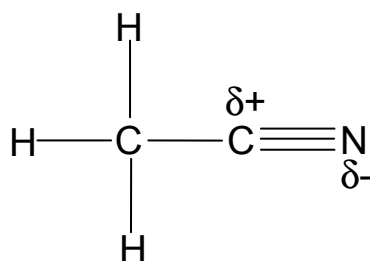
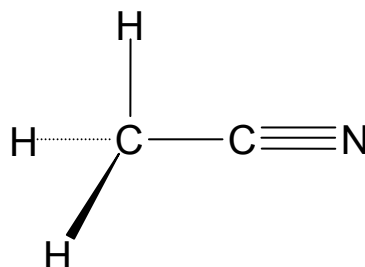


CHEM 121
Supplemental Questions for Solutions

1. Acetonitrile (structural formula: CH_3CN) is a liquid that is commonly used as a solvent.
- a. Draw the Lewis dot structure of acetonitrile (only one resonance structure contributes). Use VSEPR theory to predict the overall structure of the molecule, indicate the geometry about each of the two carbon atoms, and determine its polarity.



Lewis dot structure



Structure

The left C is tetrahedral and the right C is linear. Overall the molecule is tetrahedral. There are partial charges on the C and N because of the electronegativity difference between the two atoms (N is more electronegative than C). Since these charges are asymmetrically distributed, the molecule is polar.

- b. Why is acetonitrile miscible with water?

When acetonitrile dissolves in H_2O relatively strong dipole-dipole interactions between the CH_3CN molecules and strong hydrogen bonds between the H_2O molecules must be overcome. These are replaced by dipole-dipole interactions between CH_3CN and H_2O molecules. Since CH_3CN and H_2O are miscible, we know that ΔH for solution formation must be negative, or is positive and not large (intermolecular interactions in pure compounds are not much different than in solution) and that ΔG will be negative because ΔS is positive for solution formation.

- c. Why is VCl_3 soluble in acetonitrile?

VCl_3 is an ionic compound. When it dissolves it will interact with the polar CH_3CN molecules through an ion-dipole interaction, which may actually lead to a formal bond if the N lone pairs are donated to the V^{3+} ion. The ion-dipole interaction must be sufficiently strong that it negates the energy required to overcome E_{lattice} of VCl_3 and to break up the dipole-dipole interactions in CH_3CN , thus making ΔH for solution formation negative or positive and very small. In either case solution formation is favorable ($\Delta G < 0$) because ΔS is positive for solution formation.

2a. What is the sign of ΔG for the formation of a saturated sodium acetate solution from a supersaturated one? Why?

The term supersaturated means that there is more solute present than normally can be accommodated in solution. A supersaturated solution will precipitate the excess solute and become saturated, if it can. Since the spontaneous direction of the reaction is from supersaturated to saturated, ΔG for the formation of a saturated solution from a supersaturated one is negative.

b. As long as the supersaturated solution is not disturbed in some way (e. g., stirring it, adding a small amount of a solid), no sodium acetate will precipitate. Why?

The supersaturated solution must have an E_a that is sufficiently large to keep the spontaneous reaction from occurring or there is no kinetic pathway open for the reaction. Disturbing it either gives it enough energy to overcome E_a (stirring) or provides a pathway for the precipitation to occur (adding solid).

3. Predict the solubility (soluble or insoluble) of the following compounds in the given solvent. Explain your predictions.

a. Methanol (CH_3OH) in water (H_2O).

Both compounds are polar and form hydrogen bonds between their molecules. In the solution the hydrogen bonds present in each individual compound are replaced by hydrogen bonds between the solvent and solute molecules. The energy required to break apart the solute and solvent molecules is nearly equal to the energy given off by the formation of the new hydrogen bonds between the solute and solvent molecules. Therefore, methanol is soluble in water.

b. Hydrogen chloride (HCl) in methanol (CH_3OH).

Both compounds are polar and both have hydrogen bonding possible between the molecules. As with methanol and water, the strong interactions between the solute molecules and between the solvent molecules are replaced by equally strong interactions between the solute and solvent molecules. So, HCl is expected to be soluble in methanol.

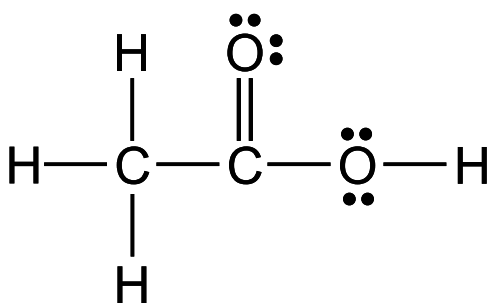
FYI. You might expect that HCl would be a strong acid in methanol, like it is in water, if the interaction between the H^+ ion and the methanol is stronger than the interaction between the hydrogen and the chlorine.

c. Hexanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) in hexane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$)

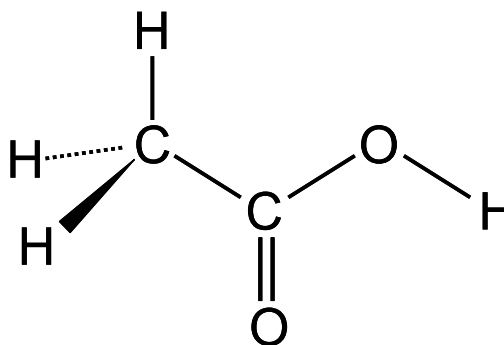
Hexanol has dispersion forces between the alkyl chain portion of the molecules and hydrogen bonding between the polar $-\text{OH}$ portions. Hexane has only dispersion forces between the alkyl chains. If hexanol dissolves in hexane the hydrogen bonds

between the hexanol molecules are disrupted, but the dispersion forces between the alkyl chains of hexanol are replaced by similar forces between hexane and hexanol molecules. However, the polar portion of hexanol accounts for only a relatively small portion of the entire molecule, so it is expected that the dispersion forces will dominate. Because the dominant dispersion forces between the solute molecules and between the solvent molecules are replaced by equal interactions between the solute and solvent molecules, it is expected that hexanol will be soluble in hexane.

4a. Draw the Lewis dot structure of acetic acid, CH_3COOH . Use the Lewis dot structure and VSEPR to draw the overall structure of the molecule.



Lewis Dot Structure



Structure from VSEPR

b. Predict ΔT_{FP} , the freezing point depression, of a solution which contains 5.00 g of acetic acid in 100.0 g of benzene relative to the freezing point of pure benzene. You are given the molar mass of acetic acid is 60.05 g/mole, and K_{FP} for benzene is $-5.12\text{ }^\circ\text{C}/m$.

$$\Delta T_{\text{FP}} = K_{\text{FP}} \cdot m_{\text{solute}}$$

$$m_{\text{solute}} = \frac{5.00\text{ g} \left(\frac{1\text{ mole}}{60.05\text{ g}} \right) \text{ acetic acid}}{0.100\text{ kg benzene}} = 0.833m$$

$$\Delta T_{\text{FP}} = (-5.12\text{ }^\circ\text{C}\cdot m^{-1})(0.833m) = -4.26\text{ }^\circ\text{C}$$

The predicted freezing point depression for this solution is $-4.26\text{ }^\circ\text{C}$.

c. The solution in part (b) actually freezes at 3.37 °C. Calculate the apparent molality of acetic acid in the solution. You are given that the normal melting point of benzene is 5.50 °C.

$$\Delta T_{FP} = K_{FP} m_{solute}$$

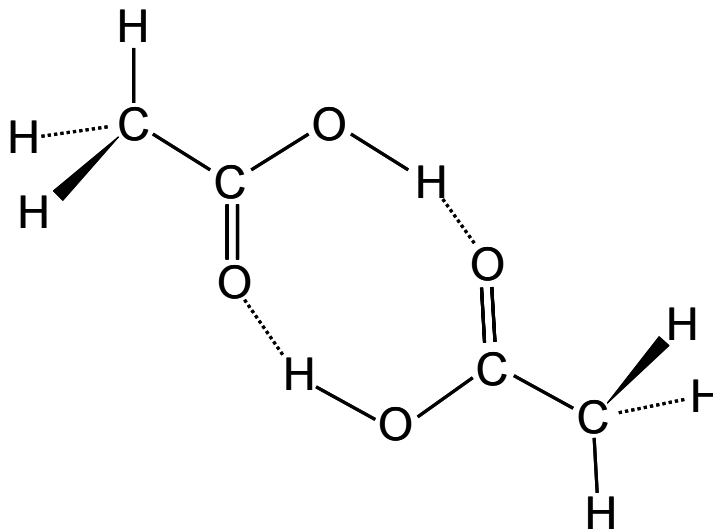
$$3.37 - 5.50 \text{ } ^\circ\text{C} = (-5.12 \text{ } ^\circ\text{C}\cdot\text{m}^{-1}) m_{solute}$$

$$m_{solute} = 0.416 \text{ m}$$

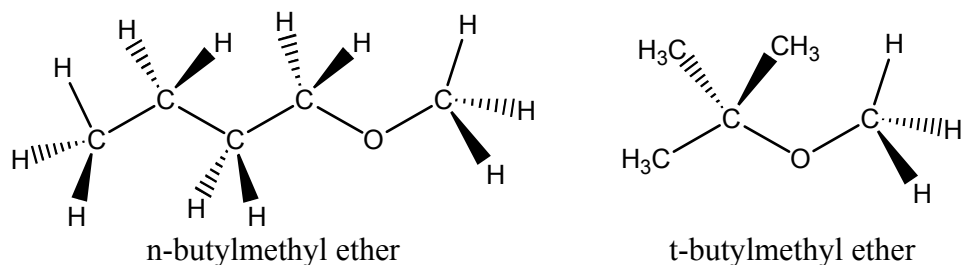
The apparent molality of this solution is 0.416 m.

d. Compare your answer to part (c) with the value you calculated to solve part (b). What does this tell you about how acetic acid exists when it is dissolved in benzene? Draw a picture showing the relationship between acetic acid molecules in benzene solution.

There are half as many acetic acid particles in solution then we expected. The molecules must, therefore, be associating in solution. Since acetic acid can form hydrogen bonds between molecules, it is likely that this is what is holding the molecules together.



5. n-Butylmethyl ether, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$, is not very soluble in water and has a boiling point of $71\text{ }^\circ\text{C}$, while t-butylmethyl ether, $(\text{CH}_3)_3\text{COCH}_3$, is moderately soluble in water and has a boiling point of $55.2\text{ }^\circ\text{C}$. Explain. Hint: predict the structure of each compound.



Both compounds have the same molar mass, but differ in shape. n-Butylmethyl ether is linear, which results in the magnitude of the dispersion forces being larger (more electrons are exposed) than in compact-shaped t-butylmethyl ether.

Because n-butylmethyl ether has more dispersion forces to overcome than t-butylmethyl ether, its boiling point will be higher.

Solubility of a compound is dictated by ΔG for the dissolution process. All mixing processes are entropically favorable ($\Delta S > 0$), so ΔH determines the sign of ΔG , and therefore the extent of dissolution. ΔH will depend on the intermolecular interactions present in the solute and solvent before mixing and then after mixing.

Both compounds have a polar ether end, which will hydrogen bond effectively with water, but it is the non-polar end that controls the solubility. When n-butylmethyl ether dissolves in water the strong hydrogen bonds between molecules are disrupted and are replaced by weak dispersion force interactions between the water molecules and the n-butyl functional group. There is some interaction of water molecules with the polar ether group, but because the solubility of this ether is very low, we may conclude that replacement of strong hydrogen bonds with weak dispersion forces causes ΔH for the dissolution of n-butylmethyl ether to have a more positive ΔG . The compact shape of t-butylmethyl ether means that there are fewer dispersion force interactions between it and the solvent water molecules. One might expect that this would lead to a decreased solubility, but that would be forgetting that fewer strong hydrogen bonds between the water molecules are disrupted when this compound dissolves in water. Because a smaller energy cost is required to rearrange the water molecules (some of which is recovered by hydrogen bonding to the ether) in t-butylmethyl ether than in n-butylmethyl ether, we expect ΔG for dissolving t-butylmethyl ether to be more negative (or less positive).