

HW5 Rubrics

Problem 1 (20)

Part a	Rank	2
	Reasoning	4
Part b	Rank	2
	Reasoning	4
Part c	Reasoning	8

Problem 4 (20)

Correct Grouping	2 for each
a, b values	1 for each
plots	5
Reasoning	6

Problem 6 (20)

Use correct formula	5
Make gamma assumption	2
Solubility assumption or temperature adjustment	3
Chloroform, $C_{i,w}$	5 (1 for answer, 4 for process)
Vinyl chloride, $C_{i,w}$	5 (1 for answer, 4 for process)

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**12-725: Fate, Transport, and Physicochemical Processes of Organic Contaminants
in Aquatic Systems and their Measurement in Environmental Samples**

Problem Set #5 Spring 2020
Due February 20 by 5pm

1. Given the following information:

Compound	ΔH_{vap} (kJ/mol)	H_{wE} (kJ/mol)	$\Delta H_{\text{vap}} - H_{\text{wE}}$
Benzene	34	4	30
Dipropylether	27	-19	46
Methylbenzene	38	6	32
1-hexanol	62	-14	76

- Rank the compounds in order of increasing vapor pressure (lowest to highest). Explain your reason.
- Rank these compounds on order of increasing aqueous solubility (lowest to highest). Explain your reasoning.
- Which compound's air-water partition coefficient should be the most sensitive to changes in temperature? Explain your reasoning.

a) Benzene and dipropylether are about the same size. They actually have very similar vapor pressure, but dipropylether is a monopolar compounds, where as benzene is mostly apolar (it is an H acceptor). Thus, we'd predict benzene to have a slightly higher vapor pressure than dipropylether. Methylbenzene vapor pressure will be slightly lower than that due to its larger size, and 1-hexanol will have the lowest VP due to its ability to H-bond in a pure liquid of itself.

Highest to lowest VP

Benzene > dipropylether > methylbenzene > 1-hexanol

b) Solubility is based on its ability to interact with water. 1-hexanol for form H-bonds with water so it is most soluble, followed by dipropylethere which can also form H-bonds (but not as many per molecule). Benzene and methylbenzene will have the lowest solubility. Benzene is slightly ore soluble than methylbenzene because it is smaller.

Highest to lowest solubility:

1-hexanol > dipropylether > benzene > methylbenzene

c) The sensitivity of the air-water partitioning coefficient is $\Delta H_{\text{vap}} - H_{\text{Eiw}}$. I've added those values in the table above. The higher the magnitude of the value, the greater the effect of

T on K_{iaw} . So, from lowest to highest effect is:
Benzene < Methylbenzene < dipropylether < 1-hexanol.

2. Estimate the aqueous solubility of the following compounds at 25 °C in mg/L using two different estimation methods. Cite sources for the estimation methods, data, and experimental/reported values used. Compare the estimated values with reported values and calculate the error (%). (Note: I have provided a chapter from a book on solubility estimation methods).
(a) chloroform, (b) anthracene

Various methods are available for estimating the solubility of these compounds including 1) using known values of the activity coefficient and knowing T_m and T_b (to correct for a phase change of the compound at 25 °C if needed,

(a) For chloroform, $T_m = -63.5^\circ\text{C}$ and $T_b = 61.15^\circ\text{C}$.

At 25°C, chloroform is in liquid phase. Thus: $C_{iw}^{sat} = \frac{1}{\bar{v} \times \gamma_{iw}^{sat}}$

According to EOC Table 9.1, $\gamma_{iw}^{sat} = 7.9 \times 10^2$ for chloroform.

Thus: $C_{iw}^{sat} = \frac{1}{\bar{v} \times \gamma_{iw}^{sat}} = \frac{1}{\frac{0.018\text{L}}{\text{mol}} \times 7.9 \times 10^2} = 0.07 \text{ mol/L}$

Molecular weight of chloroform is: 119.38 g/mol.

Concentration in mg/L is: $C_{iw}^{sat} = 0.07 \times 1000 \times 119.38 = 8357 \text{ mg/L}$

Reported water solubility for chloroform is: $\log C_{iw}^{sat} = -1.15$ (Appendix C)

$$C_{iw}^{sat} = 0.071 \text{ mol/L}$$

$$\text{Error \%} = \frac{|C_{iw}^{sat \text{ est}} - C_{iw}^{sat}|}{C_{iw}^{sat}} \times 100 = 1.4\%$$

(b) For anthracene, $T_m = 216^\circ\text{C}$. At 25°C, it is in solid phase.

Thus, $C_{iw}^{sat} = \frac{1}{\bar{v} \times \gamma_{iw}^{sat}} \left(\frac{P_{is}}{P_{iL}} \right)$

According to EOC Table 9.1, $\gamma_{iw}^{sat} = 2.5 \times 10^6$ for anthracene.

$$\ln \left(\frac{P_{is}}{P_{iL}} \right) = -(6.8 + 1.1\tau - 2.3\log\sigma) \left[\frac{T_m}{T} - 1 \right]$$

Where $\tau = 0.5$ and $\sigma = 4$

$$\ln \left(\frac{P_{is}}{P_{iL}} \right) = -(6.8 + 1.1 \times 0.5 - 2.3\log 4) \left[\frac{216 + 273}{298} - 1 \right] = -3.82$$

$$\frac{P_{is}}{P_{iL}} = 0.022$$

Thus,

$$C_{iw}^{sat} = \frac{1}{\bar{v} \times \gamma_{iw}^{sat}} \left(\frac{P_{is}}{P_{iL}} \right) = \frac{1}{0.018 \times 2.5 \times 10^6} \times 0.022 = 4.89 \times 10^{-7} \text{ mol/L}$$

Molecular weight of anthracene is: 178.23 g/mol

Concentration in mg/L is: $C_{iw}^{sat} = 4.89 \times 10^{-7} \times 1000 \times 178.23 = 0.087 \text{ mg/L}$

Reported water solubility for anthracene is: $\log C_{iw}^{sat} = -6.60$ (Appendix C)

$$C_{iw}^{sat} = 2.51 \times 10^{-7} \text{ mol/L}$$

$$\text{Error \%} = \frac{|C_{iw \text{ est}}^{sat} - C_{iw}^{sat}|}{C_{iw}^{sat}} \times 100 = 94.8\%$$

2) estimating solubility based on LFERs using relating Kow and aqueous solubility. You can find these in the book by Boethling and Mackay (Chapter 7).

$\log S = -0.01(T_m - 298) - \log K_{ow} + 0.54$ for hydrophobic compounds. (eqn 14 in Boethling and Mackay)

(a) According to Appendix C:

For chloroform, $\log K_{iow} = 1.95$ and $T_m = -63.5^\circ\text{C}$

$$\log S = -0.01(273 - 63.5 - 298) - 1.95 + 0.54 = -0.525$$

$S = 0.29 \text{ mol/L}$.

Molecular weight of chloroform is: 119.38 g/mol.

Concentration in mg/L is: $C_{iw}^{sat} = 0.29 \times 1000 \times 119.38 = 34620 \text{ mg/L}$

Reported water solubility for chloroform is: $\log C_{iw}^{sat} = -1.15$ (Appendix C)

$$C_{iw}^{sat} = 0.071 \text{ mol/L}$$

$$\text{Error \%} = \frac{|C_{iw \text{ est}}^{sat} - C_{iw}^{sat}|}{C_{iw}^{sat}} \times 100 = 308\%$$

(b) For anthracene, according to Appendix C, $\log K_{iow} = 4.68$ and $T_m = 216^\circ\text{C}$

$$\log S = -0.01(273 + 216 - 298) - 4.68 + 0.54 = -6.05$$

$S = 8.91 \times 10^{-7} \text{ mol/L}$

Molecular weight of anthracene is: 178.23 g/mol

Concentration in mg/L is: $C_{iw}^{sat} = 8.91 \times 10^{-7} \times 1000 \times 178.23 = 0.16 \text{ mg/L}$

Reported water solubility for anthracene is: $\log C_{iw}^{sat} = -6.60$ (Appendix C)

$$C_{iw}^{sat} = 2.51 \times 10^{-7} \text{ mol/L}$$

$$\text{Error \%} = \frac{|C_{iw \text{ est}}^{sat} - C_{iw}^{sat}|}{C_{iw}^{sat}} \times 100 = 255\%$$

The most rigorous approach here is to apply several estimation methods and then compare those methods with the values reported in the back of your book and/or in Chemical Abstract (Scifinder Scholar) or PubChem.

3. Q10.2 and Q 10.4 in EOC

10.2

$$\Delta_{w,\ell} G_i = -2.302RT \log \gamma_{iw}/\gamma_{il}$$

$$K_{i\ell w} = \frac{C_{i\ell}}{C_{iw}} = \frac{\gamma_{iw} \bar{V}_w}{\gamma_{i\ell} \bar{V}_\ell}$$

The first colleague is right. When $\Delta_{w,\ell} G_i = 0$, the ratio of $\gamma_{i,w}/\gamma_{i,\ell} = 1$, but we still need to calculate $K_{i\ell w}$ based on the molar volume of each liquid. We get 0.22, 0.11, and 0.06 for trichloromethane (chloroform)–water, n-octanol–water, and n-hexadecane–water systems respectively after plugging in molar volume.

10.4

These differences result from the intermolecular interactions in the organic liquid phase since the second phase is water in all three cases and is the same. Amphetamine is bipolar and can only form Van der Waals interactions (London forces) with heptane thus it has the lowest partition coefficient. Amphetamine can form H bonds with n-octanol, but it also needs to break octanol H-bonds for the cavity formation and thus is energy expensive. Chloroform is an H-donor and can form relatively strong interaction with amphetamine (H-acceptor), and the energy cost for cavity formation in chloroform is low. Thus, K_{icw} is higher than K_{iow} .

4. P10.5 in EOC

Using excel, one plots $\log K_{ioctw}$ vs. $\log K_{iow}$. The data naturally align themselves into three distinct trends. The compounds in each group are as follows

Group 1: Phenol, 3-CP, 4-CP, and 3,5-DCP

Group 2: 2-CP, 2,3-DCP, 2,4-DCP, 2,5-DCP, and 2,4,5-TCP

Group 3: 2,6-DCP, 2,4,6-TCP, 2,3,4,6-TetraCP, PCP

The regressions are linear of the form $\log K_{ioctw} = a \log K_{iow} + b$. Values for a and for b for each group are as follows.

Group 1: a=1.4, b=3.05

Group 2: a=1.7, b=1.1

Group 3: a=1.2, b=1.1

The reason that these compounds group in this manner becomes apparent when you draw the structures of the compounds for each group. The group one compounds have zero chlorines in the meta position next to the OH group. The group 2 compounds all have ONE chlorine in the meta position next to the OH group. The third group has two chlorines in the meta positions next to the OH group. The chlorine, which is electronegative, interacts with the OH group to provide a significant electron withdrawing from the ring structure. This greatly affects the compounds interactions

with the solvents and leads to different behaviors depending on the number of chlorines adjacent to the OH group, zero, one, or two. Pretty cool, huh!

5. Starting with equation 10-2 in your textbook:

$$K_{i,lw} = \frac{C_{il}}{C_{iw}} = \frac{\gamma_{iw}}{\gamma_{il}} \frac{V_w}{V_l} \text{ (eqn 10-2)}$$

Derive the expression to calculate the $C_{i,w}$ from an organic mixture containing species i.

$$C_{i,w} = x_{i,mix} \gamma_{i,mix} C_{i,wL}^{sat} \text{ (eqn 10-31)}$$

Where $x_{i,mix}$ the mole fraction of species i in the organic mixture and $\gamma_{i,mix}$ is the activity coefficient of species i in the organic mixture. Also, derive an expression for the partitioning of species I from an organic mixture and water, $K_{i,mix,w}$.

From rearranging eqn 10-2

$$C_{iw} \gamma_{iw} V_w = C_{il} \gamma_{il} V_l$$

For a liquid that is a mixture of organics this is denoted as:

$$C_{iw} \gamma_{iw} V_w = C_{i,mix} \gamma_{i,mix} V_{mix}$$

Since, $x_{i,mix} = \frac{C_{i,mix} V_{mix}}{V_w \gamma_{iw}}$

$$C_{iw} \gamma_{iw} V_w = x_{i,mix} \gamma_{i,mix} V_{mix}$$

$$C_{iw} = \frac{x_{i,mix} \gamma_{i,mix} V_{mix}}{V_w \gamma_{iw}} = x_{i,mix} \gamma_{i,mix} C_{i,wL}^{sat}$$

Since

$$C_{iw} = \frac{x_{i,mix} \gamma_{i,mix} V_{mix}}{V_w \gamma_{iw}} = C_{i,mix} \gamma_{i,mix} V_{mix} C_{i,wL}^{sat}$$

Rearranging this yields:

$$K_{i,mix} = \frac{C_{i,mix}}{C_{i,w}} = \frac{1}{V_{mix} \gamma_{i,mix} C_{i,wL}^{sat}} \text{ (eqn 10-33)}$$

6. What is the concentration of chloroform and vinyl chloride in groundwater at 15 °C at equilibrium with a large volume of methylene chloride (dichloromethane) containing chloroform and vinyl chloride at 1wt% and 0.01wt%, respectively?

Using

$$C_{iw} = \frac{x_{i,mix} \gamma_{i,mix}}{V_w \gamma_{iw}} = x_{i,mix} \gamma_{i,mix} C_{i,w}^{sat} \quad (5) \text{ or giving eqn for } K_{ilw}$$

Assume that $\gamma_{i,mix} = 1$ for both chloroform and vinyl chloride in methylene chloride (dichloromethane). (2)

We need to know $x_{i,mix}$ for these compounds in the mixture and their water solubility. Looking up solubility in appendix C (at 25C) we find $10^{-1.15}M$ for chloroform and $10^{-1.35}M$ for vinylchloride. We will assume that the solubility is not affected **much by the 5C range in temperature**. This is OK for chloroform (a liquid) but perhaps not as good of an assumption for vinyl chloride (a gas at 25C). (3) **temperature assumption or T adjustments**

Calculating $x_{i,mix}$ for these compounds

For chloroform at 1wt% in the mixture

$$x_{i,mix} = \frac{n_{chloroform}}{(n_{chloroform} + n_{dichloromethane})} = \frac{(1g/119.4g/mol)}{((1g/119.4g/mol) + (99g/84.9g/mol))} = 0.008$$

so:

$$C_{i,w} = 0.007 * 1 * 10^{-1.15}M = 5 \times 10^{-4} M \text{ for chloroform (5) answer 1, eqn 4}$$

For vinyl chloride

$$x_{i,mix} = \frac{n_{VC}}{(n_{VC} + n_{dichloromethane})} = \frac{(0.001g/96.9g/mol)}{((0.001g/96.9g/mol) + (99g/84.9g/mol))} = 8.6 \times 10^{-6}$$

$$C_{i,w} = 8.6 \times 10^{-6} * 1 * 10^{-1.35}M = 3.8 \times 10^{-7} M \text{ for vinyl chloride (5) answer 1, eqn 4}$$