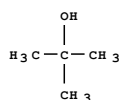


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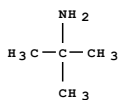
12-725: Fate, Transport, and Physicochemical Processes of Organic Contaminants in Aquatic Systems

Problem Set #2 Spring 2020-solutions
Due January 30 by 5pm

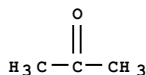
1. Label each of these compounds below as apolar, monopolar, or bipolar. Which compounds would form hydrogen bonds in a pure phase liquid? Explain your answers in terms of the compound's chemical properties.



2-methyl-2-propanol



t-butylamine



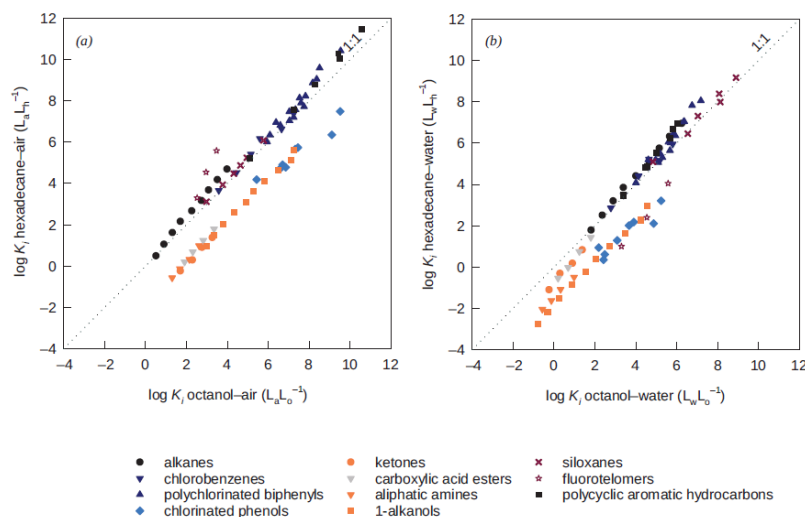
2-propanone

2-methyl-2-propanol: bipolar. The OH group allows this compound to form hydrogen bonds with itself.

t-butylamine: bipolar. The R-NH₂ group on this compound allows it to hydrogen bonds with itself.

2-propanone: monopolar. This compound has dipole-induced dipole interactions and London forces, but it cannot hydrogen bond with itself.

2. Using your knowledge of intermolecular forces and compound properties, explain the trends in the figure below.



For hexadecane-air vs. octanol-air partitioning you need to consider the intermolecular forces of the compound in hexadecane (i.e. activity coefficient or chemical potential in hexadecane) compared to octanol. For apolar compounds that only interact primarily by van der Waals, the interactions with hexadecane and octanol are all similar and roughly fall on the 1:1 line. For compounds that can interact with the OH group on the octanol (ketones, amines, alcohols), they prefer octanol over hexadecane (or you can say they are at a lower energy state or lower activity or lower chemical potential in octanol vs. hexadecane and therefore fall below the 1:1 line).

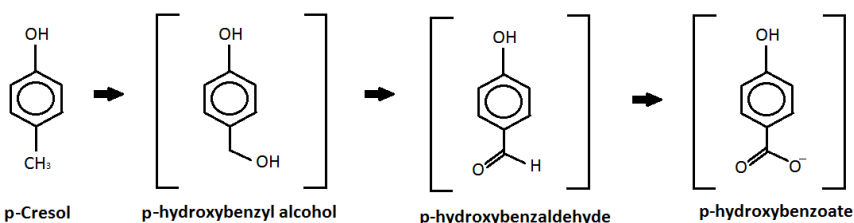
Comparing hexadecane-water with octanol-water you get very similar trends. However, considering the one also needs to consider the interactions with water, ketones and carboxylic acid esters no longer fall on exactly the same line as the bipolar compounds. And the fluorotelomers are more in line with bipolar compounds due to their negative charge and that interaction with water.

- Trichloromethane (chloroform) is a common chlorinated solvent. It is also a byproduct from the biological reduction of tetrachloromethane. When using the pure liquid compound as reference state, in which types of solvents (give examples) would you expect that trichloromethane has an activity coefficient of (a) close to 1, (b) smaller than one, and (c) larger than one? Repeat this analysis for tetrachloromethane (aka. Carbon tetrachloride).

Trichloromethane is an H donor or electron acceptor. It is therefore monopolar. It would have an activity coefficient close to 1 in a similar solvent, e.g. dichloromethane. It would be smaller than one in a solvent that is an H acceptor such as acetone or benzene. It would be larger than one in a bipolar solvent like water where H-bonds needed to be broken to make a cavity for it.

Tetrachloromethane is an apolar compound. It can only form dipole induced dipole and London dispersive force with other compounds. Unlike trichloromethane, it is NOT an H donor. The activity coefficient can be close to 1 for similar solvents like chloroform and dichloromethane. Activity coefficient cannot be lower than 1 since no strong intermolecular force (H-bonding and e^- donor acceptor interaction) can form. The activity coefficient would be larger than one in a bipolar solvent like water where H-bonds between solvent molecules needed to be broken to make a cavity for it.

4. Below shows the transformation scheme for p-cresol (a component of coal tar). Name each of these compounds. What kind of reactions are occurring at each step of the process, i.e. oxidation, reduction, etc.?



The three transformations are all oxidation reactions, moving from the alcohol to the aldehyde, to the carboxylic acid.

5. Q7.5 and Q7.6 in your EOC textbook (online version).

Q7.5

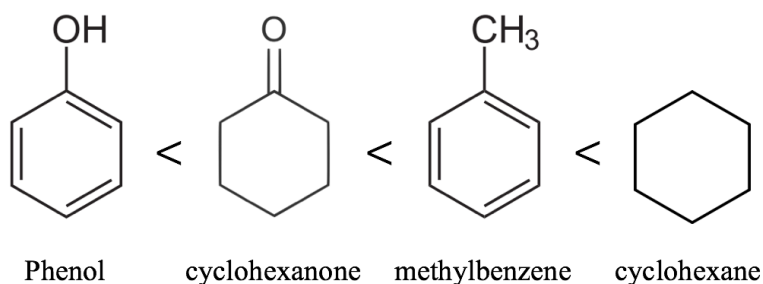
a, Case I b, Case I c, Case III, H bond would form between solute and solvent d, Case II e, Case IV f, Case I g, Case I h, Case III ,H in chloroform is an H donor i, Case I Case II

Q7.6

- The hexane-air partitioning depends on 1) the inherent volatility of the compound, and 2) interactions in hexane. Since hexadecane can only undergo VdW interactions, they increase with size of the molecule, and similarly for all molecules. Similarly, the inherent volatility of the compounds decreases with increasing size of the compound. Both changes are in the same direction, leading to relatively steep increase of $K_{\text{hex-air}}$ with increasing size of the solute. For $K_{\text{water-air}}$, the inherent volatility also decreases with increasing size, which should increase $K_{\text{water-air}}$. However, as the size of compound increases, the energy to form cavity in water also increases because H-bonds between water molecules must be overcome to make a cavity. This tends to decrease $K_{\text{water-air}}$. The net result is a much weaker dependence on the size of the molecules.
- As size goes up, the fluorotelomer alcohols and siloxanes become less volatile, increasing solvent-air partition coefficient. However, fluorotelomer alcohols and siloxanes are neither hydrophilic nor lyophilic. So, the larger size does not increase the

- interactions with the solvent as much as for the other compounds, leading to a smaller overall effect of size on $K_{\text{hex-air}}$.
- The hexadecane only interacts with alkanes and 1-alkanols by van der Waals force. Thus, with similar interactions, the hexadecane-air partition coefficient for these two compound classes are similar. Octanol interacts with alkanes only through van der Waals force, while the 1-alkanols can form H-bonding with octanol, which makes their interaction stronger. Since the interaction between 1-alkanol and octanol is stronger than between alkane and octanol, the octanol-air partition coefficient can be much higher for 1-alkanol.
 - Unlike the octanol-air partition coefficient, the value of the octanol-water partition coefficient is also affected by the interactions with water. The higher K_{ow} for alkanes compared to 1-alkanols indicates that the partitioning is affected by the water more than by the octanol. The former cannot H-bond with water, but the latter can, making it much more easy to partition into water.
6. Rank the four compounds below in order of increasing vapor pressure at 25 °C. Phenol, cyclohexane, cyclohexanone, methylbenzene. Provide an **EXPLANATION** for your assignments. The explanation is worth more than the assignments. Compare your assignments with reported values.

The rank of increasing vapor pressure for phenol, cyclohexane, cyclohexanone and methylbenzene is:



Phenol: Phenol is a bipolar compound with a hydroxyl group that can serve as both electron donor (H acceptor) and electron acceptor (H donor). Thus, hydrogen bonding can form between phenol molecules in liquid phase, causing strongest intermolecular attraction among these four compounds and lowest vapor pressure at 25 °C.

Cyclohexane is an apolar compound that will only undergo Van der Waals interactions (mainly London dispersive forces). Thus, the intermolecular attraction between cyclohexane molecules is the smallest among all four kinds of compounds. Cyclohexane also has the lowest boiling point in these four compounds (81°C at 1atm). Thus, the vapor pressure of cyclohexane is the lowest at 25 °C among all four compounds.

Methylbenzene and cyclohexanone are both monopolar compounds and are electron donors (H acceptor). The boiling point of cyclohexanone (155.65 °C) is higher than that of methylbenzene (111 °C), this is because the intermolecular attractions (dipole-dipole and dipole induced dipole interactions) between cyclohexanone molecules in pure liquid phase is stronger than methylbenzene (C=O induced higher polarity than the benzene ring). Thus, the vapor pressure of cyclohexane is lower than methylbenzene.

7. Q 8.5 and Q8.8 in EOC.

Q8.5

Subcooled liquid: A liquid cooled to a temperature below its melting temperature but not allowed to crystallize.

Superheated liquid: A liquid that has been heated above its boiling point, but not allowed to vaporize.

A supercritical fluid: any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid.

Q 8.8. a) Phenanthrene and anthracene are both solids at 25°C. Their BPs are the same because they roughly have the same size and their intermolecular forces are the same. This means that the vapor-liquid equilibrium is nearly the same at the BP where they are both liquids. The difference therefore must be in their transition from a solid to a liquid, i.e. melting/fusion. ΔH_{fus} would be similar, but ΔS_{fus} is not. This is because anthracene has more symmetry than phenanthrene. As a result, it gains LESS entropy in the transition from solid to liquid than phenanthrene. So it requires more enthalpy (higher temperature) to melt. It also gives it a lower vapor pressure for a given temperature $T < T_m$ for both compounds.

b) Hexane has only London dispersive intermolecular forces and therefore has a higher vapor pressure than styrene which is monopolar (electron donor) and has stronger intermolecular forces than hexane, and much higher than for 3-methylphenol which can H-bond.

c) The methyl groups in the 2 and 6 positions are right next to the OH group. This blocks access to that group and makes the H-bonding weaker in 2,6-dimethylphenol compared to 3,4-dimethylphenol which does not shield the OH group.

8. Estimate the vapor pressure of the following compounds at 25 °C: anthracene, trichloroethylene, 2-chlorophenol. How do your estimates compare with reported values?

Commented [GVL1]: Confirm that these are good calculations.

Basically, we can use the 'KF' constant to estimate the vapor pressure.

$$\ln P_{iL}^* = -K_f(4.4 + \ln T_b) * \left(1.8 * \left(\frac{T_b}{T} - 1\right) - 0.8 * \frac{T_b}{T}\right) \quad (2)$$

If the compound is a solid at the interested temperature, you will need to convert the vapor pressure of subcooled liquid to the vapor pressure of solid

$$\ln(P_{is}^*/P_{iL}^*) = -\left((6.8 + 1.1\tau - 2.3\log\sigma)\left(\frac{T_m}{T} - 1\right)\right) \quad (3)$$

Anthracene ($T_m=214$ degree C, $T_b=340$ degree C), which is a solid
 Trichloroethylene ($T_m=-85$ degree C, $T_b=87$ degree C), which is a liquid
 2-chlorophenol ($T_m=7$ degree C, $T_b=175$ degree C), which is a liquid

For Anthracene, $K_f \approx 1$, $\tau=0$ $\sigma=4$. Convert the units of T_m , T_b from degree C to K, and plug in all the values to equation 2,

$$\ln P_{il} = -14.3$$

Because anthracene is a solid at $T=25$ °C, we need to use equation (3) to convert P_{il} to P_{is} ,

Plug in $\tau=0$ $\sigma=4$,

$$\ln (P_{is}/P_{il}) = -3.91$$

$$\ln (P_{is}) = -18.2, P_{is} = 1.2 \times 10^{-8} \text{ atm} = 0.0012 \text{ pa.}$$

Reported value: 0.08 pa ([ILO-ICSC](#))

The estimated value is lower than the reported value, but they are both pretty low and within 2 order of magnitude. I would say the estimation method worked pretty good in this case.

For Trichloroethylene, $K_f \approx 1$, plug in T_b ,

$$P_{il} \approx 0.1 \text{ atm} = 10 \text{ kpa}$$

The reported value is 7.8 kpa ([ILO-ICSC](#))

I would say this is a pretty good estimation.

For 2-chlorophenol, $K_f \approx 1.2$, plug in T_b ,

$$P_{il} = 0.0004 \text{ atm} \approx 40 \text{ pa}$$

The reported vapor pressure is 230 pa ([ILO-ICSC](#))

The estimated value was lower, but within an order of magnitude of the reported value.