Lecture 19 8/11/14

A. Solutions that Are Very, Very Non-Ideal

- In the prior lectures on non-ideal solution behavior, we have considered a lattice theory of solutions, i.e. regular solution theory, in which we explicitly assume the solution is a non-electrolyte solution, and that the solvent and solute molecules are about the same size.
- In the next two lectures we consider cases where these assumptions are violated; polymer solutions and electrolyte solutions.
- In polymer solutions, the solute is assumed to be a macromolecule composed of N monomeric units, where N is a very large number.
- In electrolyte solutions, salts dissolve in water to form ions. Ions are charged particles and they interact with each other via Coulombic forces. Unlike regular solutions where solute-solute, solvent-solvent, and solute-solvent interactions are assumed weak, Coulombic forces are not weak and the Coumbic interaction energy falls of as 1/r.

B. Polymer Solutions: Flory-Huggins Theory

- What makes polymer solutions unique is the fact that the solute (i.e. the polymer) is much larger than the solvent (i.e. water, acetone, etc.). This affects physical properties of polymer solutions in particular colligative properties.
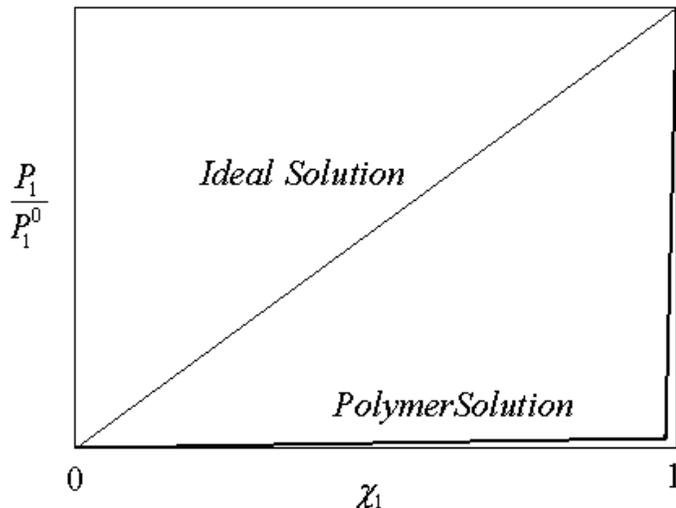
- The diagram above contrasts the solvent vapor pressure observed above an ideal solution (i.e. Raoult's Law) with the vapor pressure above a polymer solution.

- Implicit in many of our solution thermodynamic equations is the assumption that the solute and solvent particles are of similar sizes and occupy similar volumes. A good example is the entropy of mixing. If we mix gas A in volume V_A and gas B in volume V_B the final volume occupied by both gases is V_A+V_B. The entropy change is:

$$\Delta S_{MIX} = n_A \Delta \overline{S}_A + n_B \Delta \overline{S}_B = R \left(n_A \ln \left(\frac{V_A + V_B}{V_A} \right) + n_B \ln \left(\frac{V_A + V_B}{V_B} \right) \right)$$

$$= -R \left(n_A \ln \left(\frac{V_A}{V_A + V_B} \right) + n_B \ln \left(\frac{V_B}{V_A + V_B} \right) \right) = -R \left(n_A \ln \phi_A + n_B \ln \phi_B \right) \qquad \textbf{(19.1)}$$

where ϕ_A and ϕ_B are volume fractions. The volume fractions are replaced by mole fractions only after making some assumptions. First we replace each volume with the number of moles times the partial molar volume:

$$\Delta S_{MIX} = -R \left(n_A \ln \left(\frac{n_A \overline{V}_A}{n_A \overline{V}_A + n_B \overline{V}_B} \right) + n_B \ln \left(\frac{n_B \overline{V}_B}{n_A \overline{V}_A + n_B \overline{V}_B} \right) \right) \qquad \textbf{(19.2)}$$

- Now if we make the assumption that the partial molar volumes of the two gases are equal $\overline{V}_A = \overline{V}_B$ … a good assumption for gases…we obtain

$$\Delta S_{MIX} = -R \left(n_A \ln \left(\frac{n_A}{n_A + n_B} \right) + n_B \ln \left(\frac{n_B}{n_A + n_B} \right) \right) = -R \left(n_A \ln \chi_A + n_B \ln \chi_B \right) \qquad \textbf{(19.3)}$$

$$or \ldots \Delta S_{MIX,m} = \frac{\Delta S_{MIX}}{n_A + n_B} = -R \left(\chi_A \ln \chi_A + \chi_B \ln \chi_B \right)$$

which is the expression usually given for the entropy of mixing.

- The assumption $\overline{V}_A = \overline{V}_B$ is good for gases and solids. This assumption was made in the theory of regular solutions, but it is never valid in polymer solutions, where the macromolecular solute is much larger than the solvent and occupies a lot more volume than the solvent. So for polymer solutions where the solute(s) may be much larger in size than the solvent, it is better to use the volume fraction instead of the mole fraction in the entropy equation and in the equations for all state functions.
- A polymer solution can be visualized in the same way as a regular solution: the solvent and solute occupy a lattice. The difference is that the polymer occupies more than a single lattice site. We assume each monomer occupies a lattice site as shown below, where each monomer is a dark circle and the monomers are connected into a polymer. The solvent molecules are shown as open circles.
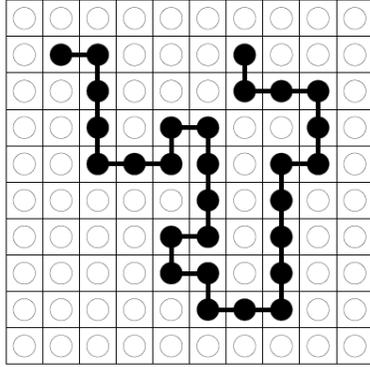
- Suppose this lattice has M sites. M plays the role of the total volume. There are n_P polymer molecules each with N monomer units and n_S solvent molecules. If the lattice is filled then $M = Nn_P + n_S$. We now define the solvent and polymer volume fractions:

$$\phi_S = \frac{n_S}{M} \text{ and } \phi_P = \frac{Nn_P}{M} \tag{19.4}$$

- Flory-Huggins theory calculates the energy, entropy, free energy, chemical potential, and activity coefficients for polymer solutions using the same lattice approach as used for regular solutions. The difference is that volume fractions are used instead of mole fractions. First of all, from our remarks about the entropy, it is obvious that the entropy of mixing a polymer and a solvent is:

$$\Delta S_{MIX} = -R\left(n_S \ln \phi_S + n_P \ln \phi_P\right)$$

$$or\ldots\Delta \overline{S}_{MIX} = \frac{\Delta S_{MIX}}{M} = -R\left(\phi_S \ln \phi_S + \frac{\phi_P}{N}\ln \phi_P\right) \tag{19.5}$$

which is identical to our entropy equation for ideal solutions if N=1.

- The energy U is derived in the same way as in regular solution theory (see Lecture 19). The internal energy u accounts for all interactions between solvent and polymer molecules:

$$U = N_{SS}\varepsilon_{SS} + N_{PP}\varepsilon_{PP} + N_{SP}\varepsilon_{SP}$$

$$where\ldots Zn_S = 2N_{SS} + N_{SP} \text{ and } ZNn_P = 2N_{PP} + N_{SP} \tag{19.6}$$

- In the same procedure as in regular solutions we get the energy of mixing. U is composed of U_S and U_P which are the energies of the pure solvent and polymer, respectively:

$$U = \frac{Z\varepsilon_{SS}}{2RT} + \frac{Z\varepsilon_{SS}}{2RT} + RTw_{SP}\frac{n_S n_P N}{M}$$

$$where\, U_S = \frac{Z\varepsilon_{SS}}{2RT} \text{ and } U_P = \frac{Z\varepsilon_{SS}}{2RT} \tag{19.7}$$

- The internal energy of mixing is obtained by subtracting U_S and U_P from U in equation 19.7. Note as before the internal energy of mixing and the enthalpy of mixing are roughly equivalent

$$\therefore \Delta U_{MIX} = U - U_S - U_P \, RTw_{SP} \frac{n_S n_P N}{M} = MRTw_{SP}\phi_S\phi_P$$

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$$\therefore \bar{U}_{MIX} = \frac{U_{MIX}}{M} \approx \Delta\bar{H}_{MIX} = RTw_{SP}\phi_S\phi_P \ldots where \ldots w_{SP} = \frac{Z}{RT}\left(\varepsilon_{SP} - \frac{\varepsilon_{SS} + \varepsilon_{PP}}{2}\right)$$

(19.8)

- We can also obtain the Helmholtz and Gibbs energies. These two energies are about equal because the internal energy and enthalpies are roughly equal. We assume the form for the internal energy of mixing in 19.8 and the expression for the entropy of mixing in 19.5:

$$\Delta\bar{G}_{MIX} \approx \bar{A}_{MIX} = \bar{U}_{MIX} - T\Delta\bar{S}_{MIX} = RTw_{SP}\phi_S\phi_P + RT\left(\phi_S \ln\phi_S + \frac{\phi_P}{N}\ln\phi_P\right)$$

(19.9)

$$\therefore \frac{\bar{A}_{MIX}}{RT} = w_{SP}\phi_S\phi_P + \phi_S \ln\phi_S + \frac{\phi_P}{N}\ln\phi_P$$

- Now as before we can calculate the chemical potential of the polymer:

$$\mu_p - \mu_p^0 = \left(\frac{\partial A_{MIX}}{\partial n_p}\right)_{V,T} = RT\ln\phi_p + wNRT\phi_s^2 + RT(1-N)\phi_s = RT\ln\phi_p + RT\ln\gamma_p$$

(19.10)

$$\therefore \ln\gamma_p = wN\phi_s^2 + (1-N)\phi_s$$

- The first term on the right of the activity coefficient expression is the same as a regular solution…it is the contribution from solvent-solute, solvent-solvent, and solute-solute interactions. The second term which goes like $(1-N)\phi_s$ needs further explanation.

- Suppose we mixed two polymers A and B together and repeated the calculation. Polymer A has length N_A and polymer B has length N_B. If we repeated this calculation assuming two polymers, the chemical potential of polymer B is, for example:

$$\mu_B - \mu_B^0 = \left(\frac{\partial A_{MIX}}{\partial n_B}\right)_{V,T,n_A} = RT\ln\phi_B + wN_B RT\phi_A^2 + RT\left(1 - \frac{N_B}{N_A}\right)\phi_A$$

(19.11)

$$\therefore \ln\gamma_B = wN_B\phi_A^2 + \left(1 - \frac{N_B}{N_A}\right)\phi_A$$

- Note that the term $\left(1 - \frac{N_B}{N_A}\right)\phi_A$ in the activity coefficient goes to zero if $N_A = N_B$. If A is a polymer of length $N_A = N$ and B is a monomer for which $N_B = 1$ we get

$$\ln\gamma_B = w\phi_A^2 + \left(1 - \frac{1}{N}\right)\phi_A$$

(19.12)

- The term $\left(1 - \frac{N_B}{N_A}\right)\phi_A$ therefore reflects contribution to the non-ideality of the solution from the difference in molecular sizes.

C. Osmotic Pressure Measurements

- Osmotic Pressure: Osmotic pressure is another example of a colligative property. Osmotic pressure is typically described for ideal solutions where it can be directly related to solute concentration. Osmotic pressure is the best way to obtain activity coefficients for polymer solutes.
- We consider the diagram below. A compartment with two stacks is separated by a semipermeable membrane. On one side of the membrane is a solvent 1 (e.g. water). On the other side is a solution consisiting of the same solvent 1 and a solute 2. The membrane is permeable to the solvent but no to the solute.
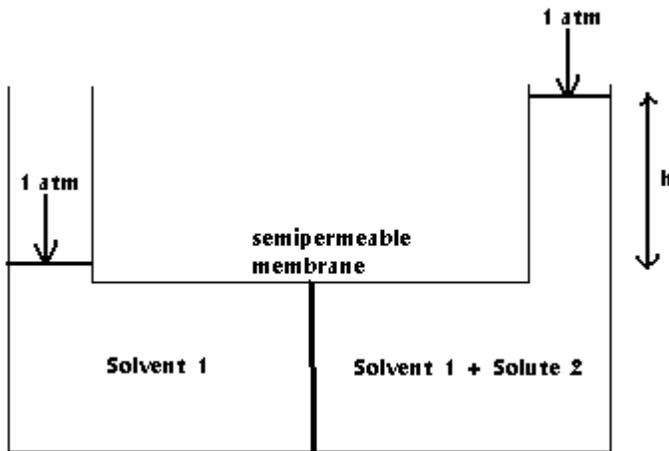
- To reach equilibrium the free energy of the solvent must be equal on both sides of the membrane i.e.
  -
  $$\mu_1\left(left\right)=\mu_1\left(right\right) \tag{19.13}$$
- In the left-hand-compartment is pure solvent so $\mu_1\left(left\right)=\mu_1^0$.
- In the right-hand-compartment is a solution so $\mu_1\left(right\right)=\mu_1^0+RT\ln a_1$
- The only way that this system can reach equilibrium is for solvent to flow from the left-hand compartment through the membrane to the right-hand compartment. However, in doing so the volume of the solution increase and a column of water rise in the right-hand stack. The difference between the liquid heights in the right-hand and left hand stacks is h.
- To push water in the right-hand stack a pressure π must be exerted in excess of the atmospheric pressure. To push a column of solution with density ρ up a height h requires $\pi=\rho gh$
- To relate the pressure π to properties of the solution consider that to produce this pressure the free energy of the solution must increase by

$$\Delta\mu=\int d\mu=\int\left(\bar{V}dP-\bar{S}dT\right)=\int_1^{1+\pi}\bar{V_1}\,dP\,(if\ dT=0) \tag{19.14}$$

- The equilibrium condition is

$$\mu_1(left) = \mu_1(right) \; or$$

$$\mu_1^0 = \mu_1^0 + RT \ln a_1 + \Delta\mu \tag{19.15}$$

$$= \mu_1^0 + RT \ln a_1 + \int_1^{1+\pi} \overline{V}_1 \, dP = \mu_1^0 + RT \ln a_1 + \pi \overline{V}_1$$

- Rearranging

$$\ln a_1 = -\pi \frac{\overline{V}_1}{RT} \tag{19.16}$$

- If the solution is non-ideal (polymer solution) we have two approaches to evaluate theacitivity coefficient from an osmotic pressure measurement:

$$\ln a_1 = \ln \gamma_1 + \ln \chi_1 = -\pi \frac{\overline{V}_1}{RT} \tag{19.17}$$

From the Flory-Huggins Model:

$$\ln a_1 = \ln(1-\phi) + \phi\left(1 - \frac{1}{N}\right) + w_{SP}\phi^2 = -\pi \frac{\overline{V}_1}{RT} \tag{19.18}$$

where ϕ is the volume fraction of the polymer. Therefore a measurement of the osmotic pressure can directly measure w_{SP} for a polymer solution and a direct measurement of the activity coefficient for the solvent and the polymer because.

$$\ln \gamma_S = \phi\left(1 - \frac{1}{N}\right) + w_{SP}\phi^2$$

$$\ln \gamma_P = (1-\phi)(1-N) + w_{SP}(1-\phi)^2 \tag{19.19}$$

- If the polymer solution is dilute then

$$\chi_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \ll 1 \tag{19.20}$$

- Using $\ln(1-x) \approx -x \quad if \; x \ll 1$ we get

$$\ln a_1 = \ln \chi_1 = \ln(1-\chi_2) \approx -\chi_2 = -\pi \frac{\overline{V}_1}{RT} \tag{19.21}$$

- Rearrange to get

$$\pi = \frac{\chi_2}{\overline{V}} RT \approx \frac{n_2}{n_1\overline{V}} RT \approx \frac{n_2}{V} RT = c_2 RT \tag{19.22}$$

- Van't Hoff's Law: In the limit of infinite dilution the osmotic pressure π is defined as $\pi = c_2 RT$.

Example: Calculate the osmotic pressure associated with a 0.1M sucrose solution at T=298K.

Solution: $\pi = c_2 RT = (0.1M)(0.0821 L \cdot atm / moles \cdot K)(298K) = 2.44\,atm.$

Note: 1 atm of pressure would push a column of mercury 0.76 m high. Therefore the osmotic pressure described above would support a column of mercury 1.85 m high. The same pressure would support a column of water 25 meters high (i.e. 78 feet).

- The molecular weight of a polymer can be determined from its osmotic pressure. Starting with the dilute limit:

$$\pi \approx c_2 RT = \frac{n_2}{V} RT = \frac{w_2}{VM_2} RT = C_2 \frac{RT}{M_2} \qquad \textbf{(19.23)}$$

Where C_2 has units of kg per m^3 or g per L and M_2 is the molecular weight. For very dilute solutions given a value for the osmotic pressure and C_2, M_2 can be determined. For more concentrated real solution the equation $\dfrac{\pi}{C_2} = \dfrac{RT}{M_2} + mC_2$. The y-intercept of this plot is RT/M_2.

Example: Use the following data to determine the molecular weight of glucose at T=283K:

C_2 (g L^{-1})	18.1	93.1	193.0
Π (bars)	2.42	11.70	24.12

Using $\dfrac{\pi}{C_2} = \dfrac{RT}{M_2} + mC_2$ plot $\dfrac{\pi}{C_2}$ versus C_2.
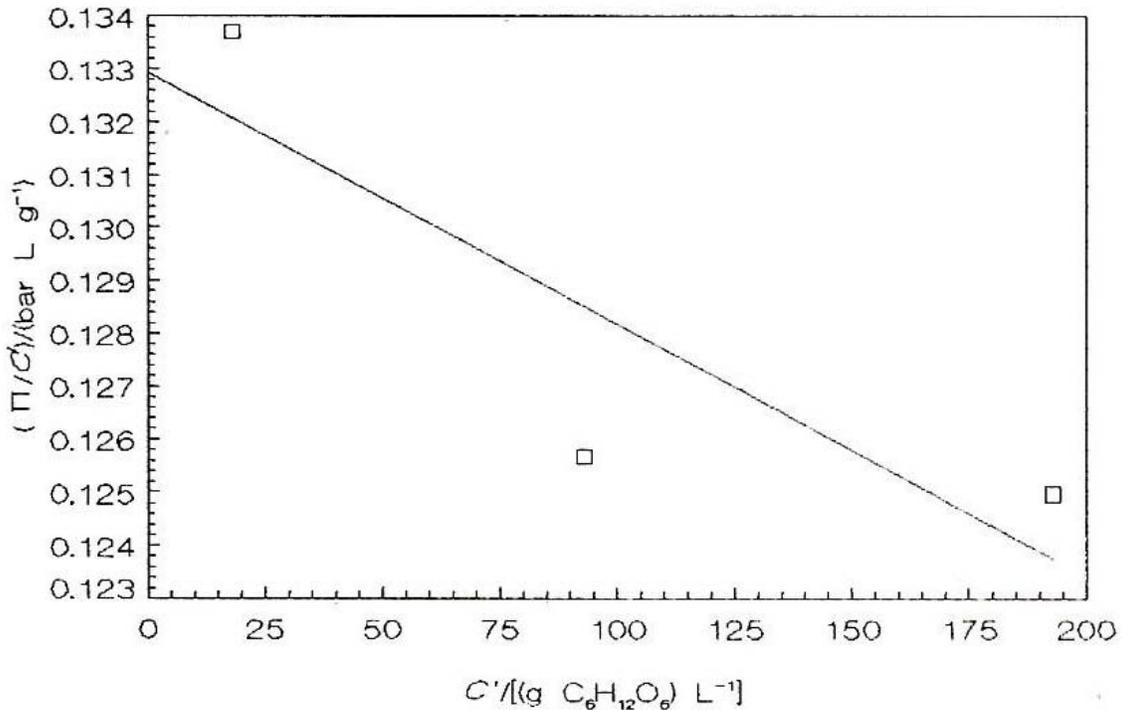
The intercept is $\dfrac{RT}{M_2} = 0.133 barLg^{-1}$. Solving M2=177gmol^{-1}.