Sperling: Dilute Solutions

3.5 Determination of number average molecular weight

3.5.1 End group analysis

▶OH groups, COOH groups: Titrated or analyzed by ir etc.

▶For MW>25,000 the method is insensitive due to the too low concentration.

3.5.2 Colligative properties

Colligative properties depend on the number of molecules in the solution, and not their chemical constitution: Boiling point elevation, melting point depression, vapor pressure lowering (Refer to Figure 9.11, Engel & Reid), osmotic pressure (Figure 9.11). MW determined by colligative method is absolute MW. (See the derivation in E&R followed by)

$$\lim_{c\to 0}\frac{\Delta T_b}{c}=\frac{RT^2}{\rho\Delta H_v}\left(\frac{1}{M_n}\right) \quad (3.35)$$

$$\lim_{c\to 0}\frac{\Delta T_f}{c}=-\frac{RT^2}{\rho\Delta H_f}\left(\frac{1}{M_n}\right) \quad (3.36)\ (- : \text{depression})$$

ρ=Solvent density ΔH_v=Heat of fusion per g of solvent, ΔH_f=Heat of fusion per g of solvent, c= Solute concentration, g/cm^3.

For small vapor pressure of solute, apply Raoult's law for solvent

$P_1 = P_1^o X_1$ (P_1^o =Vapor pressure, P_1=Partial pressure of solvent)

$P_2 = P_2^o X_2$

$P = P_1 + P_2 = P_1^o (1-X_2) + P_2^o X_2 = P_1^o + (P_2^o - P_1^o) X_2$

Then

$$\frac{P_1^O - P_1}{P_1^O} = X_2 \qquad (3.37)$$

The osmotic pressure (π) is defined by

$$\pi = \frac{nRT}{V}$$ van't Hoff eq (Engel & Reid 9-41)

n=Moles of solute, So, n x M_n = Mass of solute→

n=Mass of solute/M_n

c=Mass of solute/V, <For dilute solution $V \sim n_{solvent} \times V_m$ >

Then, n/V= (Mass of solute/M_n)/V= c/M_n

►M_n is determined by measuring osmotic pressure (π).

$$\lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M_n} \qquad (3.38)$$

Osmometry is limited to 500,000Mn because the pressure becomes too small.

Table 3.5 Typical values for colligative properties for 20000Mn.

Scan Table 3.5 here

Table 3.5 Comparison of the colligative solution properties of a 1% polymer solution with M = 20,000 g/mol (23)

Property	Value
Vapor pressure lowering	4×10^{-3} mm Hg
Boiling point elevation	1.3×10^{-3} °C
Freezing point depression	2.5×10^{-3} °C
Osmotic pressure	15 cm solvent

3.5.3 Osmotic pressure

3.5.3.1 Thermodynamic basis

Chemical potential of pure solvent>chemical potential of solvent in Solution→ Causes osmotic pressure. (See the Supplementary)

Similarity between the IG law and osmotic pressure.

For IG

$$PV = nRT \qquad (3.39)$$

Replace n/V→c/M, then

$$P = \frac{c}{M}RT \qquad (3.40)$$

Setting P=π, (38) is obtained.

3.5.3.2 Instrumentation

Osmometer includes a semipermeable membrane which allows solvent alone to pass. (See Engel and Reid Figure 9.12)

3.5.3.3 The Flory Θ temperature

As c→0, osmotic pressure gives M_n according to

$$\lim_{c\to 0}\frac{\pi}{c}=\frac{RT}{M_n} \qquad (3.38)$$

At finite concentrations, interactions between the solute and solvent results in virial coefficients, A_2, A_3... and the full eq becomes

$$\frac{\pi}{c}=RT\left(\frac{1}{M_n}+A_2c+A_3c^2+\cdots\right) \qquad (3.41)$$

►$A_1=1/M_n$

►A_2= Second virial coefficient accounts for the interactions between one polymer molecule and solvent

►A_3..... Due to multiple polymer-solvent interactions

►For medium M_n, the slope is linear below 1% solute (c).

(See Figure 3.5)

►A_2 depends on temperature and solvent (for given polymer)

If A_2=0

►A unique and much desired state arises, called Flory Θ-temperature.

►Behaves like an ideal solution

►$\frac{\pi}{c}\neq$ f(Concentration)→One concentration need to measure Mn.

►X_1=0.5