

Chemical Engineering 10.420/ 10.520
Solutions to Problem Set #2

Part I.

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, V_m = molar volume, and T is the 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.

- (a) 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 ₂ O	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.

Solution: We can estimate C by using ΔH_v as measured at room temperature for each solvent using the following equation:

$$C = \frac{\Delta H_v - R(293K)}{V_m} = \frac{\Delta H_v - (8.314J/molK)(293K)}{MW/\rho}$$

where ρ is the density (g/ cm³), MW is the molecular weight (g/ mol) and ΔH_v is the enthalpy of vaporization (J/ mol K). In the CRC, we find ΔH_v for the given solvents are:

Solvent	Π (MPa)	Density (g/ cc)	MW (g/ mol)	ΔH_v (kJ/ mol)	C (MPa)	n
H ₂ O	151	1.0	18.0	4399	2308	0.07
Benzene	379	0.879	78.1	33.83	353	1.07
Acetonitrile	379	0.783	41.05	32.94	582	0.65
Diethylether	264	0.708	74.1	27.10	235	1.12
CS ₂	377	1.26	76.1	37.51	415	0.91
CCl ₄	345	1.595	153.8	32.43	311	1.11

The ratio n is a rough comparison of dispersion interactions with all intermolecular forces present in the liquid state. Small values of n indicate large amounts of specific interactions such as H-bonding. Values of n that are close to 1.0 are found for weakly polar and non-polar solvents. Values of $n > 1$ are found for solvents with noninteracting characteristics (i.e., fluorocarbons).

- (b) The cohesive energy density, C , is related to energy changes needed to separate 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.

Solution: We can rank these solvents by comparing their C values, treating each C value as a kind of solvent parameter. Systems with similar cohesive energy densities should be more soluble in one another. Since water has a large C value, we list the solvents in order of estimated C :

Solvent	C (MPa)	n	Actual Solubility (parts/ 100)
Acetonitrile	582	0.65	∞
CS ₂	415	0.91	0.2
Benzene	353	1.07	0.08
CCl ₄	311	1.11	0.07
Diethyl ether	235	1.12	7.5

As a solubility gauge, the C value works fairly well for all solvents but diethyl ether. Acetonitrile, which is highly polar, is 100% miscible with water, and has a fairly large C value. CS₂ is more miscible than benzene and CCl₄, which are almost equally insoluble in water. The square root of C is called the Hildebrand Solubility Parameter, and it can generally be used with reasonable accuracy to predict solubilities of solute/ solvent combinations. For systems such as diethyl ether, which can undergo moderate H-bonding with water, but not with itself, the correlation can break down.

- (c) Given the following information:

Solvent	Density (g/ cm ³)	MW (g/ mol)	ΔH_{vap} (kJ/ mol)
Pyridine	0.982	79.1	40.15
CH ₃ I	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?

Solution: Again, calculating C :

Solvent	ρ (g/ cc)	MW (g/ mol)	ΔH_{vap} (kJ/ mol)	C (MPa)	Solubility (pph)
Pyridine	0.982	79.1	40.15	468	∞
CH ₃ I	2.279	142	26.09	379	1.8

So we can predict that pyridine would be more soluble from the C value. If we also consider the strong H -bond acceptor that pyridine is, it makes sense that it is more soluble. When considering solubility of CH_3I in water, we must be aware that water may act as a fairly weak nucleophile with I^- as a good leaving group. Over long periods of time, a mixture of the two would react to form CH_3OH . Pyridine and CH_3I are highly reactive and would instantaneously react if combined. Although from C values alone, these two chemicals are soluble in each other, if a small amount of pyridine is added to CH_3I , a pyridinium salt would form, which would not necessarily be soluble.

Part II.

- Consider the following isomeric compounds: heptanoic acid, isopropyl butyrate, isopropyl-2-methyl-propionate, methyl hexanoate, propyl-2-methyl-propionate, and propyl butyrate:
 - Draw the structure of each of these compounds. All compounds have the chemical formula $(C_7H_{14})O_2$.

Solution:

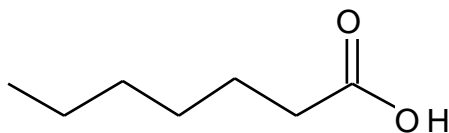


Figure 1: *Heptanoic acid*

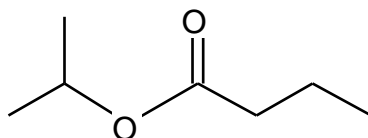


Figure 2: *Isopropyl butyrate*

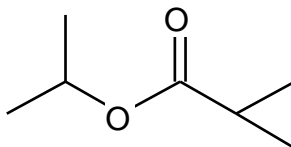


Figure 3: *Isopropyl-2-methyl-propionate*

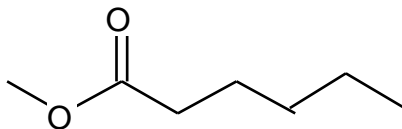


Figure 4: *Methyl hexanoate*

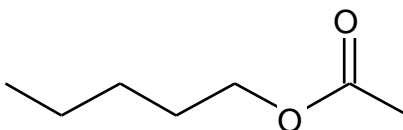


Figure 5: *Pentyl acetate*

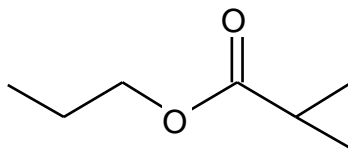


Figure 6: *Propyl 2-methyl propionate*

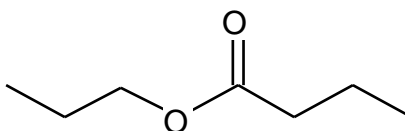


Figure 7: *Propyl butyrate*

- (b) Which compounds do you expect to have the highest boiling point and why?

Solution: Heptanoic acid has the highest boiling point because the carboxylic acid groups can form strong H-bond dimers.

- (c) Which compound do you expect to have the lowest boiling point and why?

Solution: Isopropyl 2-methyl propionate has the lowest boiling point. Esters cannot H-bond, so they must rely on van der Waals and dipole-dipole interactions. Isopropyl 2-methyl propionate is nearly symmetric (small dipole) and is branched (low area for van der Waals contact).

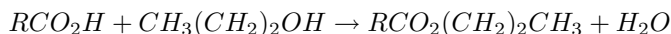
- (d) For the remaining five compounds, boiling points fall in two different temperature ranges. Based on the molecular structure of these compounds, determine which should have similar boiling points and list the two sets, noting which has higher boiling points.

Solution:

Highest Boiling Points: Pentyl acetate, methyl hexanoate, propyl butyrate.

Lowest Boiling Points: Isopropyl butyrate, propyl 2-methyl propionate.

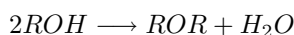
2. A convenient method to regulate the temperature of a reaction is to select a solvent that boils at that temperature and to operate the reaction at reflux. In the synthesis of a specialty chemical, a carboxylic acid is converted to a propyl ester, catalyzed by a solid acid catalyst/desiccant:



The manufacturer has traditionally performed this reaction in a refluxing mixture of 1,1,1-trichloroethane (b.p. 76 °C) and propanol (b.p. 97 °C), 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 b.p. 76 °C ± 10 °C.

- (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 available commercially, and explain your answer.

Solution: Ether based solvents with T_{bp} between 66–86 °C include di-isopropyl ether, methyl butyl ether, THF, and t-butyl ethyl ether. Symmetric ethers are the most readily available due to the ease in synthesis.



- (b) Design an ester-based solvent compatible with the temperature needs of the process that also minimizes any transesterification concerns.

R-Group	Boiling Point	
	R(CH ₂) ₂ CH ₃	RCO ₂ CH 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

Solution: To minimize trans-esterification, one must use a propyl ester that would react to yield the same alcohol reagent. Thus RCO₂(CH₂)₂CH₃. For the T_{bp} to be within our desired range, R must be a hydrogen, H, and therefore gives propyl formate.

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 (CH₃CN)?

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) $RCO_2CH_3 + R'NH_2 \longrightarrow RCONHR' + CH_3OH$

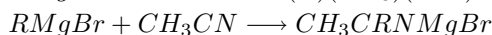
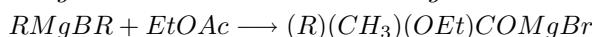
Solution: EtOH is OK. It reacts with the ester, but still yields the desired products. EtOAc cannot be used as it reacts with the amine to give RNHCOCH₃. Acetonitrile is also OK.

- (b) $RCOH + H_2/Rh \longrightarrow RCH_2OH$

Solution: Ethanol is OK because its pK_a is 16, which is greater than that of an aldehyde (approximately -10). EtOAc cannot be used because it reacts with the alcohol to give RCH₂OCOCH₃. Acetonitrile, along with EtOAc, may be reduced depending on reaction pressure. In general, the preference would be not to use an unsaturated solvent.

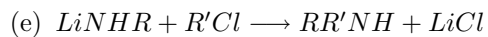
- (c) $RMgBr + CH_3COCH_3 \longrightarrow R(CH_3)_2COMgBr$

Solution: Ethanol, EtOAc, and acetonitrile cannot be used because they are all too reactive.



- (d) $NaSR + CH_3I \longrightarrow RSCH_3 + NaI$

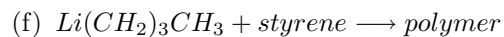
Solution: All are OK as solvents.



Solution: Ethanol cannot be used as a solvent because $^- \text{NHR}$ deprotonates ethanol. RNH_2 $pK_a = 35$, while ethanol's $pK_a = 1$.

EtOAc cannot be used as a solvent because it reacts with LiNHR .

Acetonitrile cannot be used as a solvent because $^- \text{NHR}$ deprotonates acetonitrile.



Solution: $\text{CH}_3\text{CH}_2\text{CH}_2^-$ deprotonates all three solvents, thus none will work.