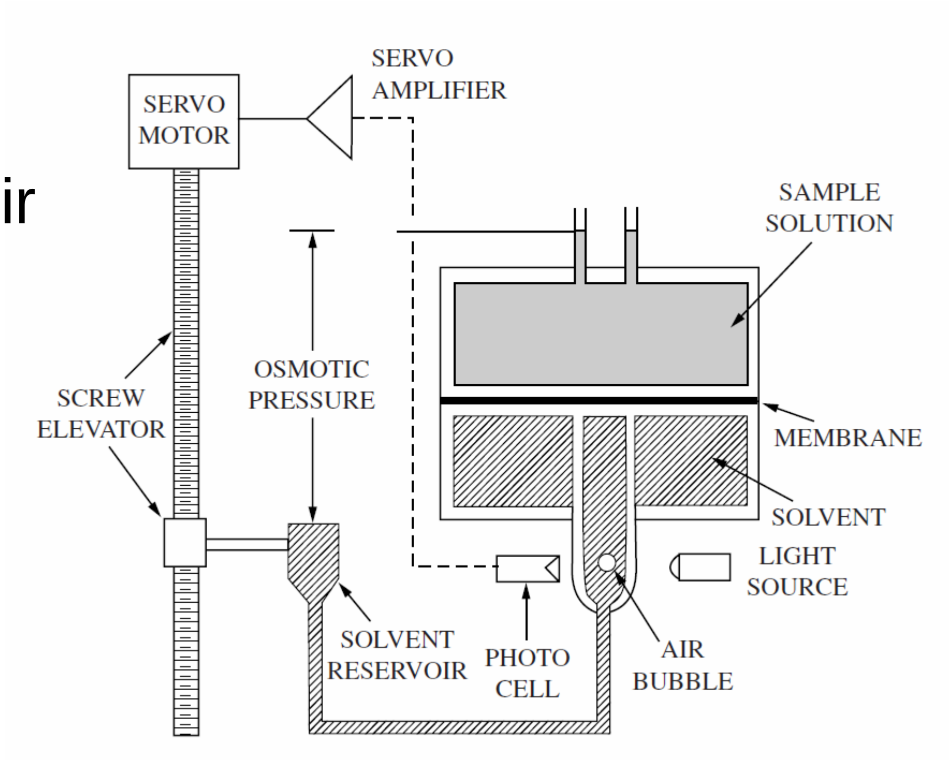


Measuring $\overline{M}_n$ by osmotic pressure

Membrane osmometers used:

➢Dynamic osometer[3]

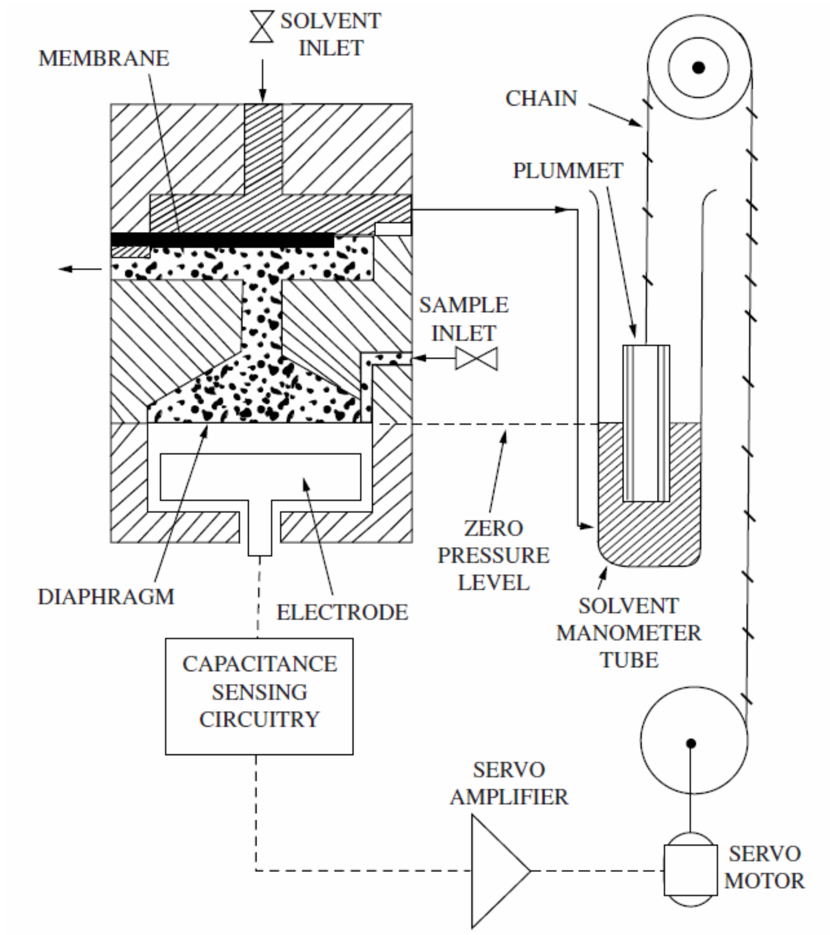
- Equilibrium by reducing pressure on solution reservoir
- Small cell volumes
- Short equilibrium times



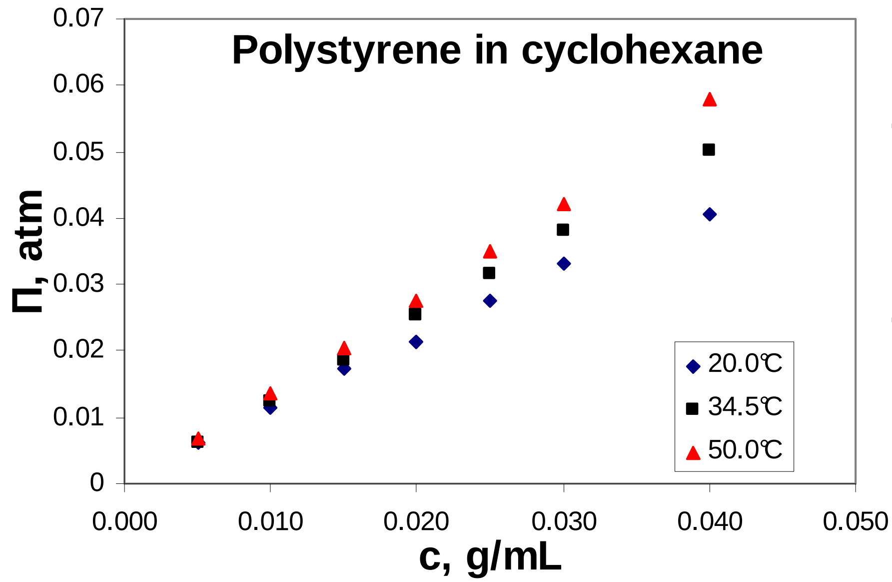
Measuring $\overline{M}_n$ by osmotic pressure

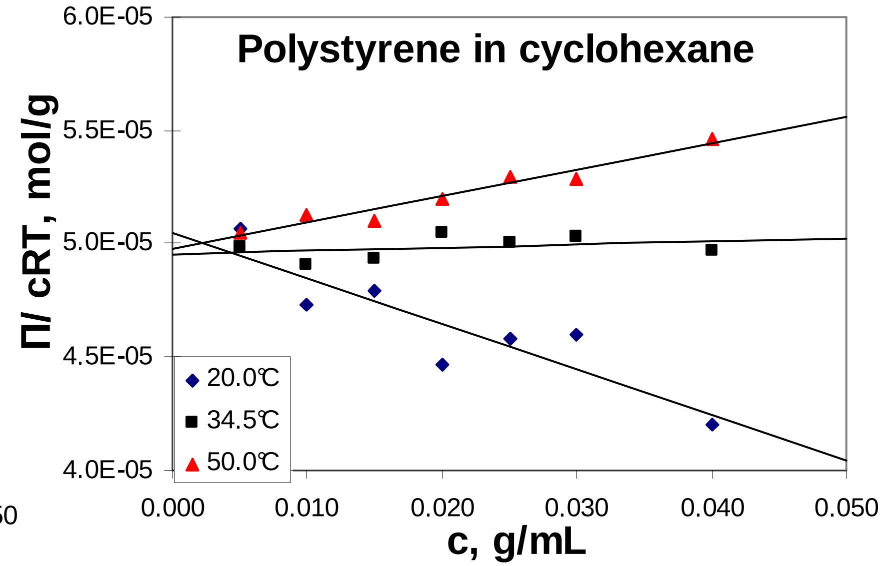
Membrane osmometers used:

- Dynamic osometer[3]



Osmotic Pressure and $\overline{M}_n$





20.0℃:Slope = A_2 = -2.0×10^{-4} cm^3 mol/g^2

1/intercept = M_n = 1.97×10^4 g/mol

34.5℃:Slope = A_2 = 1.7×10^{-5} cm^3 mol/g^2

1/intercept = M_n = 2.02×10^4 g/mol

50.0℃:Slope = A_2 = 1.7×10^{-5} cm^3 mol/g^2

1/intercept = M_n = 2.00×10^4 g/mol

Conclusion: Advantages and disadvantages

Disadvantages

- Membrane problems: leakage, asymmetry and ballooning
- Overestimation of molecular due low molecular weight molecules
- Not suitable for electrolytes

Advantages

- Absolute value of Mn
- No calibration with standards required
- Independent of chemical heterogeneity
- Applicable to polymers with broad range of molecular weights
- Measurement of Mn within 10,000 to $2x10^6$

Questions?

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