3.014 Lab 4 α_2

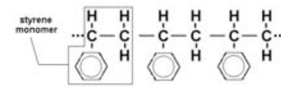
Miscibility Gaps

Zil Friend

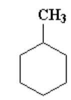
12/9, 12 & 14

Lab Procedures

- Prepare Solutions
  - Methylcyclohexane (Solvent)
  - Polystyrene (Solute)
    - **MW = 2,430**
    - **MW = 4,213**
    - **MW = 5,193**
    - **MW = 13,700**
    - **MW = 29,300**
    - **MW = 44,000**
    - **MW = 97,400**
  - Concentration = **.0001M**, **.001M**
  - 2 g samples
- Measure from ~60-~5°C.
  - Determine transition temperature.

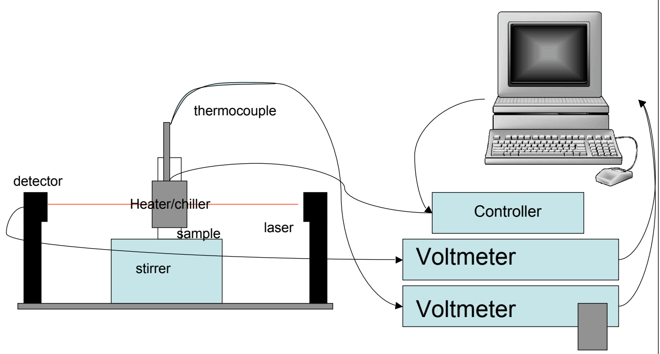


polystyrene



Methyl cyclohexane

C_7H_{14}



- Temperature range: 60°- 5°C controlled by thermal cell.
- Light from laser penetrates hole in heater/chiller, scatters in sample cell.

•Laser - Diode Pointer Laser, ~ 1 mW, 670 nm wavelength.

•Detector - Newport Si Diode, #883-SL.

•HP 3457A Multimeters w- GPIB 48 interface, 6.5 digit resolution.

•VWR 375 Hot plate- Stirrer

•Thermoelectric Chiller Modules, 1.5 in^2. Rated 4 A Max current, 70° differential.

•Pentium Processor Fans

•Type K Thermocouple.

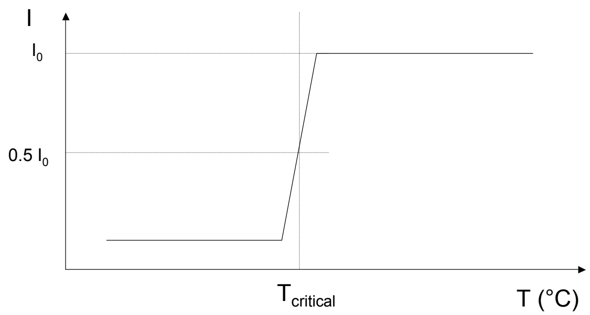
•Newport I 16C54 Thermal Process Controller with custom bipolar power supply ±20 V @2.5 A.

•Fluke 80TK Thermocouple Converter Module: 1 mV = 1°C.

•Fluke Stainless Steel Thermocouple probe.

•Labview V. 7.1, Cloud Point V. 11 written by David Bono.

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

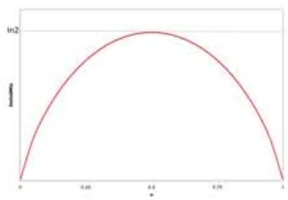
Review: Ideal Solution Theory

- 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



- ΔS_{Mix} / kN = - $x_A \ln x_A$ - $(1-x_A) \ln(1-x_A)$
- -TΔS 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
  - χ_{AB} =(z/kT) [E_{AB-} $(E_{AA}+ E_{BB})/2$]

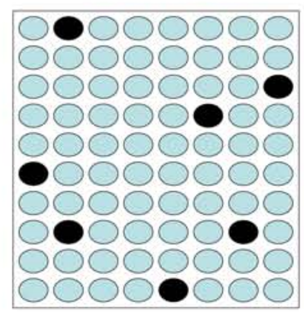
Review: Regular Solution Model

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

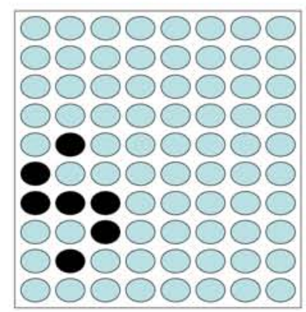
$\chi_{AB}(x_A)(1-x_A) + x_A \ln x_A + (1-x_A) \ln(1-x_A)$

- 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