The Solvent of Life

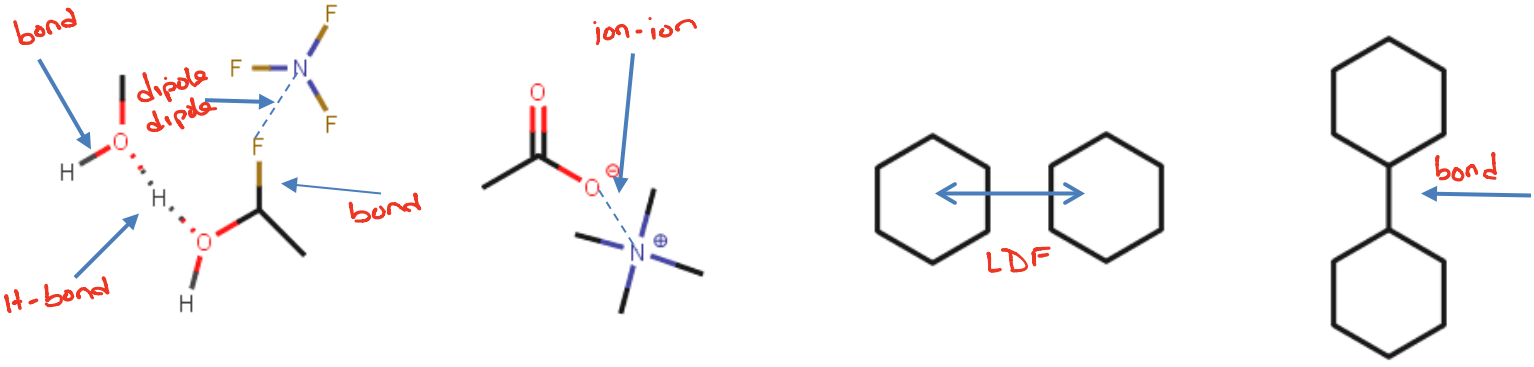
1. Intermolecular forces play an exceptionally important role in biochemistry. This first exercise aims to remind you of the central IMFs and how to identify them. The last part of this section will encourage you to think very critically about the thermodynamics of IMF and use your predictions to understand why non-polar molecules aggregate in polar solvents.
    a. Define a chemical bond. Shared electrons between two atoms. This involves the overlap of atomic orbitals to form a molecular orbital.

    b. In your own words, what is an IMF? A force holding two atoms or molecules together. It does not involve sharing electrons. All IMFs originate from the interactions between opposite charges (these can be full charges like we see in ion-ion or partial charges for the rest of the IMF).

    c. Based on your answers to the questions above, what is the difference between an IMF and a bond?

    Shared electrons.

    d. Label each of the following interactions as a bond or IMF. For the IMF, identify what kind of IMF (LDF, H-bond, ion-ion, ion-dipole, dipole-dipole).



    e. H-bonds play a ubiquitous role in biological macromolecules. In your own words, what is needed for two atoms to form an H-bond? A hydrogen atom covalently bonded to oxygen, nitrogen, or fluorine interacting with another N/O/F by sharing the hydrogen.

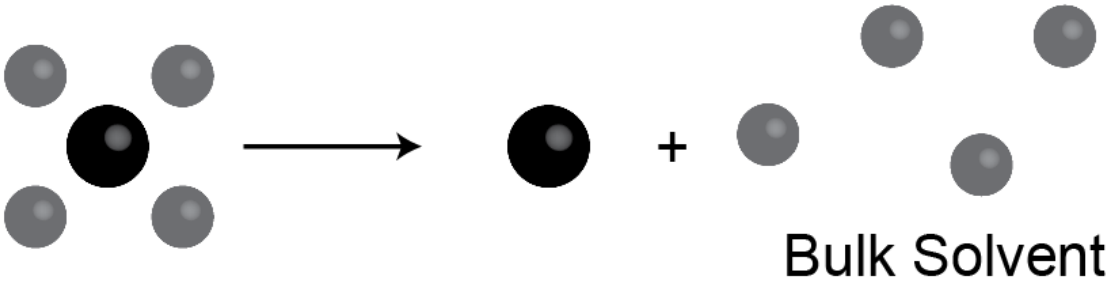
In your reading, you learned about the hydrophobic effect; the phenomenon that causes nonpolar substances to aggregate in water. This exercise aims to help you think about the role of enthalpy and entropy in the aggregation of hydrophobic molecules (this will be very important when we learn about protein folding).

Consider the dimerization of methane in water: $2\ CH_4 \rightarrow (CH4)_2$ This process can be thought of as two separate steps:

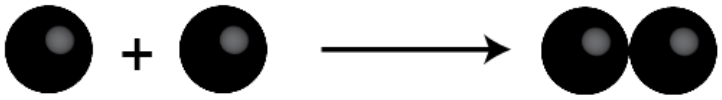
- The dehydration of each methane (several water molecules start by weakly interacting with methane and are released to the bulk solvent.

- The newly dehydrated methane molecules interact to form a dimer.

Step 1



Step 2



i. What type of IMF exist between methane and methane? LDF only
ii. What type of IMF exist between water and water? H-bonds are the strongest, but dipole-dipole and LDF also exist
iii. What type of IMF exist between water and methane? You may want to refer to Figure 2-8 in your textbook. The only IMF that CAN exist is LDF (or induced dipole); however, some current research suggests that there is no interaction at all.
iv. Rank the strength of the IMF in the three previous questions. ii > i > iii
v. The overall process (aggregation of methane in water) is spontaneous. What is the sign on ΔG?

$\Delta G = 0$ **$\Delta G < 0$** $\Delta G > 0$

vi. Consider the enthalpy and entropy of each step. Complete the table.

	Step 1 (dehydration and reorganization of water)	**Step 2** (Methane dimerization)	**Overall Process**
ΔH	Tough to predict – either choice is reasonable based on how you think about the reaction	$\Delta H < 0$ (forming an IMF)	Tough to predict because ΔH is unknown
ΔS	$\Delta S > 0$ (lots of water disordered)	$\Delta S < 0$ (2 becomes 1)	$\Delta S > 0$ ($\Delta S_1 >> \Delta S_2$)
ΔG			$\Delta G < 0$

vii. Refer to Table 2-2 in your book. Do your predictions for the thermodynamic values match up with the experimental values? If not, reevaluate ΔH and ΔS for each step and figure out why your predictions don't match up to experiment. The enthalpy of Step 1 is very hard to predict; consequently, the enthalpy of the overall process is hard to predict. You should be able to rationalize the rest of the boxes. Making a LDF in step 2 is going to be exothermic (think about this like forming a bond – it is always exothermic) but order is created as 2 things become 1. The entropy of step 1 should be very favorable because a lot of disorder is created.

viii. Based on Table 2-2 and your predictions from above, what do you think is the biggest contributor to the favorable ΔG for the overall process? Circle your answer on the table and explain your choice.

It is clear from table 2-2 that this is largely an entropically driven process. Since the only step that has a favorable entropy is step 1, this MUST be the biggest contributor.

ix. Collectively, these steps form the conceptual basis of the ***hydrophobic effect***. This name has often been criticized by biochemists.
    1. Why do you think that many consider the term misleading? The hydrophobic component of the effect has little influence on the net driving force. It is primarily a lot of favorable entropy caused by disordering of solvent
    2. Can you think of a better term to describe the aggregation of hydrophobic molecules in water? A good choice would be related to the solvent reorganization since it is the main driving force

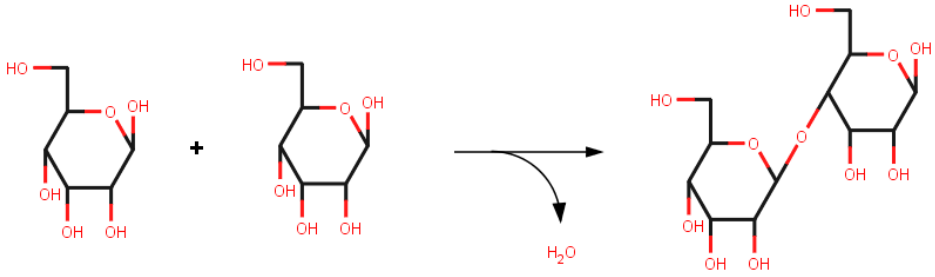
2. Most of the macromolecules that exist in your cells were formed through polymerization reactions.
    a. In your own words:
        i. What is a polymer? Chain of "links" (monomers) created through covalent bonding

        ii. What is a polymerization reaction? The reaction where monomers combine to fom a polymer

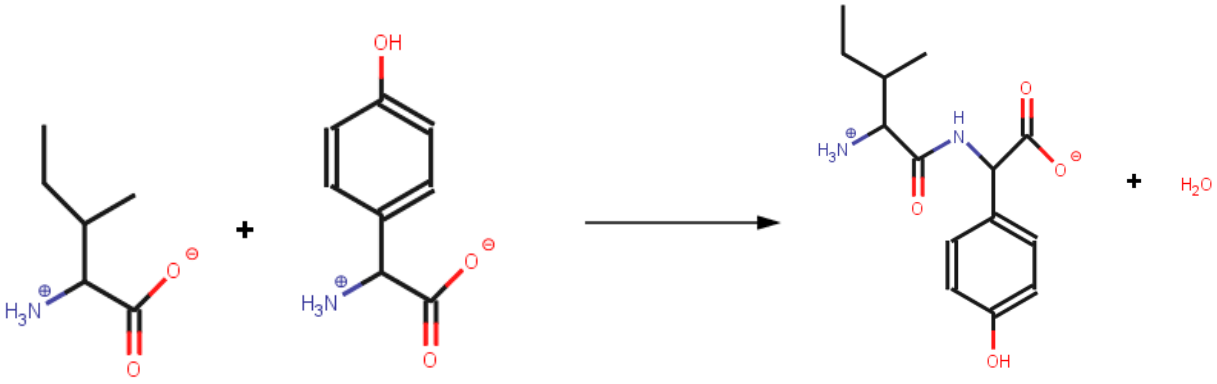
        iii. Which reaction is most likely to be an example of a polymerization?

Condensation Hydrolysis Combustion Double Replacement

        iv. What type of reaction is shown below? Condensation

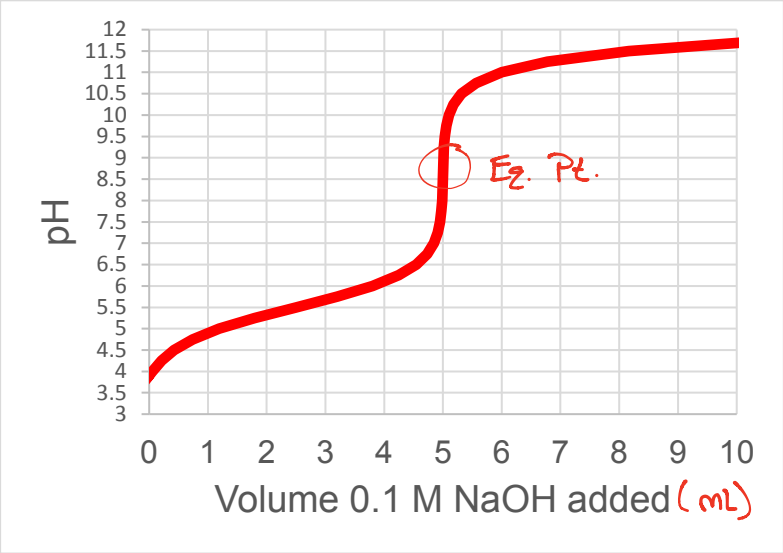


        v. Predict the product(s) of this polymerization reaction.



        vi. In the reaction shown above, do you expect the reactants or product to be more soluble in water? Explain your answer. Reactants. The products only have two charged regions on the ends while each reactant has a pair of charges. Ions interact with water very strongly, so the more charged functional groups that exist, the more soluble the molecule will be in water.

3. The titration of 0.1 M NaOH into 100 mL of a weak acid (HX) is shown below. Answer the following questions based on this information.



a. What is the pKa of the acid? How did you determine this? 5.5 – this is the pH at the ½ equivalence point.

b. How many moles of base are needed to reach the equivalence point?

$0.005\ L \times \frac{0.1\ mol}{L} = 5 \times 10^{-4}\ mol\ OH^-$

c. If the original volume of the acid solution was 100 mL, what was the original concentration of the acid?

@ Eq. Pt, mol OH^- added = moles of acid initially. So... 5×10^{-4} mol of acid in 100 mL

$\frac{5 \times 10^{-4}\ mol}{0.1\ L} = 0.005\ M = 5\ mM$

d. Determine the concentration of the conjugate base ([X-]) when:

i. pH = 5.5

$pH = pK_a$ so... $[HX] = [X^-]$

$[X^-] + [HX] = 5mM$

$[HX] = 5 - [X^-]$

$5 - [X^-] = [X^-]$

$5 = 2[X^-]$

$[X^-] = 2.5\ mM$

ii. pH = 6.0

$pH = pK_a + \log \frac{X}{HX}$ AND $[X^-] + [HX] = 5mM$

$[HX] = 5 - [X^-]$

$pH = pK_a + \log \frac{X}{5-X}$

$pH - pK_a = \log \frac{X}{5-X}$

$6 - 5.5 = 0.5$

$10^{0.5} = \frac{X}{5-X}$

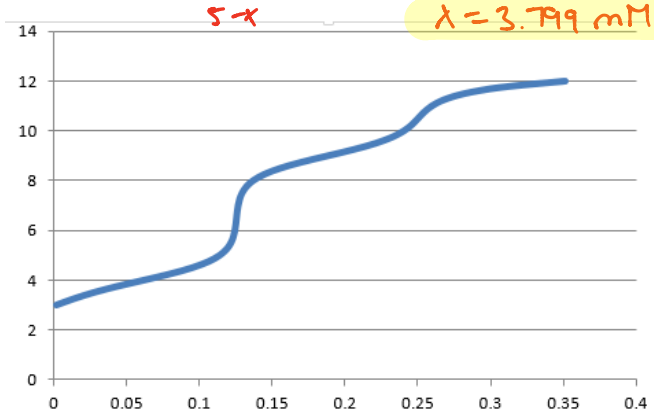
$10^{0.5}(5-X) = X$

$15.81 - 10^{0.5}X = X$

$15.81 = (1 + 10^{0.5})X$

$X = 3.799\ mM$

4. Consider the titration curve shown to the right.



a. Which acid is most likely the titrand?

HX H_2X H_3X H_4X

b. What is/are the pka values for this acid?
4 and 9 (these are the pH values that the 2 ½ equivalence points

c. Draw the two molecular species that are present at pH 4.7 (e.g. X^-) This is in the buffer range for the first pKa, so the 2 most protonated forms exist: H_2X and HX^-