CHEM 331

Problem Set #1: Inter-molecular Forces and Vapour Pressure

Hand in all worked solutions in a neat and organized format. Not all questions will be graded.

Due: Friday, Feb 2nd.

1. The water solubility of several organic compounds are provided in the table below.

a) The solubility of straight chain aliphatic hydrocarbons decreases dramatically with chain length. With the information provided, show that there is roughly an inverse linear relationship between the *molar volume* and the logarithm of the aqueous solubility for these compounds.

b) Look up the water solubility's for *n*-nonane, cyclohexane and benzene in Appendix C of your text (Schwarzenbach, 2nd Ed) and fill in the missing information below. Is their solubility predicted by the relationship established in part a (above). Explain.

Substance	Molecular formula	C_w^{sat} (μM)	Density (g/mL) at 25°C
n-pentane	C_5H_{12}	560	0.626
n-hexane	C_6H_{14}	150	0.659
n-heptane	C_7H_{16}	30	0.684
n-octane	C_8H_{18}	6.3	0.70
n-nonane	C_9H_{20}	?	?
Benzene	C_6H_6	?	?
cyclohexane	C_6H_{12}	?	?

2. The following compounds are listed in order of increasing refractive index as reported in Table 3.1 of your text (Schwarzenbach, 2nd Ed).

a) Classify each compound as *apolar*, *monopolar* or *bipolar* according to Schwarzenbach.

b) Rationalize the increase in refractive index in terms of molecular features that effect the *polarizability* of each compound.

c) How is the refractive index related to the polarizability and the magnitude of the dispersive free energy between a solute molecule '*i*' in a solvent molecule '1'.

d) Predict the order of increasing vapour pressures of these compounds at 25°C?

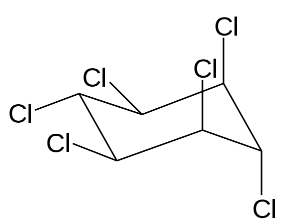
Substance	Molecular formula	n_D	BP (°C)	ΔH_{vap} (kJ/mol)
methanol	CH_3OH	1.326	65	35
2-propanone	$CH_3(CO)CH_3$	1.342	56	31
ethanol	CH_3CH_2OH	1.359	78	39
n-hexane	$CH_3(CH_2)_4CH_3$	1.372	69	29
1-octanol	$CH_3(CH_2)_6CH_2OH$	1.427	195	70
1,2-ethandiol	$HOCH_2CH_2OH$	1.429	197	66

3. a) Referring to Figure 3.6 in your text (Schwarzenbach, 2nd Ed), explain why ln K_{iah} is inversely related to the dispersive vdW parameter for all compounds whereas ln K_{iaw} is positively correlated to the dispersive vdW parameter and only within a homologous series of structurally related compounds.

b) Referring to Table 3.6 in your text (Schwarzenbach, 2nd Ed), several one-parameter linear free energy relationships (LFERs) are given for predicting equilibrium partition constants. Why are these LFERs always base on logarithmic functions of equilibrium constants and what are the advantages and limitations of using these type of LFERs?

4. In an article by Ternes *et al*. (Environ. Sci. Technol., **2004**, *38*(20), 393A-399A) on the fate and distribution of pharmaceuticals and personal care products (PPCPs) in wastewater treatment facilities, he summarizes the fate of the painkiller acetylsalicylic acid (ASA). Three chemical compounds described as 'metabolites' are identified as salicylic acid, gentisic acid and o-hydroxyhippuric acid. Look up the chemical structures of each of these compounds and propose an overall reaction scheme classifying each reaction as *oxidation*, *reduction*, *addition*, *elimination*, *substitution*, *condensation* or *hydrolysis.*

5. One of the most widely used and frequently detected organochlorine pesticides is known commonly as *lindane* (γ-HCH). Using the information provided, estimate the upper limit of the vapour pressure of the *sub-cooled* liquid state at 25^{o}C. Will the vapour pressure of solid *lindane* be higher or lower than that of the *sub-cooled* liquid state? Why?



MW = 291 g mol^{-1}
C_w^{sat}(L) = 1.9 x 10^{-4} M
T_m = 113 ^{o}C
T_b > 250 ^{o}C

6. Pure 1,4-dichlorobenzene (DCB) is still used as a disinfectant and 'air-refresher' in some public urinals. You want to calculate the concentration of DCB in g per m^3 of air at 25 ^{o}C.
a) Estimate using only melting point (T_m = 53.0 ^{o}C) and boiling point (T_b = 173.9 ^{o}C) data.
b) Refine your answer using the vapour pressure data given below.

T (^{o}C)	29.1 s	44.4 s	54.8	84.8	108.4	150.2
P^o (mm Hg)	1	4	10	40	100	400

7. The vapour pressure of 1,1,1,2-tetrafluoroethane (HFC-134a) is 132.9 kPa at -20°C and 292.9 kPa at 10°C. Estimate the normal boiling point of HFC-134a.

8. For each of the following;
a) identify the functional groups involved
b) the oxidation state changes and the number of moles of electrons transferred
c) if the reaction does not involve an overall change in oxidation state, classify the reaction as one of the following *addition*, *elimination*, *condensation* or *hydrolysis*.