INTRODUCTION TO

POLYMER PHYSICS:

THERMODYNAMICS OF POLYMER SOLUTIONS

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CONTENT

Thermodynamics of Polymer Solution:

- Dilute Solution
- Theta Condition
- Solubility Parameter

DILUTE SOLUTION

Thermodynamics of Polymer Solutions:

Dilute Solution

Theta Condition

Solubility Parameter:

<u>Using Flory-Huggins Theory:</u>

For Solvent: $$\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\mu_1 - \mu_1^0 = RT\ln a_1 = RT\ln(X_1\gamma_1) = RT\ln X_1 + RT\ln\gamma_1$$

$$= \left(\mu_1 - \mu_1^0\right)^{\text{ideal}} + \left(\mu_1 - \mu_1^0\right)^{\text{excess}}$$

$$\left(\mu_1 - \mu_1^0\right)^{\text{ideal}} = RT\ln X_1$$

$$\left(\mu_1 - \mu_1^0\right)^{\text{excess}} = RT\ln\gamma_1$$

DILUTE SOLUTION

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Solubility Parameter:

$$\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\left(\mu_1 - \mu_1^0\right)^{\text{ideal}} = RT\ln X_1$$

$$\ln(1+p) = p - \frac{p^2}{2} + \frac{p^3}{3} - \cdots \qquad \text{for } -1 < p < 1$$

$$\ln\phi_1 = \ln(1-\phi_2) = -\phi_2 - \frac{\phi_2^2}{2} - \frac{\phi_2^3}{3} - \cdots$$

$$\ln X_1 = \ln(1-X_2) = -X_2 - \frac{X_2^2}{2} - \frac{X_2^3}{3} - \cdots$$

For Dilute Solution: $X_2 \ll 1$ $\quad N_1 \gg xN_2$

$$\phi_2 = \frac{xN_2}{N_1 + xN_2} \cong \frac{xN_2}{N_1}$$

$$X_2 = \frac{N_2}{N_1 + N_2} \cong \frac{N_2}{N_1} = \frac{\phi_2}{x}$$

$$\ln\phi_1 = \ln(1-\phi_2) \cong -\phi_2 - \frac{\phi_2^2}{2}$$

$$\ln X_1 = \ln(1-X_2) \cong -X_2 = -\frac{\phi_2}{x}$$

DILUTE SOLUTION

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$$\mu_1 - \mu_1^0 = RT\left[\ln\phi_1 + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\left(\mu_1 - \mu_1^0\right)^{\text{ideal}} = RT\ln X_1$$

$$\ln\phi_1 = \ln(1 - \phi_2) \cong -\phi_2 - \frac{\phi_2^2}{2}$$

$$\ln X_1 = \ln(1 - X_2) \cong -X_2 = -\frac{\phi_2}{x}$$

$$\mu_1 - \mu_1^0 = RT\left[-\phi_2 - \frac{\phi_2^2}{2} + \phi_2\left(1 - \frac{1}{x}\right) + \chi\phi_2^2\right]$$

$$\left(\mu_1 - \mu_1^0\right)^{\text{ideal}} = -RT\frac{\phi_2}{x}$$

$$\mu_1 - \mu_1^0 = RT\left[-\frac{\phi_2}{x} + \left(\chi - \frac{1}{2}\right)\phi_2^2\right]$$

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

$$\boxed{\left(\mu_1 - \mu_1^0\right)^{\text{excess}} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2}$$

$$\mu_1 - \mu_1^0 = \left(\mu_1 - \mu_1^0\right)^{\text{ideal}} + \left(\mu_1 - \mu_1^0\right)^{\text{excess}}$$

THETA CONDITION

$$(\mu_1 - \mu_1^0)^{\text{excess}} = RT\left(\chi - \frac{1}{2}\right)\phi_2^2$$

$$\chi = \frac{1}{2} \qquad (\mu_1 - \mu_1^0)^{\text{excess}} = 0 \qquad \mu_1 - \mu_1^0 = (\mu_1 - \mu_1^0)^{\text{ideal}}$$

Theta Condition: Polymer solution behaves ideally

Theta (θ) Temperature:

For a given polymer-solvent system, the temperature at which theta condition occurs.

$$(\mu_1 - \mu_1^0)^{\text{excess}} = RT\psi\left[\left(\frac{\theta}{T}\right) - 1\right]\phi_2^2$$

ψ: Entropy Parameter

THETA CONDITION

More sophisticated theories also predict:

$$(\mu_1 - \mu_1^0)^{\text{excess}} \propto \left(\chi - \frac{1}{2}\right)$$

$$(\mu_1 - \mu_1^0)^{\text{excess}} \propto \psi\left[\left(\frac{\theta}{T}\right) - 1\right]$$

POLYMER	SOLVENT	θ TEMPERATURE (°C)
Polyethylene	Biphenyl	125
Poly(vinyl alcohol)	Water	97
Poly(vinyl acetate)	Methanol	6
Polystyrene	Cyclohexane	34
Poly(methyl methacrylate)	Pentyl acetate	41
Poly(acrylic acid)	1,4-Dioxan	29

PHASE BEHAVIOUR

$$\chi = a + \frac{b}{T}$$

$b > 0$
χ decreases with T

$b < 0$
χ increases with T

SOLUBILITY PARAMETER

First proposed by Hildebrand for liquid mixtures:

$$\Delta H_m^{\text{contact}} = V_m \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

V_m: Volume of mixture/solution
δ_1: Solubility parameter of solvent
δ_2: Solubility parameter of solute (polymer)

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V}}$$

ΔH_v: Molar Enthalpy of Vaporization $\quad$ V: Molar volume

Cohesive Energy Density, **CED** $= \delta^2$
(Measure of the strength of attraction between molecules in unit volume)

For Polymers: Additivity Approach

$$\delta = \frac{\rho_p}{}$$

ρ_p: Dens

M_0: Mola

f_i: Numb

F_i: Group

Group Molar Attraction Constants

(adapted from 'Introduction to Polymer Science and Chemistry, 2nd Ed. by Manas Chanda)

Group	F, in $(\text{cal cm}^3)^{1/2}\ \text{mol}^{-1}$
$-CH_3$	147.3
$-CH_2$	131.5
$-CH$	85.99
$>C<$	32.03
$CH_2 =$ (olefin)	126.54
$-CH=$ (olefin)	121.53
$>C=$ (olefin)	84.51
$-CH=$ (aromatic)	117.12
$-C=$ (aromatic)	98.12
$-O-$ (ether, acetal)	114.98
$-O-$ (epoxide)	176.20
$-COO-$, i.e. $-\overset{\overset{\displaystyle O}{\|}}{C}-O-$	326.58
$>C=O$ (carbonyl)	262.96
$-CHO$ (aldehyde)	292.64
$-OH$ (hydroxyl)	225.84
6-membered ring	−23.44

SOLUBILITY PARAMETER

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For Polymers: Additivity Approach

$$\delta = \frac{\rho_\mathrm{p} \sum_i f_i F_i}{M_0}$$

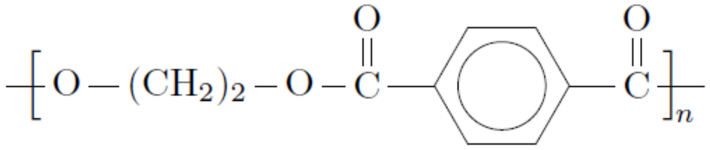
ρ_p: Density of polymer

M_0: Molar mass of repeat unit

f_i: Number of groups of type 'i'

F_i: Group molar attraction constant for group 'i'

Example: PET ($\rho_\mathrm{p} = 1.38$ g/cm³)



Group	F_i (cal.cm³)$^{1/2}$ mol^{-1}	f_i
$-\overset{\overset{\displaystyle O}{\|\|}}{C}-O-$	326.58	2
$-CH_2$	131.5	2
$-CH=$ (aromatic)	117.12	4
$-C=$ (aromatic)	98.12	2
6-membered Ring	-23.44	1

$$\sum_i f_i F_i = 1557.44 \text{ (cal.cm}^3)^{1/2} \text{ mol}^{-1}$$

$$M_0 = 10 \times 12 + 4 \times 16 + 8 \times 1 = 192 \text{ g/mol}$$

$$\delta = \frac{1.38 \times 1557.44}{192} \text{(cal/cm}^3)^{1/2} = 11.194 \text{ (cal/cm}^3)^{1/2}$$

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Example:

Polymer/Solvent	δ (cal.cm^3)$^{1/2}$ mol^{-1}
Polystyrene	9.1
Water	23.4
Ethanol	12.9
Cyclohexane	8.2
Toluene	8.9

Relation with Flory-Huggins Interaction Parameter, χ:

$$\chi_H = \frac{V_1(\delta_1 - \delta_2)^2}{RT}$$

V_1: Molar volume of the solvent

Limitations of Hildebrand Solubility Parameter Approach:

- Based on theory where negative enthalpy of mixing is not allowed
- Not applicable to highly polar systems or in the presence of hydrogen bonding