

10.520 Problem Set 3
Due Wednesday, October 13, 2004

1. The dielectric properties of a homologous series of organic compounds can be estimated by the expression:

$$\frac{1}{\epsilon_n} = \frac{1}{\epsilon_1} + \frac{n}{\epsilon_2}$$

where ϵ_n , ϵ_1 , and ϵ_2 are the dielectric constants for the substance of interest, the shortest analogous compound in the series, and the incremental change, respectively.

- a. Using dielectric constant data for primary alcohols, determine the value of ϵ_2 for a methylene (-CH₂-) unit.
 - b. Estimate the dielectric constant for CH₃CH₂OC₆H₅ using ϵ_2 and the dielectric constant for CH₃OC₆H₅. Compare your estimate with the tabulated value.
 - c. Estimate the dielectric constants for CH₃(CH₂)₂COCH₃ and CH₃CH₂OCH₃ using ϵ_2 and the dielectric constant for CH₃COCH₃. In addition, estimate the dielectric constant for CH₃(CH₂)₂COCH₃ using ϵ_2 and the dielectric constant for CH₃CH₂COCH₃. Compare your estimates with tabulated values.
 - d. Estimate the dielectric constant for CH₃(CH₂)₃CN. Note the reason for your choice of basis molecule.
2. Calculate which solution contains a higher concentration of Li⁺: LiCl in MeOH or LiBF₄ in EtOH. Atomic radii: Li⁺, 0.60 Å; Cl⁻, 1.81 Å; BF₄⁻, 2.28 Å.
3. Lithium Fluoride (LiF, MW = 25.94) is to be purified by recrystallization from water. Estimate the minimum volume of water required to obtain 1kg of filtered LiF product. Solid LiF has a cubic structure and a density of 2.635 g/mL.
4. Naphthalene is to be removed from an aqueous stream at 25 °C by the addition of NaCl, KCl, MgCl₂, or CaCl₂.
- a. Which salts will be the most and least effective on a molar basis?
 - b. Which salts will be the most and least effective on a weight basis?
 - c. Under what conditions are your answers to the first two questions valid?
 - d. Which salt can salt out the most naphthalene?

	a ₊	a ₋	K ^s (naphthalene)		
Na ⁺	1.16 Å	Cl ⁻	1.67 Å	NaCl	0.22 L/mol
K ⁺	1.52 Å			KCl	0.19 L/mol
Mg ⁺²	0.86 Å			MgCl ₂	0.30 L/mol
Ca ⁺²	1.14 Å			CaCl ₂	0.32 L/mol

5. In anionic polymerization, the relative dissociation of the "living" carbanion affects the polymerization reaction rate. (Initiators such as butyl lithium and benzyl sodium are used to initiate growth of the polymer anion). You wish to use anionic polymerization to polymerize the following vinyl monomers:
- styrene
 - butadiene
 - methylmethacrylate
 - acrylonitrile
 - octadecylmethacrylate

Choose a solvent from the following list for each monomer that will optimize the reaction rate of polymerization while achieving high molecular weights.

Solvents:

- benzene
- diethyl ether
- pentane
- cyclohexane
- dimethyl formamide
- dioxane
- tetrahydrofuran

Explain your reasoning. What would happen to the reaction rate in polar solvents on the addition of glyme: $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$? on addition of crown ethers? What would happen to the reaction rate if a soluble nonreactive ionic salt were added?

6. The osmotic pressure Π in psi of polyethylene oxide, $M_n = 35,000$, in water at 22°C varies with the fraction of polyethylene oxide as follows:

v_2	0.042	0.083	0.104	0.125	0.146	0.167
Π	3	14	24	37	51	67

Plot the Flory-Huggins parameter, X_1 as a function of v_2 over this range. Comment on the shape of the curve. What do you think is happening?

7. Estimate the temperatures at which the following polymer/solvent mixtures would be fully liquid at 40% volume fraction of polymer. Use the data table below. Would you expect any of these systems to exhibit two liquid phases?

Polyethylene oxide in benzene ($X_t = 0.10$)
 Polyethylene in p-xylene ($X_t = 0.34$)
 Polyethylene in n-decane ($X_t = 0.25$)
 Cellulose tributyrate in dioxane ($X_t = 0.51$)