Membrane Osmometry

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CH 392N

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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

<table>
<thead>
<tr>
<th>Method</th>
<th>Type of mol. wt. avg.</th>
<th>Range</th>
<th>Info.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light scattering (LS)</td>
<td>$M_w$</td>
<td>To $\infty$</td>
<td>Shape</td>
</tr>
<tr>
<td>Membrane osmometry</td>
<td>$M_n$</td>
<td>$2 \times 10^4$ to $2 \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>Vapor phase osmometry</td>
<td>$M_n$</td>
<td>To $4 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>Electron and X-ray microscopy</td>
<td>$M_{n,w,z}$</td>
<td>$10^2$ to $\infty$</td>
<td>Shape, dist</td>
</tr>
<tr>
<td>Ebulliometry</td>
<td>$M_n$</td>
<td>To $4 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>Cryoscopy</td>
<td>$M_n$</td>
<td>To $5 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>End Group Analysis</td>
<td>$M_n$</td>
<td>To $2 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>Osmiodialysis</td>
<td>$M_n$</td>
<td>500-2500</td>
<td></td>
</tr>
<tr>
<td>Centrifugation</td>
<td>$M_{z,w}$</td>
<td>To $\infty$</td>
<td></td>
</tr>
<tr>
<td>SEC, with c detector</td>
<td>Relative</td>
<td>To $\infty$</td>
<td>Mol w Dist</td>
</tr>
<tr>
<td>SEC, with c and LS detectors</td>
<td>$M_{n,w}$</td>
<td>To $\infty$</td>
<td>Mol w Dist</td>
</tr>
<tr>
<td>Viscometry</td>
<td>Relative</td>
<td>To $\infty$</td>
<td></td>
</tr>
</tbody>
</table>
Membrane Osmometry
Introduction and Theory

Osmosis and Osmotic Pressure

Osmosis and Chemical Potential
Equilibrium of Chemical Potential²

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

(I)

From \( \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P,T,n_j} \)

it follows that

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

(II)

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

\[ \left( \frac{\partial \mu_1}{\partial P} \right)_{T,n_1,n_2} = \left( \frac{\partial G}{\partial n_1} \right)_{T,P,n_2} = \bar{V}_1 \]

(III)

(IV)

\[ \mu_1^0 = \mu_1 + (P - P_0)\bar{V}_1 \]

(V)

\[ \mu_1 - \mu_1^0 = -\pi\bar{V}_1 \]

(VI)
Osmotic Pressure

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

$$\mu_1 - \mu_1^0 = -RT \phi_2 / x + RT \left( \chi - \frac{1}{2} \right) \phi_2^2$$  \hspace{1cm} (VII)$$

$$\pi = RT \phi_2 / x \bar{V} + RT \left( \frac{1}{2} - \chi \right) \phi_2^2 / \bar{V}_1$$  \hspace{1cm} (VIII)$$

$$\bar{V}_1 = V_1$$  \hspace{1cm} (IX)$$

$$\phi_2 = \frac{x n_2}{(n_1 + x n_2)} \approx \frac{x n_2}{n_1}$$  \hspace{1cm} (X)$$

$$V \approx n_1 V_1$$  \hspace{1cm} (XI)$$

$$\phi_2 / x \bar{V} = n_2 / V$$  \hspace{1cm} (XII)$$

$$\pi = RT \left( n_2 / V \right) + RT \left( \frac{1}{2} - \chi \right) x^2 V_1 \left( n_2 / V \right)^2$$  \hspace{1cm} (XIII)$$
Osmotic Pressure and $\overline{M}_n$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{m}{n_2}$$  \hspace{1cm} (XIV)

$$n_2 = \left(\frac{m}{V}\right)\left(\frac{n_2}{m}\right) = \frac{c}{\overline{M}_n}$$  \hspace{1cm} (XV)

$$\pi = \frac{RT}{c} + \left(\frac{RT}{V_1}\right)\left(\frac{1}{2} - \chi\right)\left(\frac{xV_1}{\overline{M}_n}\right)^2 c$$  \hspace{1cm} (XVI)

$$x = V_2 / V_1$$  \hspace{1cm} (XVII)

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

$$\pi = \frac{RT}{c} + \left(\frac{RT}{V_1\rho_2^2}\right)\left(\frac{1}{2} - \chi\right) c$$  \hspace{1cm} (XX)
Osmotic Pressure and $\overline{M}_n$

\[
\left( \frac{\pi}{c} \right)_{\theta} = \frac{RT}{\overline{M}_n} \quad (XXI)
\]

\[
\left( \frac{\pi}{c} \right)_{c \to 0} = \frac{RT}{\overline{M}_n} \quad (XXII)
\]

\[
\frac{\pi}{c} = RT \left( \frac{1}{\overline{M}_n} + A_2c + A_3c^2 + \ldots \right) \quad (XXIII)
\]
Osmotic Pressure and $\bar{M}_n$

Typical plot of osmometry experimental data

$\frac{n}{c}$ / J kg$^{-1}$

c/ g dm$^{-3}$
Measuring $\overline{M}_n$ by osmotic pressure

Membrane osmometers used:

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

$h \propto \pi$
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°C: Slope = $A_2 = -2.0 \times 10^{-4}$ cm$^3$ mol/g$^2$

1/intercept = $M_n = 1.97 \times 10^4$ g/mol

34.5°C: Slope = $A_2 = 1.7 \times 10^{-5}$ cm$^3$ mol/g$^2$

1/intercept = $M_n = 2.02 \times 10^4$ g/mol

50.0°C: Slope = $A_2 = 1.7 \times 10^{-5}$ cm$^3$ mol/g$^2$

1/intercept = $M_n = 2.00 \times 10^4$ 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?
References

References

11. http://www.gonotec.com/content.OSMO_090.PRODUCTS_CHEM.OSMO_090.USA.ENG.html