Vapor Phase Osmometry

For determination of the Number Average Molecular Weight of a Polymer Sample

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Outline

• Introduction & Fundamentals

• Equations

• Instrument & Experiment

• Conclusion
A relative technique used to determine the Number Average Molecular Weight ($M_n$) of a polymer in a dilute polymer solution. Most common methods for measuring $M_n$ are Membrane Osmometry and Vapor Phase Osmometry. Used for polymers with molecular weights in the range of 250 to 100,000.
Introduction & Fundamentals

• Vapor Phase Osmometry is based on the equilibrium thermodynamics of vapor pressure

• Vapor Pressure is a colligative property

Evaporation in a Closed Container
Introduction & Fundamentals

• The determination of $M_n$ operates on the principle that the vapor pressure of a solution is lower than that of the pure solvent at the same temperature and pressure.

• Magnitude of the vapor pressure decrease is directly proportional to the molar concentration of solute.

• Does not directly measure vapor pressure but measures change in voltage which is proportional to change in temperature.
Equations

Altering the chemical potential of a solvent by dissolving a non-volatile substance in it alters the colligative properties of the solvent.

- At equilibrium:
  \[ \mu_1^l = \mu_1^v \]  

- Upon adjustment to new equilibrium:
  \[ d\mu_1^l = d\mu_1^v \]

- Where:
  \[ \mu = \mu(p, T, x) \]
  
  \[ l \quad liquid \quad v \quad vapor \]
  
  \[ 1 \quad solvent \quad 2 \quad solute \]
Equations

• The total differential of the chemical potential:

\begin{align*}
(3) \quad d\mu_1^l(p, T, x_1^l) &= \left( \frac{\partial \mu_1^l}{\partial T} \right)_{p, x_1^l} \, dT + \left( \frac{\partial \mu_1^l}{\partial x_1^l} \right)_{p, T} \, dx_1^l + \left( \frac{\partial \mu_1^l}{\partial p} \right)_{T, x_1^l} \, dP \\
(4) \quad d\mu_1^\nu(p, T, x_1^\nu) &= \left( \frac{\partial \mu_1^\nu}{\partial T} \right)_{p, x_1^\nu} \, dT + \left( \frac{\partial \mu_1^\nu}{\partial x_1^\nu} \right)_{p, T} \, dx_1^\nu + \left( \frac{\partial \mu_1^\nu}{\partial p} \right)_{T, x_1^\nu} \, dP
\end{align*}

• Where:

- \( x \) – mole fraction
- \( T \) – temperature
- \( p \) – pressure
- \( p = \text{constant}, dp = 0, dx_1^\nu = 0 \)
Equations

- Simplifying and equating (3) and (4):

\[
\begin{align*}
(5) & \quad \left( \frac{\partial \mu_1^l}{\partial T} \right)_{p,x_1^l} \, dT + \left( \frac{\partial \mu_1^l}{\partial x_1^l} \right)_{p,T} \, dx_1^l = \left( \frac{\partial \mu_1^f}{\partial T} \right)_{p,x_1^f} \, dT \\
(6) & \quad \left( \frac{\partial \mu_1^{l,v}}{\partial T} \right)_{p,x_1} \, dT = -S_1^{l,v} \quad \left( \frac{\partial \mu_1^l}{\partial x_1} \right)_{p,T} \, dx_1 = RT \, d\ln x_1 \gamma_1 \\
\end{align*}
\]

- And from other Thermodynamic equations:

\[
S_1^l - S_1^v = \frac{\Delta H_v}{T}
\]

- Where

\[
R \quad \text{gas constant} \quad \quad \quad \quad S \quad \text{Entropy}
\]

\[
\Delta H_v \quad \text{enthalpy of vaporization}
\]

\[
\gamma_1 \quad \text{activity coefficient of the solvent}
\]
Equations

• Substituting equations from (6) into (5):

\[ d\ln x_1 \gamma_1 = \frac{\Delta H_v}{RT^2} dT \]  \hspace{1cm} (7)

• Where:

\[ \gamma_1 = 1 \text{ for dilute solution} \]

• Integrating (7):

\[ \int_1^{x_1} d\ln x_1 = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \text{For } dT \ll T_1 \quad \Rightarrow \quad \ln x_1 = -\frac{\Delta H_v}{RT_1^2} \Delta T \]  \hspace{1cm} (8)
Equations

• And:

\[
\ln x_1 = \ln(1 - x_2) \approx -x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{g_2 M_1}{M_2 g_1}
\]

• Where:

- \( n \) – number of moles
- \( g \) – initial weight of solvent or solute
- \( M \) – molecular weight

• Rearranging # will yield an equation of temperature in terms of the number of dissolved solute particles:

\[
\Delta T = \frac{RT^2}{\Delta H_v} x_2
\]
Instrument & Experiment

• The wick provides a vapor saturated atmosphere

• Syringes used to inject standard and sample

• Thermistors detect changes in temperature

• Voltage changes are recorded

• System at an equilibrated temperature
Instrument & Experiment

• Calibration with standards is necessary
  – Must have VP no more than 0.1% of that of the solvent
  – High Solubility

• Common solvents are:
  – Sucrose octaacetate for organic solution
  – Simple sucrose for aqueous solution

Calibration Curve

Best fit line extrapolated to zero

$\frac{\Delta V}{C}$

$C \left( \frac{g}{mol} \right)$

$(V \frac{g}{mol})$
Instrument & Experiment

- Calibration is necessary to determine the Calibration Factor, $K$
  \[ K = \frac{\Delta VM_2}{C_2} \]

- Where:
  
  $C$ – concentration  
  $V$ – voltage

- Molecular weight determine by:
  \[ M_2 = \frac{KC_2}{\Delta V} \]
Instrument & Experiment

Sample Data

Characteristic Data of Solvents and Polymers

<table>
<thead>
<tr>
<th>Materials</th>
<th>Molar volume (cm$^3$/mol)</th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/cm$^3$)</th>
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</thead>
<tbody>
<tr>
<td>Benzil</td>
<td></td>
<td>210.23</td>
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<tr>
<td>Urea</td>
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<td>60.06</td>
<td></td>
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<tr>
<td>NMP</td>
<td>96.52</td>
<td>99.13</td>
<td>1.027</td>
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<tr>
<td>DMAc</td>
<td>92.98</td>
<td>87.12</td>
<td>0.937</td>
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<tr>
<td>DMF</td>
<td>77.34</td>
<td>73.09</td>
<td>0.945</td>
</tr>
<tr>
<td>Water</td>
<td>18.05</td>
<td>18</td>
<td>0.997</td>
</tr>
<tr>
<td>PEI</td>
<td>25 486</td>
<td>32 800$^a$</td>
<td>1.287</td>
</tr>
<tr>
<td>PSU</td>
<td>31 452</td>
<td>39 000$^b$</td>
<td>1.24</td>
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<tr>
<td>PES</td>
<td>35 766</td>
<td>49 000$^b$</td>
<td>1.37</td>
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<tr>
<td>PVP</td>
<td>310 345</td>
<td>360 000$^c$</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Calibration constants, K (Volt g/mol)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
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<tr>
<td>NMP</td>
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<tr>
<td>DMAc</td>
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<tr>
<td>DMF</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>509</td>
</tr>
</tbody>
</table>

$^a$ Weight average.
$^b$ Number average.
$^c$ Data of the supplier.
Instrument & Experiment
Conclusion

• Advantages of VPO include:
  – Speed
    • Isothermal distillation & Ebullioscopy are slow
  – Accuracy
    • Cryoscopy has typical standard deviation of ~10%
  – Small amount of sample required
    • Ebullioscopy requires relatively large amount of sample
  – Useful for a wide range of temperatures
    • Cryoscopy & Ebullioscopy less flexible
Conclusion

• Disadvantages of VPO include:
  – Requires calibration
    • Membrane Osmometry does not
  – Molecular weight constraints

• Questions?
References

   http://www.chem.ufl.edu/~polymer/instrumentation/vpo.html
   http://www.sciencedirect.com.ezproxy.lib.utexas.edu/science