

CHAPTER 8 Polymers in Solution

The fundamental thermodynamic equation, to describe these systems relates the Gibbs free-energy function G to the enthalpy H and entropy S . $G = H - TS$

A homogeneous solution is obtained when the Gibbs free energy of mixing $\Delta G^M < 0$.

↳ when the Gibbs free energy of the solution G_{12} is lower than the Gibbs functions of the components of the mixture G_1 & G_2

$$\Delta G^M = G_{12} - (G_1 + G_2)$$

Raoult's law is a useful starting point, and defines an ideal solution as one in which the activity of each component in a mixture a_i is equal to its mole fraction x_i .

Ideal Mixtures

- ↳ - components of comparable size
- the intermolecular forces acting between both like and unlike molecules are equal
- component molecules of each species can interchange positions without altering the total energy of the system. (latter requirement)
as, $\Delta H^M = 0$
- it only remains for the entropy contribution ΔS^M to be calculated.

↳ the entropy can be calculated from the Boltzmann law $S = k \ln \Omega$.
 Ω is the number of statistical microstates available to the system.

Nonideal Solutions

- Athermal solutions: $\Delta H^M = 0$ but ΔS^M is not ideal
- Regular solutions: ΔS^M is ideal but $\Delta H^M \neq 0$
- Irregular solutions: both ΔS^M and ΔH^M deviate from their ideal values

- The Flory-Huggins theory forms the cornerstone of polymer solution thermodynamics.

The dissolution of a polymer in a solvent can be regarded as a two-stage process.

- a) the polymer exists in the solid state, on passing to the liquid solution
- b) the chains achieve relative freedom and can change conformations.
↳ dictated by the chain flexibility and the interactions with the solvent.

The formation of the solution depends on;

- i) the transfer of the polymer chain from a pure, ordered state to a state of disorder
- ii) the mixing process of the flexible chains with solvent molecules.

Cloud-point curve - shows the limited solubility of the components.

As the temperature is increased, the limits of this two-phase coexistence contract, until eventually they ~~coalesce~~ coalesce to produce a homogeneous, one-phase mixture at the critical solution temperature T_c .

↳ or critical consolute point

- The Flory-Krigbaum theory discards the idea of a uniform distribution of chain segments in the liquid.

↳ it considers the solution to be composed of areas containing polymer separated by the solvent.

upper critical solution temperature → the critical temperature, T_c occurs near the maximum of the cloud-point curve.

lower critical solution temperature → the critical temperature is located at the minimum of the miscibility curve.

Solubility and the Cohesive Energy

Treatment involves relating the enthalpy of mixing ~~full~~ to the cohesive energy density (E/V) and defines a solubility parameter $\delta = (E/V)^{1/2}$, where

E = the molar energy of vaporization

V = the molar volume of the component

$$\Delta H^M = V^M (\delta_1^2 - \delta_2^2)^2 \phi_1 \phi_2$$

ΔH^M is small for mixtures with similar solubility parameters, and this indicates compatibility.