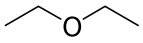
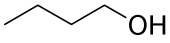
CHM 1321A
Assignment #4 Answers

1) Diethyl ether and 1-butanol have similar solubilities in water, but their boiling points are very different. Explain why these compounds have similar solubility properties but different boiling points.



solubility 8.4 mL in 100 mL H_2O

bp 35 °C



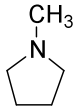
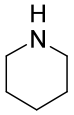
solubility 8.9 mL in 100 mL H_2O

bp 118 °C

Each molecule has about the same amount of Van der Waals interactions, and the Van der Waals surfaces are relatively large. Each compound has a dipole, lone pairs on oxygen and is able to hydrogen bond with water. Therefore each compound has similar solubility in water.

The hydrogen bonds in butanol are stronger that the dipole interactions in diethyl ether. Butanol has a higher boiling point because of the stronger hydrogen bonds. The intermolecular forces holding the butanol molecules together are stronger than those holding the diethyl ether molecules together.

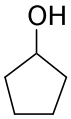
2) Explain the difference in boiling point for the following pairs of compounds:

a)  and 

bp 81 °C bp 106 °C

Each molecule has about the same Van der Waals ability. N-methyl-pyrrolidine (on the left) is capable of dipole-dipole interactions. Piperidine (on the right) has a dipole and can also hydrogen bond with itself (lone pair of electrons and hydrogen on the nitrogen atom). Therefore Piperidine has the higher boiling point.

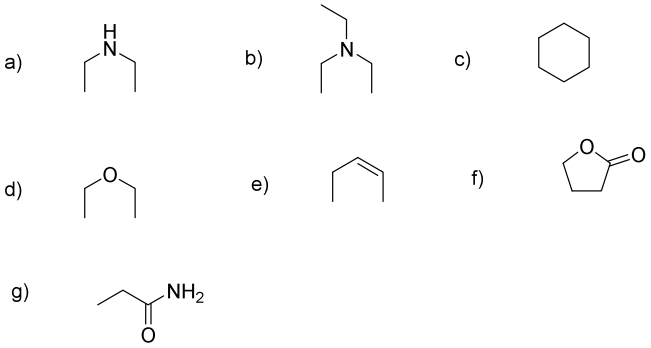
Note: The nitrogen of N-methyl-pyrrolidine has a lone pair and can hydrogen bond with water (water donates the hydrogen and is called a hydrogen bond donor). N-methyl-pyrrolidine donates the lone pair and is called a hydrogen bond acceptor. N-methyl-pyrrolidine cannot hydrogen bond with itself because there are no hydrogens on polar heteroatoms (N) in this structure.

b)  and 

bp 141 °C bp 88 °C

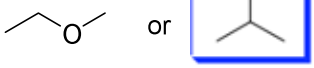
Each molecule has about the same Van der Waals ability. Both molecules have dipoles. Cyclopentanol (on the left) is capable of hydrogen bonding with itself. Tetrahydropyran (on the right) is only capable of dipole-dipole interactions. Therefore cyclopentanol has the higher boiling point since hydrogen bonds are stronger than dipole interactions.

3) Which of the following compounds can form hydrogen bonds? Which can form hydrogen bonds with water?

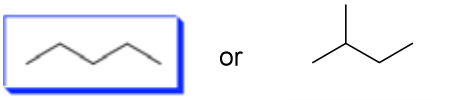


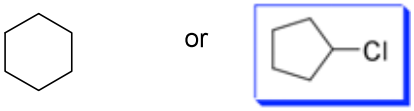
Compounds (a) and (g) can form hydrogen bonds between their own molecules. Each of these has hydrogens capable of hydrogen bonding (H's on nitrogen) and heteroatoms with lone pairs (N in structure (a); N and especially O in structure (g).
Compounds (a) and (g) can of course form H bonds with water. Compounds (b), (d) and (f) can form weaker hydrogen bonds with water. They have no hydrogens available, but do have lone pairs that can form hydrogen bonds with water.

4) Predict which of the following pairs of compounds will have the higher boiling point and explain your prediction.

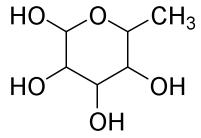
a)  Both have dipoles, however the second structure is capable of hydrogen bonding with itself (H and lone pairs on oxygen). These molecules held together by hydrogen boonds

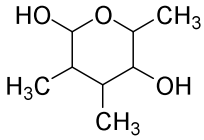
b)  Most Van der Waals forces because of larger molecules

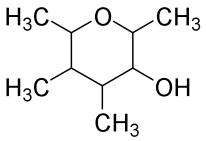
c)  Most Van der Waals forces due to least amount of branching (largest contact area)

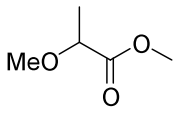
d)  Dipole-Dipole interactions, cyclohexane has Van der Waals forces only. Dipole-Dipole interactions are stronger than Van der Waals forces.

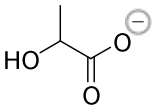
5) Predict which of the following in each set of compounds will have the highest water solubility. Which will have the lowest? Explain your answers.

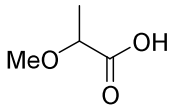
a)  highest water solubility
most hydrogen bonds possible

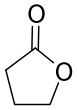


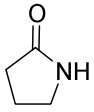
 lowest water solubility
fewest hydrogen bonds possible

b)  lowest water solubility
fewest hydrogen bonds possible

 highest water solubility
charged species have very strong dipole interactions (ionic). This makes for strong interactions with water.



c) 

 highest water solubility
most hydrogen bonds possible

 lowest water solubility
no hydrogen bonds possible