

Chapter 2

Water

Problems

1, 4, 5, 6, 7, 10

2.0 Introduction

Water is most abundant molecule in Bio systems
most biochemistry is aqueous biochemistry
interactions between water and biomolecules is what determines their structure
Thus need to study water before can even begin studying Biochem

2.1 Weak Interactions in Aqueous systems

Hydrogen bonds give extra cohesive force between water molecule not seen in organic solvents

also responsible for ice structure

polar molecules interact well with water because can H bond with water so stay in similar environment

nonpolar molecules cannot interact with water to gain E
actually disrupt water interactions with self to lose E
thus not soluble
tend to cluster into oil drops
called hydrophobic interaction

have repeated several times now H-bonding, London, hydrophobic interaction and ionic are all weak interactions, but summed together over hundred of atoms in biopolymer make big E in structure of proteins, nucleic acids, polysaccharide & membrane lipids

A. H-bond give water unusual properties

Table 2-1

water had higher MP, BP, and heat of vaporization than other common solvents

Water has electronic structure that encourages H bonds

H bond increase molecular cohesion

Make it harder to break molecules apart hence properties given

Bond dissociation E for H bond about 20 kJ/mol
(Covalent C-C bond 248 kJ/mol)

At RT kinetic E of molecule is almost balanced against H bond strength

That why you have liquid

in water lifetime of H bond is 1×10^{-9} sec

Refer to water structure as 'flickering cluster'

Look at structure H₂O may make 4 H bonds with neighbors

At RT is reorienting so on average only 3.4 H bonds. Molecules
Lack of order allows molecules to pack a little better (not in
restricted lattice) this is why liquid more dense than solid?

B. Water forms H bonds with polar substances

remember that H bond is a form of dipole -dipole interaction

What does a molecule need to make a dipole-dipole interaction?
(A dipole- electrons must be non-symmetrically distributed so get
partial +/- interaction)

What make the H bond a special Dipole?

Small size of H allows partial charges to approach more
closely to make stronger interaction

What other organic entities form H bonds?

Figure 2-3 & 2-4

C=O, N, O will H bond with H of OH

Will also H bond with H of NH

H bond strongest when oriented with e of electrons is in line with single
bond holding H

See fig 2-5

makes bond very directional required proper alignment or no good.

C. Water interacts electrostatically with charged molecules

seen in Gen Chem dipole of water interacts with + or negative ions to make
surrounding shell. This is favorable reaction. On top of this still have H
bonds between water molecules so overall E is in favorable and ions
dissolve in water

Because water 'coats' ions, it screens them from each others charge
thus don't interact as strongly

$$F = Q_1 Q_2 / \epsilon r^2$$

ϵ = dielectric constant = 78.5 for water 4.6 for benzene so can see how
much cuts down interaction

All thing being equal

$X/4.6$ / $X/78.5$ = about 20 times weaker!!!

D. Entropy increases and crystalline substance dissolves

another factor in favor of ions dissolving

as dissolve ions now much less ordered so big increase in entropy
(Slight decrease in entropy of water because oriented on ions)

E. Non polar gases poorly soluble in water

O₂, N₂ CO₂

Not charged polar or nonpolar?

(O₂ N₂ bonds non polar, molecule non polar)

CO₂ bonds polar, but molecule symmetric so no dipole nonpolar)

Will interact favorably with water?

No - no dipole -dipole for give off E

In gas phase more random than in liquid phase to no entropy drive

In fact again lose entropy as orient water molecules around

So don't dissolve well in water

Why is this a problem?

Need O₂ need to get rid of CO₂

Special proteins to binds and carry O₂ past dissolved levels

CO₂ converted to H₂CO₃ and carried as ionic acid, then converted back to gas

Other important gases

NH₃ H₂S base and acid respectively so polar, charged

F. Nonpolar compounds force unfavorable changes in water structure

now lets try nonpolar liquids + water

No favorable H interaction

water molecules oriented around outside so unfavorable entropy as well called a **clathrate**

unfavorable clathrate minimized if stick all hydrophobic into a single sphere with small surface, hence oil drop

The HYDROPHOBIC EFFECT

What if molecule a mixture of polar and nonpolar - **Amphipathic**

polar stick out into water, nonpolar stays hidden away

micelle structure (figure 4-7)

Will see this motif over and over

Detergents

protein structure

DNA structure

lipid bilayers

G. Van Der Waals interactions (London forces)

Induced dipole-dipole interactions

very weak very short range (4 kJ/mole)

molecules have to be almost touching before significant

optimum when atoms are touching each other at van der Waals radius

H. Weak interactions crucial to macromolecule structure

All forces seen are weak compared to single bond
but will use lots

Just to binding a single amino acid to a protein may have 4 H bonds,
London forces for 1-15 atoms, a couple of charge/charge interactions and
the hydrophobic force. All these little forces add up. Also as make one
interaction, other are close so they are also add, so forces add up in a
exponential manner

I. Solutes and Colligative properties

What are colligative properties
properties tied to number of solute molecules not chemistry of solute
Name me some?

Freezing point depression

Boiling point elevation

Osmotic pressure

Last is important in biological systems

$\Pi = icRT$ (Gen Chem iMRT)

C = conc

I = van't Hoff factor

ic = osmolarity of solution

Where is important to biological system

Cell

If P inside > P outside can explode (hypotonic)

If P outside > P inside collapse (hypertonic)

If equal isotonic

How to avoid

Bacteria, plants cell wall

Some protozoa have special organelle

Animals - keep fluid around cells in osmotic balance by
pumping various things around

Has significance in how things are stored

Glycogen/starch storage polysaccharides polymer of
glucose

Since not needed structurally, why not leave as glucose?

C = .001M glycogen

C = 1000 M glucose

Which has the higher osmotic pressure in cell?

Plants use osmotic pressure to keep leaves in Turgor. What does this mean?

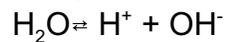
Must pay attention to this when fractionating cell (breaking open to isolate different organelles) so that you don't damage organelle you are looking at

2.2 Ionization of water, Weak Acids Weak Bases

Note this discussion will diverge from text

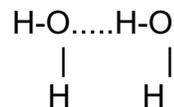
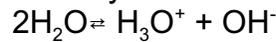
A. Pure water is slightly ionized

written



$$K_w = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Actually



Actually reflect a phenomena called proton hopping

H^+ appears to move extremely quickly in solution compared to K^+ or Na^+ movement

can be important in some places in biology, but probably won't see again until graduate school

B. Ionization of water is expressed by an equilibrium constant

$$K_{\text{eq}} = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$$

$$K_{\text{eq}} = [\text{H}^+][\text{OH}^-]/55.5\text{M}$$

$$K_{\text{eq}} \times 55.5 = [\text{H}^+][\text{OH}^-] = K_w$$

Def of a neutral solution is $[\text{H}^+] = [\text{OH}^-]$

do if $X = [\text{H}^+] = [\text{OH}^-]$

$$X^2 = K_w = 1 \times 10^{-14}$$

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

C. pH Scale designates the H⁺ and OH⁻ concentration

Remember pH scale?

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log 1 \times 10^{-7}$$

$$= -(-7)$$

$$= 7$$

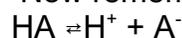
pH > 7 basic

pH < 7 acidic

pH of solution is extremely important in biochemistry. Virtually every protein is designed to work best at a single pH and moving to another pH starts to disturb performance. Your body as a whole is optimized for blood pH of 7.4. If blood chemistry shifts away for this you are one sick puppy.

D. Weak acids and bases have characteristic dissociation constants

Now remember equilibrium of weak acids?



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Also the Henderson-Hasselbach equation

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Here are a couple of problems to try...

The pK_a for H₂PO₄⁻ ⇌ HPO₄⁻² + H⁺ is 6.86

1. If [H₂PO₄⁻] = .25M and [HPO₄⁻²] = .35M what is pH?

2. If a solution is .5M total phosphate (H₂PO₄⁻ + HPO₄⁻²) what are the concentration of the two?

E. Titration Curves reveal the pKa of weak acids

Read through, we will revisit when we talk about amino acids

2.3 Buffering against pH changes in Biological Systems

Another important concept to remember is buffers

What are buffers? (Solutions that resist changes to pH when either a strong acid or base are added)

Just about every biological fluid you find is a buffer solution and resists changes in pH.

A. Buffers are mixtures of weak acids and their conjugate bases

How do you get a buffer solution?
Mixture of acid and conjugate base

Where do we see buffers most clearly? Titration curves

What would the titration curve of .5M H_2PO_4^- look like?
Buffer region 50% titrated, equal amount of acid and conjugate base,

$$[\text{HA}] = [\text{A}^-]$$

$$\text{pH} = \text{pK}_a + \log(x/x) = \log(1) = 0$$

$$\text{pH} = \text{pK}_a$$

B. The Henderson-Hasselbalch Equation

The above treatment should remind you of the Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log [\text{A}^-]/[\text{HA}]$$

This is the easiest equation to use when calculating buffer solution when you have a mixture of an acid (HA) and its conjugate base (A^-)

C. Weak acid and bases Buffer cells and Tissues against changes in pH

In fact this phosphate buffer is the main buffer used to keep the blood pH near its optimum of 7.4

Other factors as well

Carbonate system

$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_2^-$ $\text{pK}_a = 6.35$ pK_a even lower than optimum pH but still close. Why

This becomes a very important and complicated system why?



so conjugate base is coming from CO_2 that your cells are making?

And what happens in lungs?

CO_2 is released so pH could change in other direction

Also blood contains lots of proteins, each protein contains lots of ionizable groups, and these also help to keep pH of blood constant

D. Why

Blood buffered between pH 7.35 & 7.45

When get to enzymes will find that all enzymes have a pH optimum (see figure 2-21)

Presumably as blood pH changes, all enzymes in blood start to change

activity

Doesn't take much to get your Body in trouble

Diabetes

Uptake of glucose impaired (will see why later)

Body does lots of Fatty acid metabolism

This results in high levels of β -hydroxybutyric acid and acetoacetic acid in blood

High acid pH drops below 7.35

Enzyme start to malfunction

Headache, drowsiness, nausea, vomiting, diarrhea, stupor, coma, convulsions

Other conditions also produce acidosis

2.4 Water as a reactant

Water is not only the solvent for most biological reactions, it is also a reactant in many reactions. What are two reactions we have already seen?

Condensations: AA + AA to polymer + H₂O

Nuc Acid + Nuc Acid to DNA + H₂O

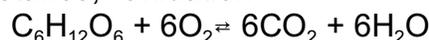
Reverse: Hydrolysis

Protein to water + AA's

DNA to Nucleic Acids + water

These are two major reactions involving water. There are other important ones as well

For instance, Oxidation



And reduction



2.5 Fitness of the aqueous environment for living organisms

1. High specific heat of water. Take much E to change temp, helps to hold temp steady
2. High heat of vaporization of water. Use to make sweat
3. Density of ice lower than water so ponds freeze from top down
4. How do you keep ice from forming in arctic fish living <freezing?