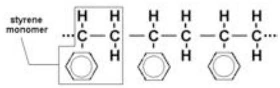
3.014 Lab 3 γ_2

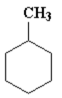
Phase Separation
Zil Friend
11/16, 11/18 & 11/21

Lab Procedures

- Prepare Solutions
- Methylcyclohexane (Solvent)
- Polystyrene (Solute)
  - MW = 13,200
  - MW = 50,000
  - MW = 29,300



polystyrene

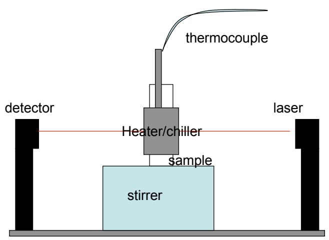


Methyl cyclohexane

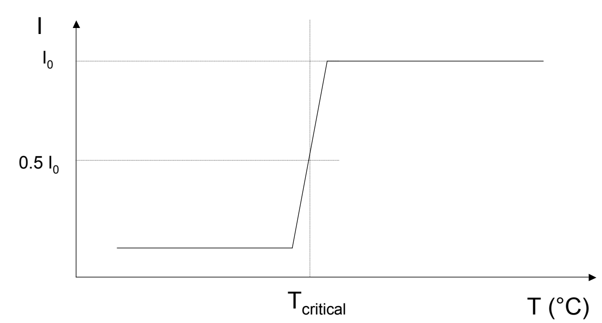
C_7H_{14}

Lab Procedures

- Temperature range: 60°- 5° C controlled by thermal cell.
- Light from laser scatters in sample cell.
- Laser signal at each T step



Results



Lab Safety

- Laser: Do not look into beam.
- Wear gloves & glasses when preparing & handling chemical solutions.
- Methyl cyclohexane: flammable, vapors should not be inhaled.

Review: Ideal Solution Theory

- Helmholtz Free Energy:
  - F=U-TS
  - U: Interaction energies between solution components
  - S: Entropy of mixing

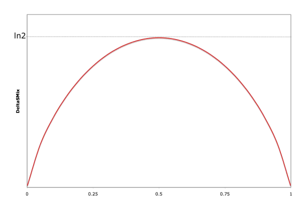
Review: Ideal Solution Theory

- S: Entropy of Mixing
- Filling N lattice sites with N_A solvent molecules & N_B solute molecules
- # states = $N!/N_A!N_B!$
- ΔS_{Mix}=k ln(#states)

  $= - k (N_A \ln x_A + N_B \ln x_b)$

$\Delta S_{Mix} / kN = - x_A \ln x_A - (1-x_A) \ln(1-x_A)$

Review: Ideal Solution Theory



- $\Delta S_{Mix} / kN = - x_A \ln x_A - (1-x_A) \ln(1-x_A)$
- $-T\Delta S$ term is negative for all x_A
- Mixing reduces free energy!
- Ideal case ONLY - assumes no energy associated with mixing.
- What about the real world?

Review: Regular Solution Model

- Interactions between A and B
- $U=(\#AA)E_{AA}+(\#BB)E_{BB}+(\#AB)E_{AB}$
- U=

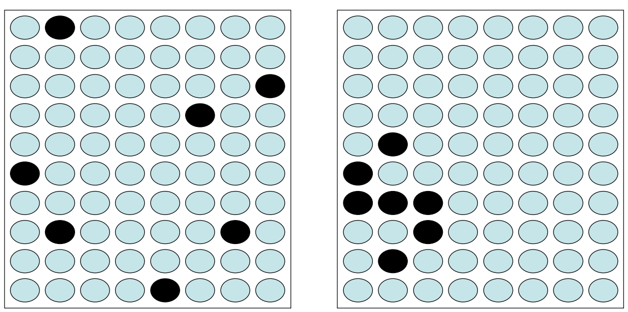
$(zE_{AA}/2)N_A+(zE_{BB}/2)N_B+kT\chi_{AB}(N_AN_B/N)$
  - z = #A nearest neighbors
  - χ_{AB} = Exchange parameter
  - $\chi_{AB} =(z/kT)\ [E_{AB-}(E_{AA}+E_{BB})/2]$

Review: Regular Solution Model

- $\Delta F = \Delta U - T\Delta S$
- **$\Delta F/NkT =$**

$\chi_{AB}(x_A)(1-x_A) + x_A \ln x_A + (1-x_A) \ln(1-x_A)$
- χ_{AB} usually >0
- Competition between Entropy and Mixing Energy terms!
  - Entropy: Pro-Mixing
  - Energy: (often) Anti-Mixing

Polymer Solutions



Small Solute-Solvent System   Polymer-Solvent System

Polymer Solutions

- Different from regular solution model.
- Why?
- Polymers are BIG CHAINS
- Use Flory-Huggins Model to describe polymer solutions

Flory-Huggins Model

- Need to take into account that polymers are long chains of N segments
- Each segment takes 1 lattice site
- $M = N\ n_p + n_s$
  - M = Total # lattice sites
  - n_p, n_s = # polymers, solvent molecules

Flory-Huggins Model

- Regular Solutions

$\Delta S_{Mix} / kN = - x_A \ln x_A - x_B \ln x_B$

  - N = #molecules

- Polymer Solutions

$\Delta S_{Mix} / kM = - \Phi_S \ln\Phi_S - (\Phi_P/N) \ln(\Phi_P)$

  - M = # lattice sites
  - Φ = Lattice fraction (of Solvent & Polymer)
  - N = #monomer units

Flory-Huggins Model

- Regular Solution Energy

$U = (zE_{AA}/2)N_A+(zE_{BB}/2)N_B +kT\chi_{AB}(N_A N_B/N)$

  - $\chi_{AB} =(z/kT) [E_{AB-} (E_{AA}+ E_{BB})/2]$

- Polymer Solution Energy

$U = (zE_{SS}/2)n_S+(zE_{PP}/2)Nn_P +kT\chi_{SP}(Nn_S n_P/M)$

  - $\chi_{SP} = (z/kT) [E_{SP-} (E_{SS}+ E_{PP})/2]$

Flory-Huggins Model

- Helmholtz Free Energy

$\Delta F_{mix}/kT = U_{mix}/kTM - S/k$

$$\Delta F_{mix}/kT = n_S \ln\Phi_S + n_P \ln\Phi_P + (zE_{SS}/2kT)n_S + (zE_{PP}/2kT)Nn_P +\chi_{SP}(Nn_S n_P/M)$$

Fun with Free Energy Curves

- (1/kT) $\delta F/\delta n = \mu$
  - "chemical potential"
  - Common tangent defines 2-phase coexistance curve
- (1/kT) $\delta^2 F/\delta n^2 = 0$
  - Spinodal decomposition curve edge
- >0 ("concave" curve) - phase split increases Free Energy
- <0 ("convex" curve) - phase split decreases Free Energy

Fun with Free Energy Curves

- (1/kT) $\delta^2 F/\delta n^2 =$ (1/kT) $\delta^3 F/\delta n^3$
  - Critical Point - where separation first occurs