

Chemical Engineering 160/260
Problem Set #3 Solutions:

1) *Why do most polymers exhibit LCST rather than UCST behavior?*

Consider an A B system. The appearance of UCST vs. LCST behavior can be determined by the sign of the enthalpy and entropy terms ΔH_{mix} and ΔS_{mix} in the free energy of mixing equation:

$$\Delta G_{\text{mix}}(\%A, T) = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}},$$

assuming that the dominant temperature dependence of ΔG_{mix} is from the T term. If ΔG_{mix} is less than zero, the two components will form a single phase. If ΔG_{mix} is greater than zero the components will phase segregate. For most solutions ΔS_{mix} is greater than zero because mixing allows increased configurational entropy (more unique ways to arrange the two components A, B on a lattice). Consider a solution with concentration eg 0.5% A and 0.5% B. If ΔH_{mix} is also greater than zero for this system, (endothermic mixing) then at low temperatures ΔG_{mix} will be greater than zero, at some critical temperature ΔG_{mix} will be equal to zero and at higher temperatures ΔG_{mix} will be less than zero. Thus we will see UCST type behavior: a two phase region at low temperatures and a single phase region at high temperatures. If ΔH_{mix} is less than zero we see complete miscibility at all temperatures.

For polymers, as Sperling points out, ΔH_{mix} is usually less than zero and ΔS_{mix} is often greater than zero (the exact opposite of the UCST case). ΔS_{mix} is greater than zero because of densification, which leads to a loss of configurational entropy due to a loss of holes or lattice sites which would allow more microstates. Qualitatively, the chains are more locked into a given configuration when densification occurs. ΔH_{mix} is negative due to exothermic mixing. Both these terms are quite small, but the important point is their signs. For a given concentration, at low temperatures ΔG_{mix} is negative and a single phase exists. At higher temperatures ΔG_{mix} becomes positive and a two phase region exists.

2) We are asked to discuss the spheres which form when a poly(styrene-co-butadiene) block copolymer phase segregates. The polystyrene blocks have a molecular weight of 20,000 g/mol and the butadiene blocks have a molecular weight of 40,000 g/mol.

a) *Size of spheres:*

$$R = 1.33 \alpha KM^{1/2}$$

$$\alpha = 1.2$$

$$K = 670 \text{ E}^{-3} \text{ A}$$

$$M = 20,000 \text{ g/mol}$$

Substituting in leads to **R = 151 A**: the spheres have a diameter of 302 Angstroms.

b) *# blocks/sphere?*

There are two approaches one can think of to obtain this number. They are both estimates, but one is a better approach than the other.

Approach #1: Assume uniform density in the spheres, use bulk density of polystyrene to approximate the total mass within one sphere, and use the given molecular weight of polystyrene blocks to obtain the # blocks/sphere.

$$V_{\text{sphere}} = 4/3\pi R^3 = 1.442 \text{ E}^{-17} \text{ cm}^3$$

$$\text{Mass}_{\text{sphere}} = \rho V_{\text{sphere}} = 1.06 \text{ g/cm}^3 * 1.442 \text{ E}^{-17} \text{ cm}^3 = 1.529 \text{ E}^{-17} \text{ g [density from Table 3.2]}$$

$$\# \text{ blocks/sphere} = \text{Mass}_{\text{sphere}} * N_A \div \text{MW} = 1.529 \text{ E}^{-17} \text{ g} * 6.023 \text{ E}^{23} \text{ blocks/mol} \div 20,000 \text{ g/mol}$$

blocks/sphere ~ 460

Approach #2: Estimate the radius of gyration of the styrene block and divide the total sphere volume by this number.

Using data from Table 3.9 in Sperling, we can obtain $\langle R_g \rangle^2 = 6.6 \text{ E}^{-12} \text{ cm}^2$ at 34.2° C (theta temperature) for polystyrene with a molecular weight of $M_w = 7.65 \text{ E}^5 \text{ g/mol}$. We can assume to first approximation that the blocks in the spheres are in a theta solvent because they are *mostly* surrounded by blocks of the same chemical structure. To be more accurate we would have to consider boundary effects. Since the ratio $(\langle R_g \rangle^2 / M_w)^{1/2}$ should be roughly constant for a given molecular weight of the same polymer in the same solvent we can estimate R_g for the block with molecular weight 20,000 g/mol as

$$\langle R_g \rangle^{2/2} = [6.6 \text{ E}^{-12} \text{ cm}^2 * (20,000 \text{ g/mol} \div 7.65 \text{ E}^5 \text{ g/mol})]^{1/2} = 4.15 \text{ E}^{-7} \text{ cm}$$

$$R_g \sim 41.5 \text{ Angstroms}$$

$$\# \text{ blocks/sphere} \sim V_{\text{sphere}} / V_{\text{block}} = (R_{\text{block}} / R_g)^3 = (151/40)^3 = 48$$

I think that the first approach will give a more accurate number, because the second assumes that no other blocks can penetrate into the volume $4/3\pi R^3$ assigned to one block. In fact we know that there is a great deal of interpenetration.

c) #spheres/cm³?

Here we need to take into account the fact that much of the space in a cubic centimeter will be filled by the matrix butadiene. The volume of butadiene required for each sphere to satisfy the stoichiometry of the block copolymer can be determined using the given molecular weights of each block in conjunction with the bulk densities of each polymer, again assuming as in approach #1 that these values are valid here.

$$\rho_{\text{polystyrene}} = 1.06 \text{ g/cm}^3$$

$$\rho_{\text{butadiene}} = 1.01 \text{ g/cm}^3$$

The volume ratio of butadiene to polystyrene is thus given by

$$80,000 \text{ g/mol} \div 20,000 \text{ g/mol} * \rho_{\text{polystyrene}} \div \rho_{\text{butadiene}} = 4.198$$

So for every sphere of polystyrene with volume V_{sphere} , we must account for $4.198V_{\text{sphere}}$ volume for the matrix. Thus the number spheres per cm^3 is $[(1+4.198)V_{\text{sphere}}]^{-1} = 1.334 \text{ E}^{16} \text{ spheres/cm}^3$.

3) What is the analytical expression for X_{blend} for the system of two copolymers $(A_x B_{1-x})_n / (C_y D_{1-y})_n$?

$X_{\text{blend}} = \sum c_{ij} X_{ij}$. This can be solved by inspection using X_{blend} for the $A/(C_x D_{1-x})_n$ as given in Sperling. The result is:

$$X_{\text{blend}} = xyX_{AC} + x(1-y)X_{AD} + (1-x)yX_{BC} + (1-x)(1-y)X_{BD} - x(1-x)X_{AB} - y(1-y)X_{CD}$$

4) We are given an equation for the enthalpy of vaporization at 25°C , the boiling point at one atmosphere pressure, density, and molecular weight of toluene and asked to calculate its solubility parameter at 25°C .

-The solubility parameter can be calculated from the equation $\delta = (\Delta E/V)^{1/2}$ where V is the molar volume and ΔE is the change in internal energy of the material on going from liquid to gas states.

-Substituting in T_b to the given $\Delta H_{\text{vaporization}}$ gives $\Delta H(25^\circ\text{C}) = 9083 \text{ cal/mol}$

-To relate ΔH to ΔE , consider the definition of enthalpy:

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

The third term is usually negligible because any pressure change occurring would be very small. There is however a significant molar volume change on vaporization so the second term is not negligible. We can approximate $dV \sim V_{\text{vapor}}$ since $V_{\text{vapor}} \gg V_{\text{liquid}}$. We can further assume the vapor behaves ideally so that from the ideal gas law

$PV_{\text{vap}} = RT$. So

$$dH \sim dE + PV_{\text{vap}} = dE + RT$$

$$\Delta E = \Delta H - RT = 9083 - 1.987(298) = 8283 \text{ cal/mol}$$

The molar volume can be found from the density and molecular weight given as

$$V = MW/\rho = 105.7 \text{ cm}^3/\text{mol}$$

$$\delta = (\Delta E/V)^{1/2} = (8283 \text{ cal/mol} \div 105.7 \text{ cm}^3/\text{mol})^{1/2} \sim 8.9 \text{ (cal/cm}^3)^{1/2}$$