# Lecture 2: Water & Hydrogen Bonds

**Assigned Reading in Campbell**: Chapter 2.1-2.2

**Online Quiz**: 1.Water, acids & bases.

Chime tutorial dates (Baker Hall 140C): Sept 6-8, Sept 12 (6-7pm)

Key Terms:

- **Molecular orbitals**
- **Lone pair electrons**
- **Electronegativity**
- **Hydrogen bond (donor and acceptor)**
- **Hydrophobic or nonpolar**
- **Hydrophilic or polar**
- **Electrostatic Interaction**
- **Amphipathic or amphiphilic**

*Understanding the properties of water is key in biochemistry because the macromolecular components of cells – proteins, polysaccharides, DNA, RNA and membranes - assume their characteristic shapes in response to water.*

## 2.1 Structure and Polar Nature of Water

**Review of Electronic Structure of Water:**

a) Oxygen has the following electronic configuration: $1s^2 2s^2 2p^4$.
b) The 2s and 2p orbitals of the outer shell form four $sp^3$ hybrid orbitals that can accommodate 4 pairs of electrons.
c) With 6 electrons in the outer shell, the outer shell orbitals are populated such that two orbitals are filled and two contain one electron.
d) The filled orbitals cannot form bonds and are called *lone pairs* of electrons.
e) The half-filled orbitals participate in the formation of a covalent bond between oxygen and hydrogen.
f) These orbitals are tetrahedral in their orientation (although the ideal bond angle of 109° is distorted to 104.5° by charge repulsion in the lone pair electrons).
g) The "bent" shape of the water molecule is polarizing, creating a permanent dipole for the molecule as a whole.

## 2.2 Hydrogen Bonds

### 1. Characteristics of H-Bonds

a) Formation of H-bonds is primarily an electrostatic attraction between:
   - A *donor* hydrogen atom attached to an electronegative atom (*e.g.* NH or OH)
   - An *acceptor* electronegative atom (*e.g.* the lone pair electrons of nitrogen or oxygen in the case of water) (See Campbell, Table 2.1 for electronegativities)

b) Typical length: 1.8Å (from hydrogen to oxygen, 2.7 Å from nitrogen to oxygen)

c) Typical angle: 180° ± 20° (the closer to linear the stronger the hydrogen bond)

d) Typical energy: 20 kJ/mole. How does this compare to a covalent bond?

**2. Significance of hydrogen bonds**

a) Defines the solvent properties of water.

b) Strong intermolecular cohesion responsible for its high boiling point, melting point, heat of vaporization and surface tension.

c) Large heat capacity, important for temperature regulation.

d) Low density of ice. H-bonds in ice are directional and straight, resulting in strong H-bonds and an open, lattice structure.

e) Water molecules in liquid water form a random H-bonded network with non-ideal orientations. (The average lifetime of an H-bond between two water molecules is 10 picoseconds.) Thus each individual H-bond is easily made and broken, resulting in fluidity.

f) Important role in recognition at the molecular level as well as the formation of the structure of complex bio-molecules: most, if not all hydrogen bonds must be satisfied in these interactions.

**2.3 Solvation** *(Oil and Water don't mix, at least not very well)*

**a) Solvation of ions**: Ions dissolve readily in water. Interaction by electrostatic forces.

The force between two charged particles is:

$$F = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{Dr^2} \qquad \varepsilon_0 = 8.854 \times 10^{-12}\, C^2/N \cdot m^2$$

The force depends on the distance between the two charges and the dielectric constant (D) of the medium. A high dielectric constant, such as that found in water, is important because the forces between charges are attenuated. Thus, unlike charges will not be strongly attracted to each other, instead, they will remain in solution and interact with the water.

The dielectric constant is related to the dipole moment of the solvent, as illustrated below:

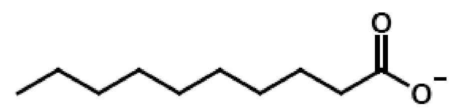
| Compound | Dielectric Constant(D) | Dipole Moment ($\mu$) |
|---|---|---|
| **Formamide** | 110 | 3.37 |
| **Water** | 79 | 1.85 |
| **Methanol** | 32 | 1.66 |
| **Benzene** | 2 | 0.00 |

The dipole moment reflects the charge distribution of a molecule. It is defined by the following equation: $\mu = \sum qr$. A large dipole moment means that the solvent molecules can interact favorably with charged solute molecules. Consequently, a high dipole moment usually implies a high dielectric constant.

**b) Hydrophilic** (polar) compounds (*e.g.* ethanol): interaction by hydrogen bonds.

**c) Hydrophobic** (apolar) compounds (*e.g.* butane): do not form hydrogen bonds to water; rather, they are excluded from water and are forced to interact with each other.

**d) Amphipathic** (or amphiphilic) compounds are both polar (or charged) and non-polar (*e.g.* fatty acids). These can form micelles if the non-polar part is sufficiently large. Micelles are aggregates of amphipathic molecules that sequester the non-polar part on the inside, much like the inside of an orange.



**Take home question: Draw, and then describe how water will interact with the following:**

| | |
|---|---|
| 1) Water with itself | 2) Propanol |
| 3) Hexane | 4) Potassium sulfate |
| 5) Phenol | 6) Acetamide |

**2.4 Ionization of Water:**
Water has a slight tendency to ionize and pure water consists of hydronium and hydroxide ions.

$$H_2O \rightleftharpoons H_3O^+ + OH^-$$

The equilibrium constant for the dissociation of $H_2O$ can be written:

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]}$$

Since the concentration of $H_2O$ is high (55.5 M) and practically constant, we can incorporate it into the equilibrium constant and define a dissociation constant for $H_2O$:

$$K_w = K_{eq}(\mathbf{55.5}M) = [H^+][OH^-] = \mathbf{1} \times \mathbf{10}^{-14} M^2$$

Pure $H_2O$ is neutral. Therefore ionization produces equal concentrations of $H^+$ and $OH^-$, and

$$[H^+] = [OH^-] = \mathbf{1} \times \mathbf{10}^{-7} M$$

However, not all aqueous solutions are neutral. When acid is dissolved in water, $[H^+]$ increases and the solution becomes acidic. Because the ion product for water is always $\mathbf{1} \times \mathbf{10}^{-14}$, there is a reciprocal relationship between $[H^+]$ and $[OH^-]$. In solutions that are acidic, $[H^+]$ is high and $[OH^-]$ is low. Conversely, in solutions that are alkaline, $[H^+]$ is low and $[OH^-]$ is high. Note that the ion product is always $\mathbf{1} \times \mathbf{10}^{-14}$.