Lab 4 – Module α_2

Miscibility Gaps

OBJECTIVES

- ✓ Review miscibility gaps in binary systems
- ✓ Introduce statistical thermodynamics of polymer solutions
- ✓ Learn cloud point technique for experimentally determining miscibility gaps
- ✓ Study effect of chain length on miscibility of polymer-solvent mixtures

SUMMARY OF TASKS

1) Prepare solutions of polystyrene / methyl cyclohexane of varying concentration
2) Measure cloud points of prepared solutions by light scattering methods
3) Compare results to values published in archival literature

READINGS

See Dill, K. A., & S. Bromberg, *Molecular Driving Forces*. New York, NY: Garland Publishing, 2002. Chapters 15 "Solutions and Mixtures" & 31 "Polymer Solutions."

BACKGROUND

In 3.012 we've studied how ideal solutions of two components tend to mix together to increase the total entropy of the system, while regular solutions can have a miscibility gap in which the system phase separates into 2 distinct compositions of the same structure.

This lab will explore how this tendency is affected when one component is a macromolecule or polymer, and experimentally determine phase diagrams for the polymer-solvent system polystyrene-methyl cyclohexane.

Recall from 3.012 that the molar Gibb's free energy for an ideal mixture is given by:

$$\overline{G}_{sol} = \sum_{i=1}^{C} \mu_i X_i \quad,$$

where C is the number of components in the mixture and X_i is the mole fraction of the i*th* component, whose chemical potential is given by:

$$\mu_i = \mu_{i,0} + RT \ln X_i$$

For an A-B mixture:

$$\overline{G}_{sol} = \mu_{A,0} X_A + X_A RT \ln X_A + \mu_{B,0} X_B + X_B RT \ln X_B$$

In the heterogeneous (demixed) state, the free energy is given by the sum of the free energies of the unmixed components:
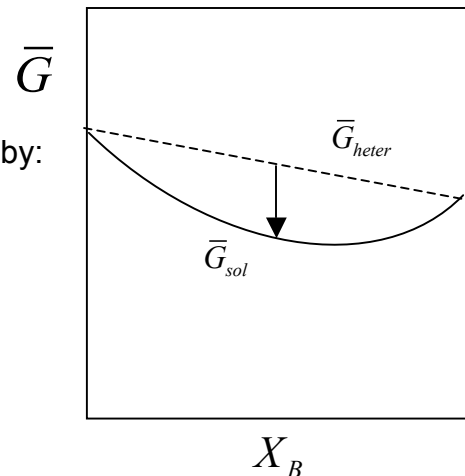
$$\overline{G}_{heter} = X_A \mu_{A,0} + X_B \mu_{B,0}$$

The change in molar free energy on mixing is thus given by:

$$\Delta \overline{G}_{mix} = RT \left(X_A \ln X_A + X_B \ln X_B \right)$$

In an ideal solution, the mixing enthalpy is zero so that:

$$\Delta \overline{G}_{mix} = -T \Delta \overline{S}_{mix}$$

$\overline{G}$

$\overline{G}_{heter}$

$\overline{G}_{sol}$

X_B

$$\Delta \overline{S}_{mix} = -R\left(X_A \ln X_A + X_B \ln X_B \right)$$

The ideal solution remains miscible at any temperature because the change in free energy on mixing is zero.

The ideal solution can be contrasted with a regular solution. In a regular solution, interactions between components result in a mixing enthalpy given by:

$$\Delta \overline{H}_{mix} = \Theta X_A X_B$$

The total change in free energy is then:

$$\Delta \overline{G}_{mix} = RT\left(X_A \ln X_A + X_B \ln X_B \right) + \Theta X_A X_B$$

For $\Omega > 0$, a regular solution can undergo phase separation as temperature decreases. The two-phase region of the T-composition phase diagram is known as a misibility gap.
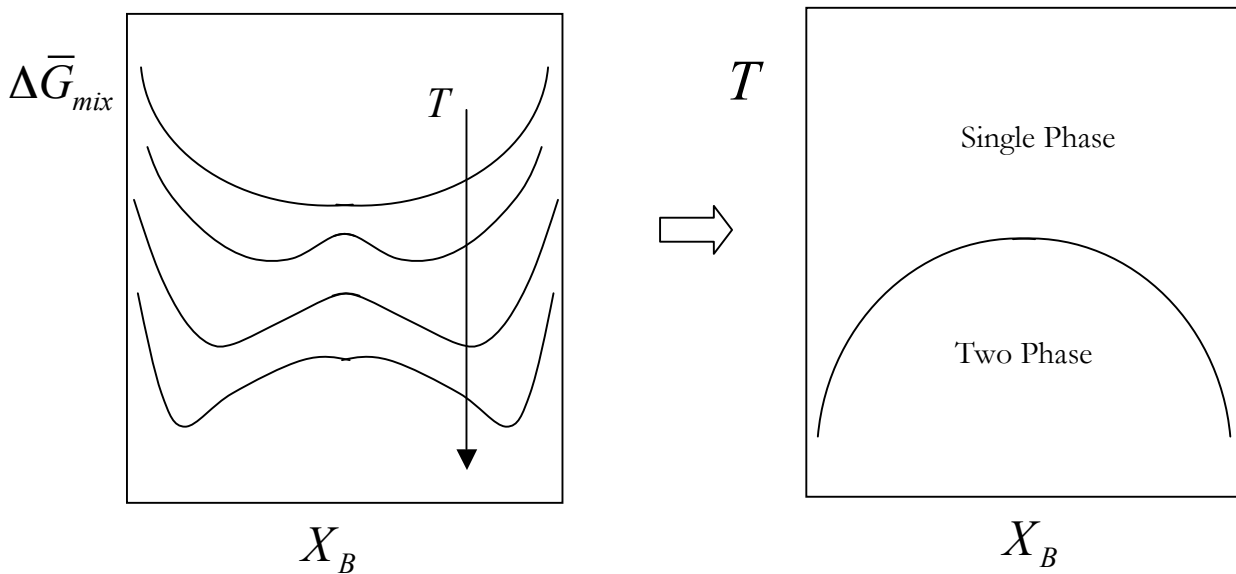
The boundary between the one- and two-phase regions which defines the miscibility gap is obtained by:

$$\frac{\partial \Delta \overline{G}_{mix}}{\partial X_B} = RT \left(\ln X_B - \ln \left[1 - X_B \right] \right) + \Theta \left(1 - 2X_B \right) = 0$$

The critical point occurs at:

$$\frac{\partial^2 \Delta \overline{G}_{mix}}{\partial X_B{}^2} \bigg|_{X_B = 0.5} = RT \left(\frac{1}{X_B} + \frac{1}{1 - X_B} \right) + -2\Theta = 0$$

An example of a miscibility gap is found in the Ir-Pd phase diagram, shown below. In the solid state, mixtures of iridium and palladium exhibit an FCC structure. Above 1450 °C, the system is single phase. Below this temperature, however, is a miscibility gap where the system splits into separate Pd-rich and Rh-rich compositions. Similar to the regular solution model above, the critical composition is near 50 at% (M_{Ir}=192.2 g/mol; M_{Pd}=106.4 g/mol). Plotting the phase diagram in weight fraction introduces asymmetry to the miscibility gap.

Figure removed for copyright reasons.
Ir-Pd phase diagram. From Baker, H., ed. *ASM Handbook Alloy Phase Diagrams*.
Vol. 3. 10th ed. Materials Park, OH: ASM International, 1992, p. 265. ISBN: 0871703815.

How does the result change for polymer solutions?

Polymers are long chain molecules of repeating chemical units called monomers. The molecular weight of a polymer increases with the number of monomers per chain.

Styrene
monomermonomer

Polystyrene
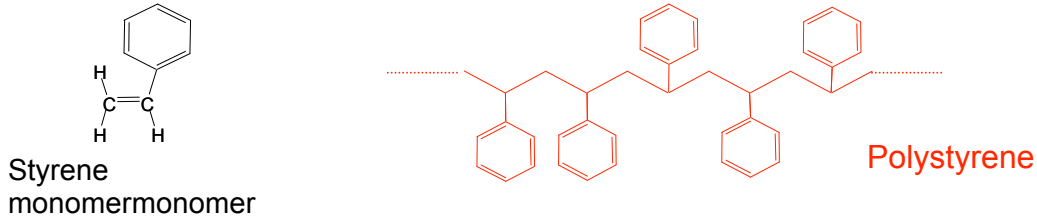
For polymers, molecular weights typically range from 10,000 g/mol to 1M g/mol while solvents have molecular weights typically ~100 g/mol.

For given mass ratio of polymer and solvent, m_P/m_S, the molar fraction of polymer is:

$$X_p = \frac{\left(\dfrac{m_p}{m_s}\right)\left(\dfrac{1}{NM_{mer}}\right)}{\left(\dfrac{1}{M_s}\right)+\left(\dfrac{m_p}{m_s}\right)\left(\dfrac{1}{NM_{mer}}\right)}$$

while that of the solvent is:

$$X_s = \frac{\left(\dfrac{1}{M_s}\right)}{\left(\dfrac{1}{M_s}\right)+\left(\dfrac{m_p}{m_s}\right)\left(\dfrac{1}{NM_{mer}}\right)} = 1 - X_p$$

where M_s is the solvent molecular weight, M_{mer} is the molecular weight of the monomer repeat unit and N is the number of repeat units.

Table 1 gives values of X_p for given values of m_P/m_S and N. For equal mass fractions, the mole fraction is increasingly asymmetric, introducing similar asymmetry into the phase diagram. We can see this qualitatively by calculating $\Delta \overline{S}_{mix}$ for the ideal solution.

N	m_P/m_S	$w_p = m_P/(m_S+m_p)$	X_p	$\Delta \bar{S}_{mix}/R$ (K^{-1}) *(ideal soln)*
100	0.1	0.0909	0.0010	0.008
100	0.2	0.1667	0.0012	0.009
100	0.5	0.3333	0.0050	0.031
100	1	0.5000	0.0099	0.056
100	2	0.6667	0.0196	0.096
100	5	0.8333	0.0476	0.191
100	10	0.9090	0.0909	0.305
100	50	0.9804	0.3333	0.636
100	100	0.9901	0.5000	0.693
100	1000	0.9990	0.9091	0.305
1000	1	0.5000	0.0010	0.008
1000	2	0.6667	0.0020	0.014
1000	5	0.8333	0.0050	0.031
1000	10	0.9090	0.0099	0.056
1000	100	0.9901	0.0909	0.305
1000	500	0.9980	0.3333	0.636
1000	1000	0.9990	0.5000	0.693
1000	10000	0.9999	0.9091	0.305
1	0.1	0.0909	0.0909	0.305
1	0.2	0.1667	0.1667	0.451
1	0.5	0.3333	0.3333	0.636
1	1	0.5000	0.5000	0.693
1	2	0.6667	0.6667	0.636
1	5	0.8333	0.8333	0.451
1	10	0.9090	0.9090	0.305

As the polymer chain length increases, there is less entropy gained by adding small amounts of polymer (e.g., by weight) into solvent compared to that gained by adding small amounts of solvent to polymer. This introduces strong asymmetry to the phase diagram.
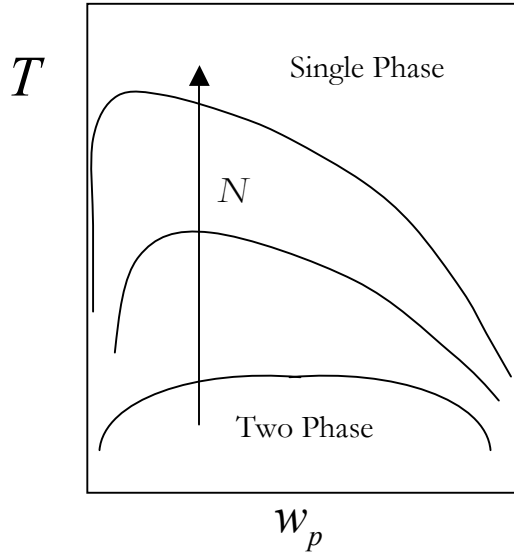

Although qualitatively correct in showing that entropy of mixing diminishes with increasing chain length, the regular solution model cannot rigorously be applied to polymer mixtures and solutions. An improved model for predicting phase behavior of polymer solutions was put forth by P.J. Flory,[1] who won the Nobel Prize for his contributions to polymer science. Flory's model employs statistical mechanics, a field that connects macroscopic behavior to the microscopic properties of systems. His model builds off the statistical mechanics development of the regular solution model.

Consider, for example, a small molecule mixture of n_A molecules of component A and n_B molecules of component B. The number of *distinguishable* ways we could arrange these components on a lattice of n_A+n_B sites is:

$$\Omega = \frac{(n_A + n_B)!}{n_A! n_B!}$$

For example, the total number of configurations for a system with $n_A = 4$ and $n_B = 2$ is:

$$\Omega = \frac{6!}{4!2!} = 15$$
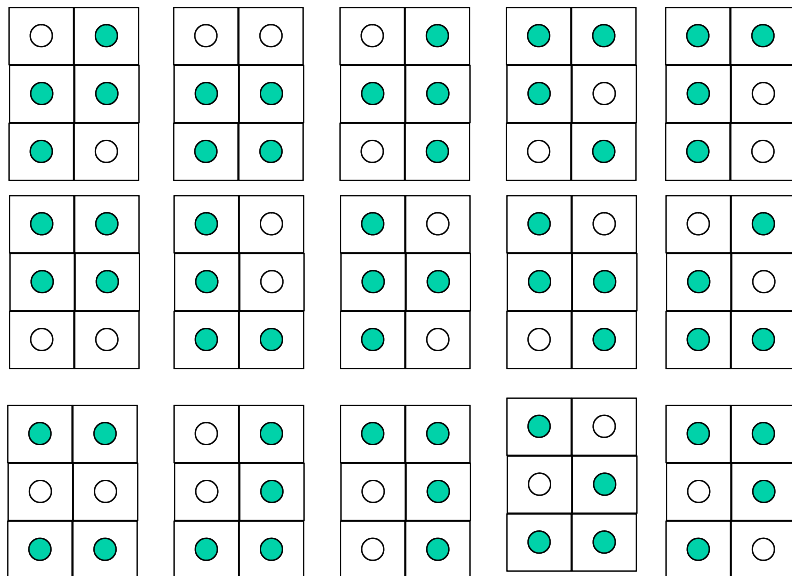
The entropy of the system is related to the number of configurations of the system Ω by:

$$S = k \ln \Omega$$

where k is Boltzmann's constant, $k = R/N_{Av} = 1.381 \times 10^{-23}$ J/K. Using Stirling's formula:

$$\ln(x!) = x \ln x - x$$

we obtain the total entropy for the system:

$$S_{sol} = -k \left[n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right]$$

In the heterogeneous state, the number of distinguishable B configurations is:

$$\Omega_B = \frac{n_B!}{n_B!} = 1 \quad ,$$

and similarly for A. The change in entropy on mixing is given by subtracting off the pure state entropy. For the small molecule mixture:

$$\Delta S_{mix} = S_{sol} - S_{heter} = -k \left[n_A \ln X_A + n_B \ln X_B \right]$$

Since our molecules A and B have equal volume, we can also write:

$$\Delta S_{mix} = -k \left[n_A \ln \phi_A + n_B \ln \phi_B \right]$$

Or, per lattice site we have:

$$\Delta s_{mix} = -k\left[\phi_A \ln \phi_A + \phi_B \ln \phi_B\right]$$

where
$$\phi_i = \frac{V_i}{V} = \frac{n_i v_o}{n_A v_o + n_B v_o}$$

and v_o is the volume of the lattice site.

For polymer solutions, we can use a similar lattice model to obtain the entropy of mixing, according to the model developed by Flory[1]. Here we consider a polymer whose segmental volume is equal to the volume of a lattice site. Due to the connectivity of the segments, the number of configurations available to the system decreases.
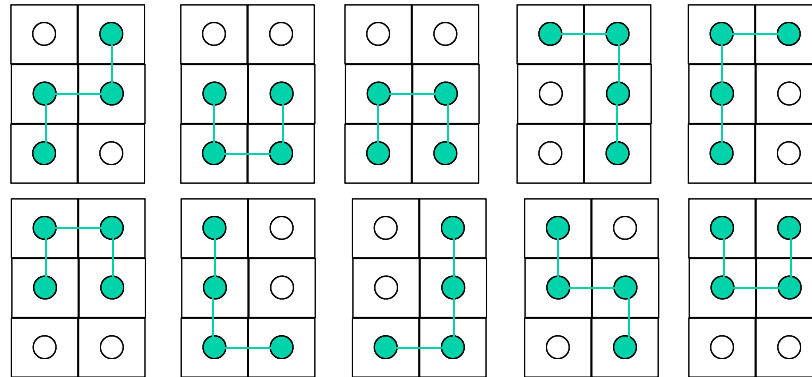
For a mixture of n_c polymers and n_s solvent molecules, the total number of lattice sites is now:

$$N_o = n_p N + n_s$$

where N is the degree of polymerization of the polymer, i.e., the number of segments per chain.

Incorporating connectivity into the placement of the polymer segments, the total number of ways of arranging the system was first shown by Flory to be[1]:

$$\Omega = \frac{(N_o)!}{n_C!\, n_S!}\left(\frac{z-1}{N_o}\right)^{n_p(N-1)}$$

where z is the number of neighbors in the lattice.

Again applying Stirling's formula, we obtain the total entropy for the system:

$$S_{sol} = -k\left[n_s \ln\frac{n_s}{n_s + Nn_p} + n_p \ln\frac{n_p}{n_s + Nn_p}\right] + kn_p(N-1)\ln\left[\frac{z-1}{e}\right]$$

Setting $n_s = 0$ in the above expression gives the entropy associated with the various configurations of the polymer coil:

$$S_{pol} = -k\left[n_p \ln\frac{1}{N}\right] + kn_p(N-1)\ln\left[\frac{z-1}{e}\right]$$

We are interested in the entropy gained by mixing solvent and polymer molecules together:

$$\Delta S_{mix} = S_{sol} - S_{pol}$$

$$\Delta S_{mix} = -k\left[n_s \ln\phi_s + n_p \ln\phi_p\right]$$

If we consider the entropy of mixing per site,[2]

$$\Delta s_{mix} = -k\left[\frac{n_s}{N_o}\ln\phi_s + \frac{n_p}{N_o}\ln\phi_p\right]$$

$$= -k \left[\phi_s \ln \phi_s + \frac{\phi_p}{N} \ln \phi_p \right]$$

Here we see quantitatively the effect of chain length on molecular weight. *As N increases, the amount of entropy gained by mixing the polymer into the solvent is reduced by 1/N.*

The enthalpy of mixing is analogous to that obtained for the regular solution model for atomic mixtures. In the demixed or *phase-separated* state, the total interaction energy can be obtained by counting the number of pair-wise interactions between monomer-monomer and solvent-solvent pairs:[3]

$$H_{heter} = n_p N \times \left(\frac{1}{2} z \varepsilon_{pp} \right) + n_s \times \left(\frac{1}{2} z \varepsilon_{ss} \right)$$
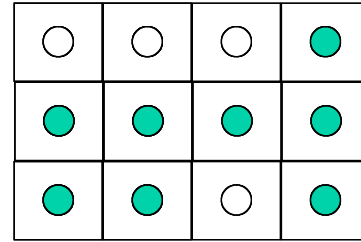
where ε_{ii} is the attractive (negative) interaction energy of the *j-j* pair. In the mixed state, the energy is calculated as:

$$H_{sol} = n_p N \phi_p \times \left(\frac{1}{2} z \varepsilon_{pp} \right) + n_s \phi_s \times \left(\frac{1}{2} z \varepsilon_{ss} \right) + n_p N \phi_s \times \left(\frac{1}{2} z \varepsilon_{ps} \right) + n_s \phi_p \times \left(\frac{1}{2} z \varepsilon_{sp} \right)$$

where the volume fractions account for the reduced probability of the adjacent site being a polymer (ϕ_p) or solvent (ϕ_s) species. The change in enthalpy on mixing per site is given as:

$$\Delta h_{mix} = \frac{H_{sol} - H_{heter}}{N_o} = \frac{z}{2} \left(2\varepsilon_{sp} - \varepsilon_{ss} - \varepsilon_{pp} \right) \phi_s \phi_p$$

The resulting expression for the free energy of mixing per site can be written as[2]:

$$\frac{\Delta g_{mix}}{kT} = \phi_s \ln \phi_s + \frac{\phi_p}{N} \ln \phi_p + \chi \phi_s \phi_p$$

where χ is known as the Flory-Huggins interaction parameter, defined as:

$$\chi = \frac{z}{kT}\left(\varepsilon_{sp} - \frac{\varepsilon_{ss} - \varepsilon_{pp}}{2}\right)\phi_s\phi_p$$

Phase diagrams can be constructed by taking the derivative of the free energy with respect to ϕ. The boundary of the miscibility gap, also called the *binodal* or *coexistence curve*, is defined by:

$$\frac{\partial \Delta g_{mix}}{\partial \phi_p} = 0$$

The limit of stability of the one phase mixture, called the spinodal, is obtained by equating the second derivative of the F-H free energy to zero:

$$\frac{\partial^2 \Delta g_{mix}}{\partial \phi_p^2} = \frac{1}{N\phi_p} + \frac{1}{1-\phi_p} - 2\chi = 0$$

For values of $\chi > \chi_s$ (or $T < T_s$), the solution will spontaneously decompose into polymer-rich and solvent-rich phases.[2] It is debated whether cloud point measurements are a measure the spinodal rather than the coexistence curve. Between the spinodal and coexistence lines, demixing occurs by nucleation and growth mechanisms.

The *critical point* is the extrema of the spinodal:

$$\frac{\partial^3 \Delta g_{mix}}{\partial \phi_p^3} = 0$$

$$\phi_{p,cr} = \frac{1}{1 + N^{1/2}}$$

$$\chi_{cr} = \frac{\left(1 + N^{1/2}\right)^2}{2N}$$

χ

Two Phase

One Phase

ϕ_p
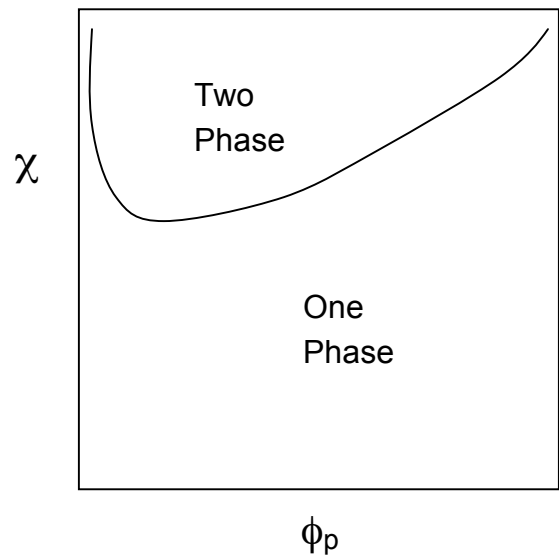
The critical concentration of polymer in a polymer-solvent mixture scales as $N^{-1/2}$. Note that the critical temperature (defined by χ_{cr}) is also fixed, in accordance with the phase rule.

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The Flory-Huggins free energy of mixing expression can be used to calculate phase diagrams of polymer solutions using the using the Hildebrand solubility parameter formalism[4]:

$$\chi = v\frac{(\delta_p - \delta_s)^2}{kT}$$

where v is an averaged volume of the polymer segment and solvent species, and δ_j is the solubility parameter of species j. For the system investigated here, the solubility parameter value is 17.52 $(MPa)^{1/2}$ for polystyrene and 16 $(MPa)^{1/2}$ for methyl cyclohexane.[5]

Previous studies investigating phase diagrams of polystyrene-methyl cyclohexane are described in the archival literature.[6-8] Recently, this system has also been exploited for microencapsulation.[9]

References

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5. Polymer Handbook, 3rd Edition, J. Brandup and E.H. Immergut, Eds., John Wiley & Sons: New York, 1989.

6. S. Saeki, N. Kuwahara, S. Konno, and M. Kaneko, "Upper and lower critical solution temperatures in polystyrene solutions", *Macromolecules* **6**, 246 (1973).

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9. T. Narita, et al., "Gibbs free energy expression for the system polystyrene in methylcyclohexane and its application to microencapsulation", *Langmuir* **19**, 5240 (2003).