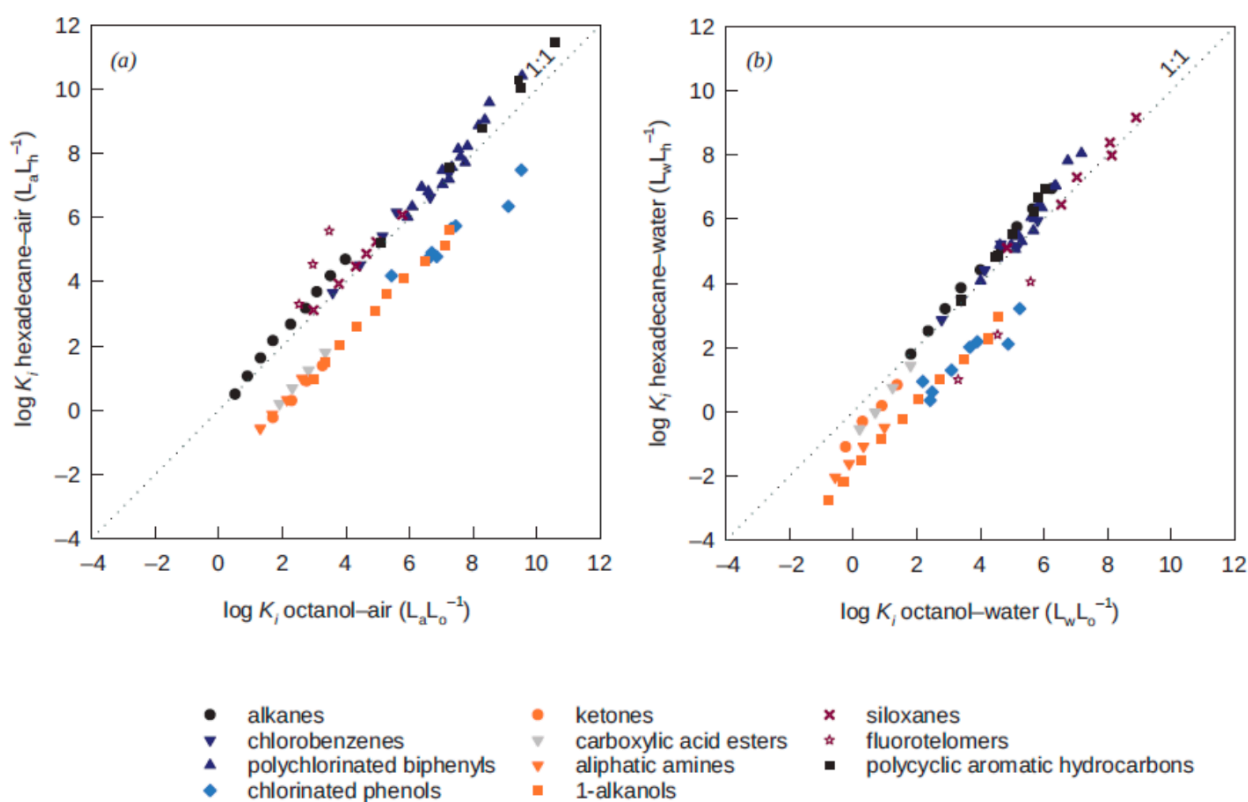


1.

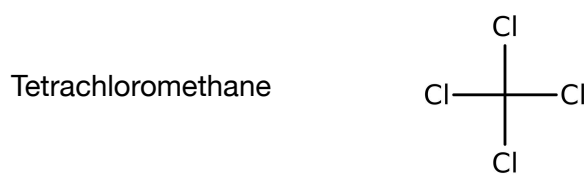
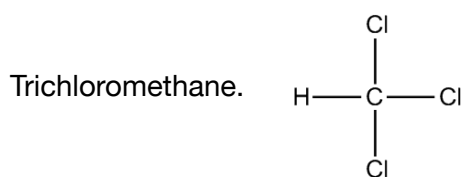
IUMPC name	2-methyl-2-propanol	T-butylamine	2-propanone
Polarity	Bipolar	Bipolar	Monopolar
Explain	The bipolar compounds exhibit both, which means have both H-donor (electron acceptor) or H-acceptor (electron donor) properties. -OH contains both H-acceptor and donor	The bipolar compounds exhibit both, which means have both H-donor (electron acceptor) or H-acceptor (electron donor) properties. -NH ₂ contains both H-acceptor and donor	The bipolar compounds have in addition either H-donor (electron acceptor) or H-acceptor (electron donor) properties. -ROR- contains only H-acceptor
H-bond in pure liquid	Yes	Yes	No
Explain	-Oδ- - Hδ+ ··· Oδ- -	-Nδ- - Hδ+ ··· Nδ- -	

2.



- As can be seen in Fig. A , in both cases, no single sp-LFER of the $\log K_{i12} = a \log K_{i32} + b$ can fit the whole data set. Good linear relationship can, however, be found for structurally closely related subsets of compounds.
- Highlighting the importance of molecular interactions, the linear relationships seen in Fig. A are quite different for bipolar compounds capable of H-bonding interactions, such as alcohols
- as for apolar compounds only capable of vdW interactions in both phases, such as the *n*-alkanes.
- When the h-bonding existed in the system, more than one kind interactions molecular force (vdW). The compound classes which can form H-bond with solvent, its logarithms linear will move forward the solvent axis. For example, ketones, 1-alkanols, carboxylic acid esters and aliphatic amines can form h-bond with octane-air.
- On the other hand, when axis changes to hexadecane-water and octanol-water, some compounds are closer to the 1:1 linear, since it not only can form h-bond with octanol-water, but also can it form with hexadecane-water. For example, ketones and carboxylic acid esters.

3.



Example

Close to 1: CH_3CCl_3

Close to 1: CH_3CHCl_3

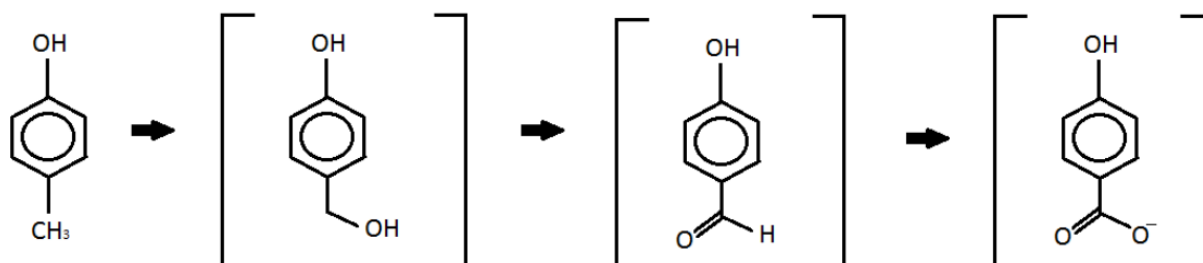
Smaller than 1: Phenol

Smaller than 1: $\text{C}_2\text{H}_5\text{OH}$

Larger than 1: H_2O

Larger than 1: H_2O

4.



Step 1: 1-Methyl-4-hydroxybenzene

Step 2: 4-(Hydroxymethyl)benzyl alcohol

Step 3: 4-Hydroxybenzaldehyde

Step 4: 4-Hydroxybenzoate

Step 1 - Step 2 : Oxidation (the oxidation state from $-\frac{6}{7}$ to $-\frac{4}{7}$), or substitution (H is replaced by OH)

Step 2 - Step 3 : Oxidation (the oxidation state from $-\frac{6}{7}$ to $-\frac{4}{7}$), Oxidation of primary alcohols to aldehydes.

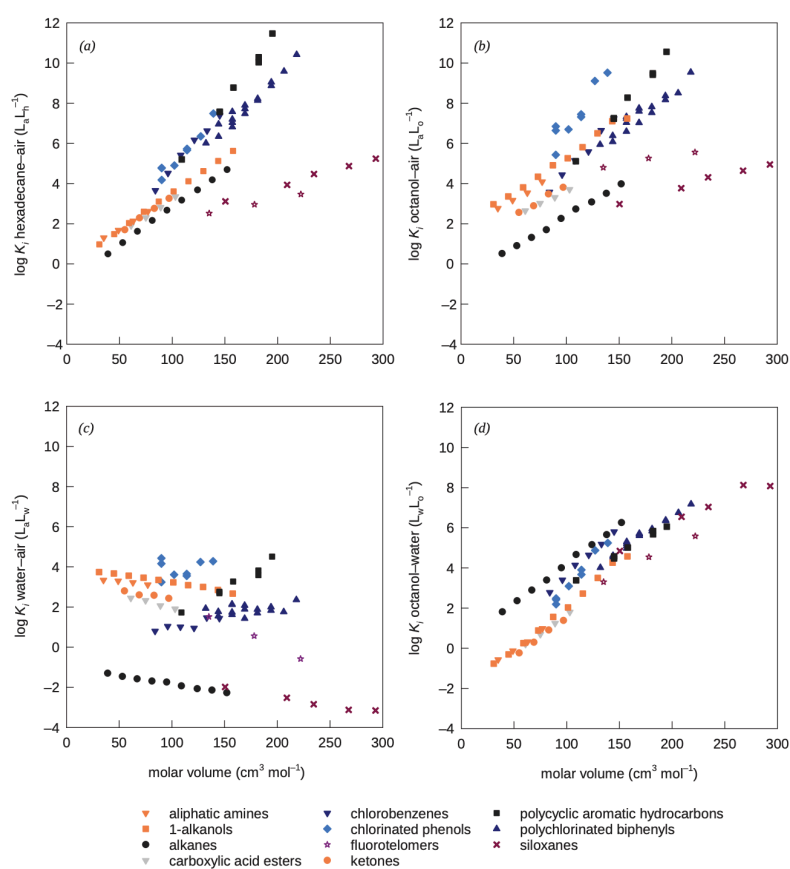
Step 3 - Step 4 : Oxidation (the oxidation state from $-\frac{6}{7}$ to $-\frac{4}{7}$), Oxidation of primary aldehydes to carboxylic ions

5.

(1)

Solvent	Polarity	Solute	Polarity	Appropriate case
Dichloromethane	Apolar	Methyl-t-butylether	Monopolar	Case I
Tetrachloroethene	Apolar	Perfluorooctylethanol	Bipolar	Case II
Diethylether	Monopolar	17-ethinylestradiol	Bipolar	Case III

Octanol	Bipolar	PCB 153	Aploar	Case I
Ethanol	Bipolar	Atrazine	Bipolar	Case IV
Toluene	Apolar	PBDE 99	Monoploar	Case I
Hexane	Apolar	Triclosan	Bipolar	Case II
Cholroform	Apolar	4-nonylphenol	Bipolar	Case IV
Ethyacetate	Monopolar	Phenanthrene	Aploar	Case I
Water	Bipolar	N-decane	Apolar	Case I



(2)

(a) The organic solvent–air partition constants increase with size of the compound (Figs. 7.2a and b), whereas for the water–air partition constants (Fig. 7.2c) a much smaller, and in some cases even negative, trend is observed.

The H-bond in water is much stronger than other h-bond in other compounds, which means dissolving into water needs more energy to break these h-bond then in some cases even negative, trend in Fig a. On the other hand, in organic solvent–air, with an increase in molecular volume, the vdW will increase, then the $\log K$ will increase in Fig and alb

(b) The organic solvent–air partition constants of the fluorotelomer alcohols and of the siloxanes increase much less with size as compared to all other compound classes (Figs. 7.2a and b).

Compared to other compounds, the fluorotelomer alcohols and the siloxanes have a more complex chemical structure, then, they are less likely to dissolve.

(c) The difference between the hexadecane–air partition constants (Fig. 7.2a) of a homologues series of alkanes and the corresponding 1-alkanols is rather small, whereas for the octanol–air partition constants (Fig. 7.2b), this difference is more than two orders of magnitude.

The main factor should be H-bond, in hexadecane-air condition, alkanes and 1-alkanols cannot form h-bond with hexadecane, then shows a little difference in portion constants, on the other hand, 1-alkanols is able to form h-bond with octanol, but alkanes cannot, thus they shows a bigger difference under this conditions due to H-bond existed.

(d) The octanol–air partition constants of the 1-alkanols are more than two orders of magnitude larger than those of the n-alkanes (Fig. 7.2b), exactly the opposite is true for the octanol-water partition constants (Fig. 7.2d).

The 1-alkanols are able to form H-bond with octanol and water, but n-alkanes cannot. For fig.d, the 1-alkanols has H-bond with water and it is not likely to bond with octanol, since breaking h-bond with water needs energy, other other hand, n-alkanes cannot form h-bond with water or octanol then it shows little difference in partition constants in Fig b and d.

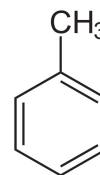
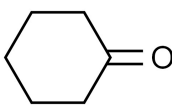
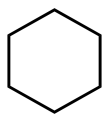
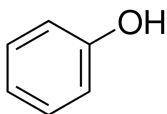
6.

Phenol

Cyclohexane

Cyclohexanone

Methylbenzene



	Phenol	Cyclohexanone	Methylbenzene	Cyclohexane
K_F	1.15	1	1	1
Boiling point K	455K	428K	384K	354K
$p_{iL}^*(298K)$ bar	0.041	0.105	0.243	0.411

The order of increasing vapor pressure at 25C

Phenol < Cyclohexanone < Methylbenzene < Cyclohexane

Equation 8-17

$$\log p_{iL}^*(T) = -\frac{1}{2.303} \times K_F \times (4.4 + \ln T_b) \left[1.8 \left(\frac{T_b}{T} - 1 \right) - 0.8 \times \ln \frac{T_b}{T} \right]$$

This equation 8 - 17 is particularly useful for prediction of vapor pressures of relatively low boiling compounds. ($T_b < 300^\circ\text{C}$)

Where T = 298 K

7.

- Explain in words the terms subcooled liquid, superheated liquid, and supercritical fluid.

Subcooled liquid: The term subcooling refers to a liquid existing at a temperature below its normal boiling point. It tells us something about the molecular interactions of the compound in its pure liquid form at a temperature where the compound is actually a solid.

Superheated liquid: Superheated is a liquid when it has been heated above its boiling point, but by increasing pressure, it is still in the liquid state and the system has both a liquid phase and a gas phase, and the liquid phase is referred to as a "Superheated".

Supercritical fluid: It is any substance at a temperature and pressure above its critical point, where the compounds existed only as one phase, which is commonly referred to as a "supercritical fluid"

- Explain the following observations:

(a) The two isomeric polycyclic aromatic hydrocarbons, phenanthrene and anthracene, are solids at 25°C. Although these compounds have almost the same boiling point (339°C and 341°C respectively), their vapor pressures at 25°C differ by more than one order of magnitude.

The main reason should be the structure difference between these two compounds.

According to the equation Eq 8-23, $\ln \frac{p_{is}^*}{p_{il}^*} = -(6.80 + 1.1\tau - 2.3 \log \sigma) \left[\frac{T_m}{T} - 1 \right]$, the σ

of phenanthrene is 2, meanwhile, the one of anthracene is 4. As a result, the boiling point,

although, are the same between these two compounds, the ratio of $\frac{p_{is}^*}{p_{il}^*}$ of phenanthrene

will be less than the one of the anthracene. Thus, p_{is}^* of these two compounds will be different at 25 C.

(b) Although they have approximately the same size, n-hexane ($V_i = 95 \text{ cm}^3 \text{ mol}^{-1}$) exhibits a 20 times larger vapor pressure than styrene ($V_i = 96 \text{ cm}^3 \text{ mol}^{-1}$), and a 1000 times larger vapor pressure than 3-methylphenol ($V_i = 92 \text{ cm}^3 \text{ mol}^{-1}$).

The intermolecular forces of these three compounds are different, to be specific, 3-methylphenol is bipolar molecular and it will form h-bond in its pure phase liquid, this molecular is more likely to stick to each others. On the other side, styrene has a ring system, which means it should be more stable than n-hexane that do not have. As we know, the more stable of compounds, less vapor pressure should they have. Moreover, the boiling point (68C, 145C, 203C, respectively) of these three compounds also tell the order of these vapor pressure at the same temperature should be different.

(c) The liquid vapor pressure of 2,6-dimethylphenol is almost one order of magnitude larger than the one of its isomer, 3,4-dimethylphenol.

The mean factor should be H-bond forming, which is more important than compounds structure difference in this case, to be more specific, the H in -OH of 3,4-dimethylphenol is more likely exposure to each others, on the other hand, the O in -OH is more likely to be H-acceptor. Thus, compared to 2,6-dimethylphenol, the H-bond has higher chance to form in 3,4-dimethylphenol, as a result, 3,4-dimethylphenol has a lower boiling point and more stable.

8. Estimate the vapor pressure of the following compounds at 25 C:

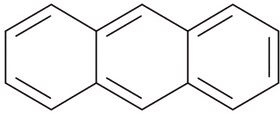
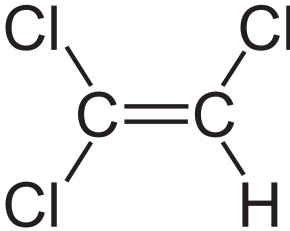
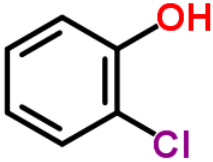
There are two equations used to estimate the vapor pressure

$$\log p_{iL}^*(T) = -\frac{1}{2.303} \times K_F \times (4.4 + \ln T_b) \times \left[1.8 \left(\frac{T_b}{T} - 1 \right) - 0.8 \times \ln \frac{T_b}{T} \right] \quad \text{Eq 8-17}$$

This equation 8 - 17 is particularly useful for prediction of vapor pressures of relatively low boiling compounds. ($T_b < 300^\circ\text{C}$)

If compounds's melting point is greater than 25C, then we need to use Eq 8-23 to calculate solid vapor pressure.

$$\ln \frac{p_{is}^*}{p_{iL}^*} = - (6.80 + 1.1\tau - 2.3 \log \sigma) \left[\frac{T_m}{T} - 1 \right] \quad \text{Eq 8-23}$$

	anthracene	trichloroethylene	2-chlorophenol
Structure			
Polarity	Monopolar	Monopolar	Bipolar
Equation Used	Entropy of fusion and Vapor pressure of Solids Equation 8-17 Equation 8-23	Trouton's rule of constant Entropy at the boiling point Equation 8-17	Trouton's rule of constant Entropy at the boiling point Equation 8-17
Melting / Boiling point	T _m = 489K	T _b = 334.1K	T _b = 447.9
K _F	1	1	1.15
σ τ	4 2		
p _{iL} [*] (298K) bar	4 × 10 ⁻⁵	0.571	0.04

