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

Introduction & Fundamentals

- 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
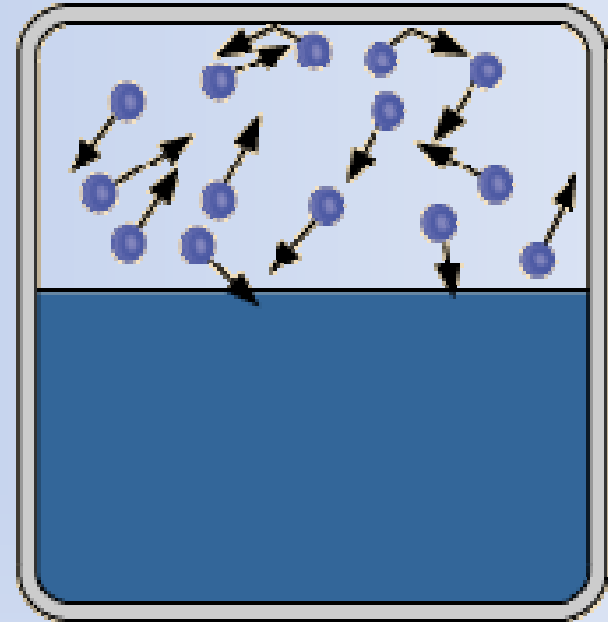
Evaporation in a Closed Container

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:

$$(1) \quad \mu_1^l = \mu_1^v$$

- Upon adjustment to new equilibrium:

$$(2) \quad d\mu_1^l = d\mu_1^v$$

- Where:

$$\mu = \mu(p, T, x)$$

$$l - liquid \qquad v - vapor$$
$$1 - solvent \qquad 2 - solute$$

Equations

- The total differential of the chemical potential:

(3) $$d\mu_1^l(p, T, x_1^l) = \left(\frac{\partial \mu_1^l}{\partial T}\right)_{p, x_1^l} dT + \left(\frac{\partial \mu_1^l}{\partial x_1^l}\right)_{p, T} dx_1^l + \left(\frac{\partial \mu_1^l}{\partial P}\right)_{T, x_1^l} dP$$

(4) $$d\mu_1^v(p, T, x_1^v) = \left(\frac{\partial \mu_1^v}{\partial T}\right)_{p, x_1^v} dT + \left(\frac{\partial \mu_1^v}{\partial x_1^v}\right)_{p, T} dx_1^v + \left(\frac{\partial \mu_1^v}{\partial P}\right)_{T, x_1^v} dP$$

- Where:

$x -$ mole fraction $T -$ temperature

$p -$ pressure $p = constant, dp = 0, dx_1^v = 0$

Equations

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

(5) $$\left(\frac{\partial \mu_1^l}{\partial T}\right)_{p,x_1^l} dT + \left(\frac{\partial \mu_1^l}{\partial x_1^l}\right)_{p,T} dx_1^l = \left(\frac{\partial \mu_1^v}{\partial T}\right)_{p,x_1^v} dT$$

- And from other Thermodynamic equations:

(6) $$\left(\frac{\partial \mu_1^{l,v}}{\partial T}\right)_{p,x_1} dT = -S_1^{l,v} \qquad \left(\frac{\partial \mu_1^l}{\partial x_1}\right)_{p,T} dx_1 = RT d\ln x_1 \gamma_1 \qquad (S_1^l - S_1^v) = \frac{\Delta H_v}{T}$$

- Where

$$R - gas\ constant \qquad\qquad\qquad S - Entropy$$

$$\Delta H_v - enthalpy\ of\ vaporization$$

$$\gamma_1 - activity\ coefficient\ of\ the\ solvent$$

Equations

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

(7) $\quad dln\,x_1\gamma_1 = \dfrac{\Delta H_v}{RT^2}\,dT$

- Where:

$\gamma_1 = 1 \; for \; dilute \; solution$

- Integrating (7):

(8) $\quad \displaystyle\int_1^{x_1} dln\,x_1 = \dfrac{\Delta H_v}{R}\int_{T_1}^{T_2}\dfrac{dT}{T'^2} \qquad \xrightarrow{\;For\; dT \ll T_1\;} \qquad ln\,x_1 = -\dfrac{\Delta H_v}{RT_1^2}\Delta T$

Equations

- And:

$$\ln x_1 = \ln(1 - x_2) \cong -x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{g_2 M_1}{M_2 g_1}$$
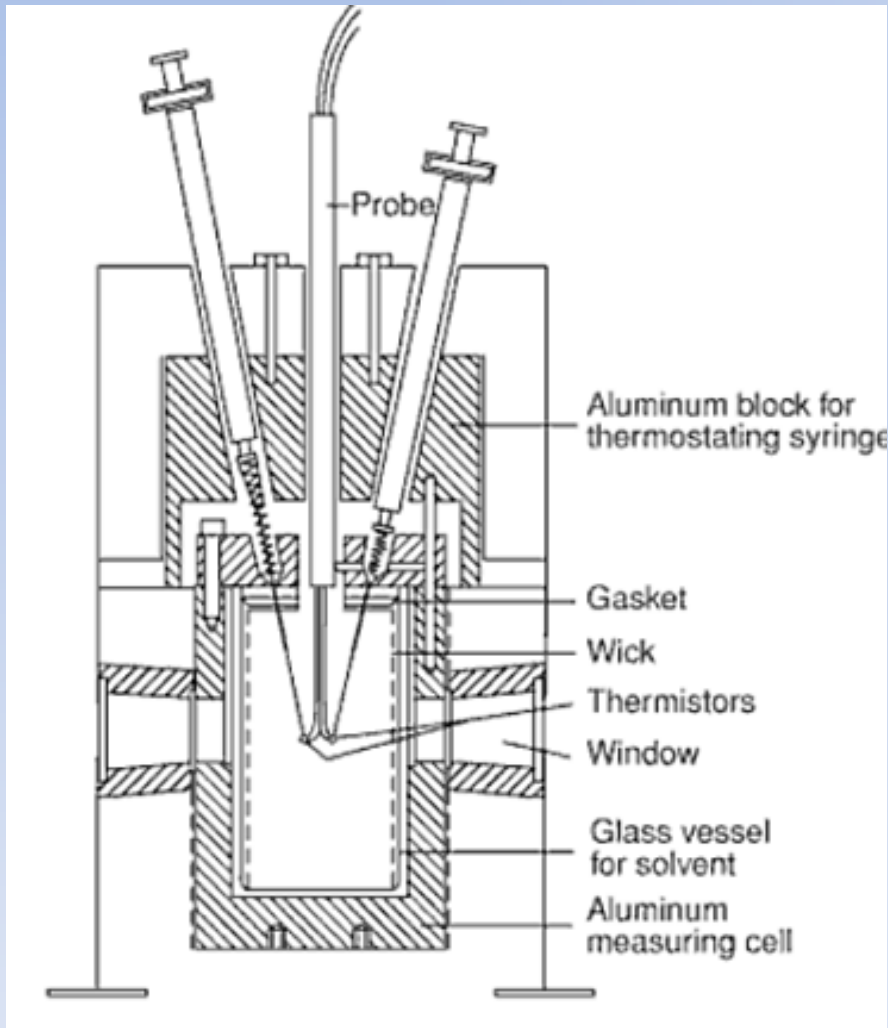
- Where:

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:

(9) $$\Delta T = \frac{RT^2}{\Delta H_v} x_2$$

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
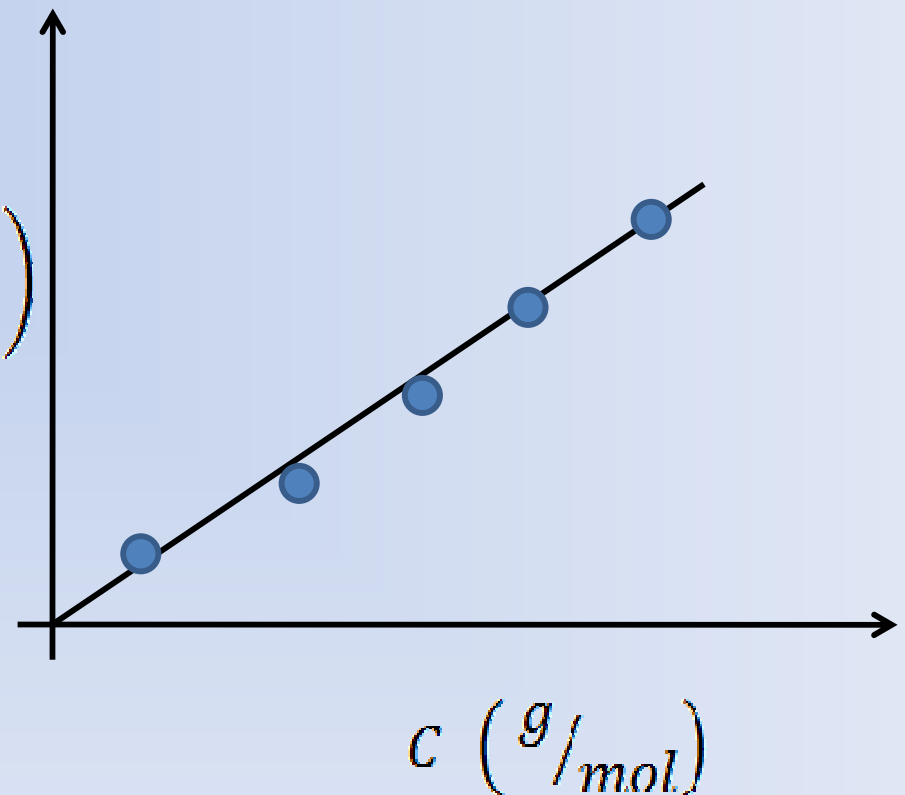 - High Solubility
- **Common solvents are:**
  - Sucrose octaacetate for organic solution
  - Simple sucrose for aqueous solution

Calibration Curve

Best fit line extrapolated to zero

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

$$\left(V \, g/_{mol} \right)$$

$$c \left(g/_{mol} \right)$$

Instrument & Experiment

- Calibration is necessary to determine the Calibration Factor, K

$$K = \frac{\Delta V M_2}{C_2}$$

- Where:

$$C - concentration$$
$$V - voltage$$

- Molecular weight determine by:

$$M_2 = \frac{K C_2}{\Delta V}$$

Instrument & Experiment

Sample Data

Characteristic Data of Solvents and Polymers

Materials	Molar volume (cm³/mol)	Molecular weight (g/mol)	Density (g/cm³)
Benzil	–	210.23	–
Urea	–	60.06	–
NMP	96.52	99.13	1.027
DMAc	92.98	87.12	0.937
DMF	77.34	73.09	0.945
Water	18.05	18	0.997
PEI	25 486	32 800[a]	1.287
	13 986	18 000[b]	
PSU	31 452	39 000[b]	1.24
PES	35 766	49 000[b]	1.37
PVP	310 345	360 000[c]	1.16

[a] Weight average.
[b] Number average.
[c] Data of the supplier.

Calibration constants, K (Volt g/mol)

Solvent	Temperature (°C)				
	25	50	70	90	110
NMP	–	–	685	1246	1744
DMAc	–	–	3919	2978	–
DMF	–	1373	2394	4977	–
Water	509	832	–	–	–

Instrument & Experiment

Conclusion

- Advantages of VPO include:
  - Speed
    - Isothermal distallation & 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
        - Membrame Osmometry does not
    - Molecular weight constraints

- Questions?

References

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