Carnegie Mellon University
12-725, Spring 2020

Department of Civil and Environmental Engineering
Instructor: G. Lowry

Physicochemical Processes and Organic Compounds in Aquatic Systems
Midterm Exam 1 (2/25/20)
Three pages of notes allowed
(64 points total) Solutions

1. 1. (**12 points**) Below shows values for $G^E_{i,w}$ and aqueous activity coefficients at infinite dilution along with the compounds that they correspond with. Note that **each list is in a random order**.
a) Match the compounds with their correct values of activity coefficient and $G^E_{i,w}$
b) briefly explain the reasons form your assignments.

Compounds: chlorobenzene, methanol, phenanthrene, trichloromethane
$G^E_{i,w}$, (kJ/mol): 36, 1.2, 16.6, 23.7
$\gamma^\infty_{i,w}$: 1.6, 1.4×10^4, 7.9×10^2, 2.0×10^6

4

a)

Compound	$G^E_{i,w}$ (kJ/mol)	$\gamma^\infty_{i,w}$
Phenanthrene	36	2×10^6
Chlorobenzene	23.7	1.4×10^4
trichloromethane	16.6	7.9×10^2
Methanol	1.2	1.6

8 b)

Phenanthrene (1) is the largest apolar compound. It will be (2) most "non-ideal" in water and thus has the largest $G^E_{i,w} + \gamma^\infty_{i,w}$

Methanol is (3) small and can form (4) H-bonds with water. Thus it will be (5) most "ideal" and will have the lowest $G^E_{i,w} + \gamma^\infty_{i,w}$

Chlorobenzene + trichloromethane are (6) mono-polar. The (7) chlorobenzene is larger, thus

(8) $G^E_{\text{chlorbenz},w} > G^E_{\text{trichloromeath},w}$

$\gamma^\infty_{\text{chlorobenz},w} > \gamma^\infty_{\text{trichloromeath},w}$

2. **(12 points)** What types of intermolecular forces occur for the compounds 1,2-dichloroethane and n-propanol in the solvents water, acetone, and hexane. *Note that you only need to consider the intermolecular forces between the compounds and the solvent.* Make a 3x2 Table showing your responses. **Be as specific as you can**.

	Solvent: Water	Solvent: Acetone	Solvent: Hexane
1,2- dichloroethane	vdw forces: London dispersive forces; dipole-dipole; dipole-induced dipole	vdw forces	London dispersive forces; dipole-induced dipole
n-propanol	H-bonding; vdw forces	H-bonding; vdw forces	London dispersive forces; dipole-induced dipole

2 points for each grid

3. **(12 points)** The pure *liquid* solubility of naphthalene in water is 8.9×10^{-4} mol/L at 25 °C. Calculate the activity coefficient for naphthalene in octanol, $\gamma_{i,oct}$, at 25 °C from knowledge of the octanol/water partition coefficient, $K_{ow} = 2.3 \times 10^{3}$. The molar volume for octanol is 0.157 L/mol, and for water is 0.018 L/mol. **Does this answer agree with your expectations? Explain.**

2' $K_{iow} = \frac{C_{io}}{C_{i,w}} = \frac{\gamma_{i,w}\bar{V}_w}{\gamma_{i,o}\bar{V}_o}$ $\qquad \gamma_{i,oct} = \frac{\gamma_{i,w}\bar{V}_w}{K_{iow}\bar{V}_o}$

2' $\gamma_{i,w}^{sat} = \frac{1}{\bar{V}_w C_{i,w(L)}^{sat}} = \frac{1}{(0.0181\ L/mol)(8.9\times10^{-4}\ mol/L)}$

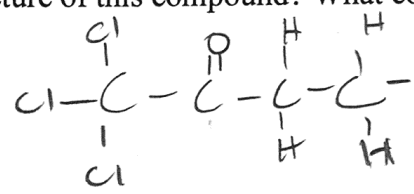
$= 6.2\times10^{4}$

2' $\gamma_{i,oct} = \frac{(6.2\times10^{4})(0.0181\ L/mol)}{(2.3\times10^{3})(0.015\ L/mol)} = 3.11$

This value is reasonable. It is near 1 (ideal) (2') but larger because naphthalene and octanol are not identical. The H-bonds in (2') octanol dissociated to make a cavity for naphthalene are not recovered in the (2) octanol–naphthalene interactions. This non-ideal behavior increases $\gamma_{naphth,w} > 1$.

4. **(28 points)**
1,1,1-trichloro-2-butanone is being considered as an antifungal agent in paint. **(T_b=115 °C, T_m=-24 °C)** Answer the following quesitons about this compound.

a. (8 points) What is the structure of this compound? What compound class or classes does this chemical belong?



(4')

it is a ketone and an organohalide

(4')

b. (8 points) Would you expect 1,1,1-trichloro-2-butanone to be hydrophobic or hydrophilic? Estimate the K_{iow} of this compound to confirm your estimate.

The compound should be moderately hydrophobic due to the chlorines and the C4 chain. The ketone group partly off-sets this, so it could be moderately hydrophilic tw. (2')

(2')

$\log K_{ow\,(25°)} = \sum n_k f_k + 0.23$ (no corrections needed)

(3')

Frag	n_k	f_k	value
$-CH_3$	1	0.55	0.55
$-CH_2$	1	0.49	0.49
al-CO-al	1	-1.56	-1.56
al-Cl	3	0.31	0.93
			+0.23
		$\log K_{ow}$	0.64

$K_{ow} = 4.4$ → only slightly hydrophobic as expected.

(1')

T_1

c. (12 points) If this compound were present in a paint at a mol fraction of 0.1 (i.e. x_i=0.1), what would be the concentration of 1,1,1-trichloro-2-butanone in air in equilibrium with the paint at 25 °C? You can assume that 1,1,1-trichloro-2-butanone *behaves ideally* in the paint.

To estimate this we need the vapor pressure of the compound.

$$\ln P_{i,L}^{*} = -K_F(4.4 \ln T_b)\left[1.8\left(T_b/T - 1\right) - 0.8 \ln\left(T_b/T\right)\right]$$ (3')

assume $K_F = 1.03$ (1') $(1.1 \geq K_F > 1)$

$T_b = 115\,^{\circ}C = 388\,K$

$$= -1.03(4.4 \ln(388))\left[1.8\left(\tfrac{388}{298} - 1\right) - 0.8 \ln\left(\tfrac{388}{298}\right)\right]$$

$$= -3.55$$

$$P_{i,L} = 2.9 \times 10^{-2}\ \text{bar} \sim \text{atm}$$ (2')

Solvent is present @ $x_i = 0.1$

assuming Raoult's Law

$$P_i = \gamma_{i,e}\, x_{i,e}\, P_{i,L}^{sat}$$ (3') assume $\gamma_{i,e} = 1$

$$= (1)(0.1)(2.9 \times 10^{-2}\ \text{atm})$$

$$= 2.9 \times 10^{-3}\ \text{atm}$$

$$\frac{n}{V} = \frac{P}{RT} = \frac{2.9 \times 10^{-3}\ \text{atm}}{0.0821\left(\frac{L\ \text{atm}}{\text{mol K}}\right)(298\ K)} = 1.1 \times 10^{-4}\ \frac{\text{mol}}{L}$$ (3')

$$= 19.1\ g/m^3$$

$MW = 174\ g/\text{mol}$