10.520 Problem Set 2

Fall 2004 - Due Monday Sept. 27 2004

Part 1:

The cohesive energy density, C, is the overall molecular cohesion of a liquid, and is given by the total change in energy of the solvent from a liquid to a noninteracting vapor at zero pressure, which can generally be represented by the internal energy change of vaporization as follows:

$$C = \frac{\Delta U_v}{V_m} = \frac{\Delta H_v - RT}{V_m}$$

where U = internal energy, Vm = molar volume and T = absolute temperature

For most liquids, it can be assumed that all intermolecular solvent-solvent interactions will be broken on vaporization to zero pressure.

A second solvent parameter that may be used is the expansion coefficient "*X*", which is the change in internal energy with a differential volume expansion:

$$X = \left(\frac{\partial U}{\partial V_m}\right)_T$$

This expansion coefficient is a measure of the degree by which attractive forces overcome repulsive forces in a solvent, and is thought to be primarily due to dispersion and dipole-dipole interactions.

i) Values of *X* for several solvents are given below, along with some physical constants. Using standard entropy or enthalpy of vaporization data, estimate the values of the cohesive energy density for each of these solvents at 25°C. Take a ratio of the two parameters, n = *X*/c. Discuss what you think the physical significance of these ratios are.

Solvent	*X* MPa	density g/cm^3	MW g/mol
H_20	151	1.0	18
benzene	379	0.879	78.1
acetonitrile	379	0.783	41.05
diethyl ether	264	0.708	74.1
carbon disulfide	377	1.26	76.1
CCl_4	345	1.595	153.8

(Note: Enthalpies of vaporization at 25°C for several organic compounds can be found in the CRC Handbook of Chemistry and Physics)

Lide, David R. *CRC Handbook of Chemistry and Physics*. 86th ed. Boca Raton, FL: CRC, 2005. ISBN: 0849304865.

ii) The cohesive energy density, C, is related to energy changes needed to separate like molecules from each other during the mixing or solvation process with a second solvent.

One may think of it as the energy required to create cavities in a solvent in which solute molecules may reside during solvation. Rank the above organic solvents with respect to their expected solubility in water based on C values. Discuss the ranking and the use of this parameter in general. Which solvent, if any, could be expected to be 100% miscible in water? Give your reasoning.

iii) Given the following information:

Solvent	density g/cm^3	MW g/mol	ΔH_{vap}(kJ/mol)
pyridine	0.982	79.1	40.15
CH_3I	2.279	142	26.09

Calculate the C values of these two solvents. Which would you expect to be water soluble, and to what degree? Would these two solvents be miscible with each other? Along with the C values, which other factors would you take into account?

Part 2:

1. Consider the follwing isomeric compounds: heptanoic acid, isopropyl butyrate, isopropyl-2-methyl-propionate, methyl hexanoate, propyl 2-methyl-propionate, and propyl butyrate:
   a. Draw the structure of these compounds. (hint: all compounds are $(C_7H_{14})O_2$).
   b. Which compounds do you expect to have the highest boiling point and why?
   c. Which compound do you expect to have the lowest boiling point and why?
   d. For the remaining five compounds, boiling points fall in two different temperature ranges. Based on the molecular structure of these compounds, determine which should have similar boiling points and list the two sets, noting which has higher boiling points.

2. A convenient method to regulate the temperature of a reaction is to select a solvent that boils at that temperature and to operate the reaction at reflux. In the synthesis of a specialty chemical, a carboxylic acid is converted to a propyl ester (eqn1, catalyzed by a solid acid catalyst/dessicant):

$$RCO_2H + CH_3(CH_2)_2OH \text{ ----------> } RCO_2(CH_2)_2CH_3 + H_2O$$

   The manufacturer has traditionally performed this reaction in a refluxing mixture of 1,1,1-trichloroethane (b.p. 76C) and propanol (b.p. 97C), using the 1,1,1-trichloroethane to regulate the temperature of the reaction. Under pressure to reduce the use of halocarbons in the process, a new solvent is needed that will have a boiling point of about 76C (i.e. +/- 10C).
   a. Design three ether-based solvents that are compatible with the temperature needs of the process. Of these three, note which one you think would be readily commercially available and why.
   b. Design an ester-based solvent compatible with the temperature needs of the process that also minimizes any transesterification concerns.

	Boiling Point	
R	$R(CH_2)_2CH_3$	RCO_2CH_3
CH_3	0 °C	58 °C
$CH_3(CH_2)_2$	69 °C	102 °C
$CH_3(CH_2)_4$	126 °C	151 °C

3. In selecting a solvent for replacement, the chemical reactivity of the solvent must be considered. In which of the following reactions might ethanol be substituted as a solvent? In which of the following reactions might ethyl acetate be substituted as a solvent? Acetonitrile CH_3CN)? For those cases in which ethanol, ethyl acetate, and/or acetonitrile cannot be used as solvents, detail the competing reaction that limits the solvent's usefulness.

   a) $RCO_2CH_3 + R'NH_2$ ---> $RCONHR' + CH_3OH$
   b) $RCOH + H_2/Rh$ ---> RCH_2OH
   c) $RMgBr + CH_3COCH_3$ ---> $R(CH_3)_2COMgBr$
   d) $NaSR + CH_3I$ ---> $RSCH_3 + NaI$
   e) $LiNHR + R'Cl$ ---> $RR'NH + LiCl$
   f) $Li(CH_2)_3CH_3$ + styrene ---> polymer