Lab 2B • 09/29/11

Extraction is used in the following situation: imagine that you're doing a chemical reaction that produces more than one product, or produces a product but a number of byproducts. We want some way to be able to target and isolate the one or sequence of compounds we really want to get out of the solution. There's ways we can play solubility tricks to target a compound and extract it out of a solution. We need to review molecular polarity. Polarity takes us into solubility, this trick that we use in order to do extraction. We're not doing a normal extraction, we're doing an acid-base extraction, where we use acid-base reactions to change polarity.

Let's start with an example of polarity. CH3-CH3, a simple two-carbon hydrocarbon; has the name ethane. Eth- is one of these common names that we still use even though we have a systematic nomenclature. Ethane has a molar mass of about thirty grams per mole. In comparison, water has a molar mass of 18 grams per mole. Even though ethane is the more massive molecule, it is a gas at room temperature. Water, the less massive molecule, is a liquid at room temperature. Why is this true? Why is the one that's heavier a gas and the one that's lighter a liquid? Water is a polar molecule. Intermolecular forces (IMF) are electrostatic forces, meaning they involve plus and minus charges. These attractive forces are what hold molecules together. At room temperature, there's too much kinetic energy, too much thermal energy, for water molecules to stay together as a solid. But because they do have the IMF, they do stick together as a liquid. Ethane has a non-polar structure. Because of that, it doesn't have as much of these intermolecular forces, so there's not as much to hold it together, so not only can it not stay together as a solid, but, in fact, it just goes completely flying apart and turns into a gas. Intermolecular forces (IMF) are attractive electrostatic (involving plus and minus charges) forces between molecules.

What is the prime root cause of polarity? Electronegativity. What is electronegativity? Electronegativity is the tendency of an atom to pull electrons towards itself when it's part of a bond. If I were to make this cartoonish picture of the periodic table, which ways along the periodic table does electronegativity increase? Towards the right and up. We exclude the noble gasses. Because they have octet configurations, they don't tend to bond. We'll make our destination point here fluorine. Why is it that electronegativity increases as you go to the right and up? As you have a smaller and smaller atom, those electrons are closer and closer to the nucleus, and the nucleus has a strong and stronger effect. Why is it that, as we go from left to right, we have this change? The closer you get to being an octet configuration, the easier it is to satisfy an atom by getting those electrons, and that translates into having higher electronegativity.

A dipole – this is what forms when you do have atoms in a bond that are of differing electronegativity. What is a dipole? It's not when they attract each other. Dipoles do cause the attraction, but what is a dipole itself. Dipole means two poles, either north and south if we're talking about magnetism, or, since we're going to confine ourselves to just talking about charge, it's going to mean plus or minus charge. A dipole is charge separation in space. It has a plus and minus end. Bonds have dipoles when the atoms in a bond have different electronegativities. When we do have a dipole, we can say something is polar.

There's a couple of different ways I could write a dipole. If I have something like water, where, yes, the whole molecule is polar, each individual bond is polar. One way to show that is to write an arrow. This is not a mechanism arrow. You can tell the difference by the plus sign that's part of that arrow. The plus sign shows which element is less electronegative, so it's having its electrons taken away, and the tip of the arrow shows where the electrons are going towards. Since this is an arrow, this is highlighting the fact that dipoles are vector quantities, which means you have a magnitude – the amount of charge separation – and you also have which way charge separation is being pointed towards. Another way of indicating this is by using a delta symbol, writing delta plus for the element that's slightly more positive and delta minus for the element that's slightly more negative. Make sure that when you're writing these deltas you don't confuse it with the letter sigma. Sigma is like a zero with a line coming off of it; a delta is more like a sloppily-written d. The delta in this case means "a little bit", so a little bit positive, little bit negative.

This tells us why bonds will be polar, when we have these different electronegativities. But it doesn't, therefore, directly talk about molecules are or are not polar. Let's look at an example molecule, carbon tetrachloride, CCl4. If we write a structure for it, you could do it as follows. Notice that I've used different kinds of lines to draw this molecules, the dash-wedge system. So the wedge is the thicker-look line; that represents something that's pointed out towards you. The dash represents something that's pointed away from you. This is a way to suggest three-dimensionality from this structure. Since this is carbon with four bonds, no lone pairs, what kind of shape does this molecule have? It's a tetrahedral shape. Because this molecule is tetrahedral, tetrahedral means having a shape that the sides, edges, angles, everything is exactly equal. That means the dipoles from each of the bonds are also exactly balanced with each other. We end up in a kind of tug-of-war effect. To simplify, if we have a linear system, where we have just two bonds, you could imagine that one bond is pulling in one direction, but the other bond is then pulling in exactly the opposite direction. If you have those two things exactly balanced with each other, it's as if electrons are never pulled anywhere. So even though the bonds might be polar, the molecule, as a whole, is non-polar. That's true in this linear case, that's true in a slightly more complicated situation like this, a tetrahedron, that has everything balances. So although the bonds in this molecule may be polar, because the dipoles exactly balance each other, the molecule as a whole is non-polar.

What could we say, then, must be true structurally about a molecule in order for it to be polar? It has to not cancel out. A molecule must have some kind of asymmetry in its structure in order for it to be polar. Coming back to ethane and water. If you look at the shape of water, it's got two bonds and two lone pairs. We can imagine that the lone pairs have their own space, so this is a derivative shape of a tetrahedron, cause there's four things. But it can't be a tetrahedron because tetrahedron means four equal things. What shape do we call this? Bent. Because of it's bent shape, it's asymmetric, and so it's polar. Since it's bonds are really polar, that's why water itself is really, really polar. What about ethane? If you look at each carbon individually, it's almost, but not quite, a tetrahedron. You can imagine this as being two tetrahedra that somewhat overlap with each other. But, in general, if you have a hydrocarbon, even if it's not totally symmetric, they're normally non-polar, because the difference between a carbon-hydrogen and carbon-carbon bond is so small that, especially for large molecules, any of these differences in electronegativity average out. In this specific case, even though there's this difference between the carbon-carbon and carbon-hydrogen bonds, the molecule, if you chop it in the middle, is exactly symmetric with itself. So one half of the molecule, it's dipole would cancel with the other half still, and so this is symmetric, so it's non-polar.

Thermal energy is just kinetic energy. It's the fact that, at any temperature, temperature is due to the fact that molecules are wiggling around. So, water is a liquid at room temperature because its intermolecular forces exceed the kinetic energy and keep the molecules together. Whereas because ethane is non-polar, it doesn't have as much in the way of intermolecular forces, so therefore it can only exist as a gas.

{About water} It would be tetrahedral if every position was exactly the same thing that was attached. In fact, by having the lone pairs, there's only a minor deviation from being tetrahedral in terms of shape, 105° angle instead of 109.5°. Even if it had exactly-equal angles, the fact that you have a bond, an atom over here, can't be balance out by the lone pair that's on the other side. So even if shape-wise it was exactly a tetrahedron, it still would be geometrically asymmetric. {Can molecules that are large enough stay together} That is what is due to what are called temporary dipoles. Everything that we've discussed so far are permanent dipoles caused by structure. For large molecules, you can have momentary asymmetry caused by the molecule moving around. That temporarily generates the dipole, and on a large enough molecule you have enough of them that occur at one instant that it can bring molecules together. Temporary dipoles, when you have a large enough molecule, can accumulate and cause molecules to stick together, but if you were directly comparing one with the other, temporary dipoles are much weaker. Whenever you have a permanent dipole, that going to have a more dramatic effect.

Non-polar molecules, since there's nothing for one molecule to grab on to another molecule with, there's not the plus and minus distribution, that's why they're not able to stay together.

In this first case, the intermolecular forces are greater than kinetic energy, and in this other case, the intermolecular forces are not able to overcome the effects of kinetic energy.

Solubility

Of these two molecules (benzoic acid and naphthalene), which one would you say is the least polar? Why would you guess naphthalene? It's symmetric, and it's only got carbon and hydrogen, and again carbon-carbon and carbon-hydrogen bonds are not normally different enough from each other to cause polarity. Naphthalene is very non-polar. If you had to make a hard choice between polar and non-polar, which way would you classify benzoic acid? Does benzoic acid go into water? Not at room temperature, no. That's one piece of evidence you could use to say that it's also non-polar. Better said, it is very slightly polar. Why would it only be slightly polar? It is slightly polar because it does have these carbon-oxygen and oxygen-hydrogen bonds, which are a bit polar. But if were took the carboxylic acids as a substituent to benzene, ignore this substituent, how many atoms are in the rest of this molecule? Six? That's a common answer, but that's only looking at the carbons. How many hydrogens are attached? Five. Because at the position where you have the carboxylic acid, at this juncture we have a double bond, a single bond, and another single bond already, so there's not a hydrogen there. But, every other position does have a hydrogen, so there's eleven atoms there, benzene therefore being the large part of this molecule and very non-polar because it's symmetric. That outweighs the polarity of the functional group, so benzoic acid as a whole is non-polar. Benzoic acid is non-polar because the large, very non-polar benzene portion outweighs the polarity of the carboxylic acid.

{Isn't easier if you have a number?} There is a way to quantify it. You can assign an intensity, a number, to that dipole. There is a unit of measure that you can specify how strong a dipole is.

Terminology

What is a solution? It is a mixture of solute and solvent, but can you define it without using terms that have that "sol" root in it? A solution is nothing more than a homogenous mixture, which means that you have these components that are equally spread out throughout the solution, so if you zoom in on one part of the solution you can't tell one part of the solution from another. What is the solvent? It is the major component of the solution. If you have something like water and ethanol, both dissolve each other. Which one is the solvent, then, is the one in greater quantity.

So the solvent is the major component of a solution (sol'n). The solute would be the minor component. What does soluble mean? Able to form a solution, with a particular solvent. You can say salt is soluble – yes, in water, but not in something like benzene. Miscible. Extractions usually involve immiscible solvents. What does miscible mean? The fact that two solvents will dissolve no matter what their proportions are, so as much or as little as each one that you've got, you're going to form a solution. Miscible means two solvents that form a solution regardless of proportions. The opposite of that would, therefore, be immiscible, which mean unable to mix regardless of the proportions. Miscible, mixable; you could think of it that way. Miscible systems generally involve only liquid, so that one component could completely envelop the other. The most common example of a miscible pair: water and ethanol. In fact, they're so miscible that you cannot use normal distillation techniques to separate water and ethanol completely from each other.

For extraction, we generally use immiscible solvents. We usually use water and some kind of organic solvent. The two normally with form two layers, and then, if you have a compound that's non-polar, it's going to greatly prefer the organic phase, and if you have a compound that's polar, it's going to greatly prefer the water phase.

Let's see a selection of common organic solvents. A simple hydrocarbon solvent is hexane, but even more common that hexane is something called hexanes, with an "s", which is a mixture of hexane isomers. What are isomers? They have the same molecular formula but different connectivity, different geometry, something about their shape is different. Molecules with the same formula but different structures. Hexanes is a mixture of different six-carbon compounds. If we take a carboxylic acid and we replace the hydrogen of the carboxylic acid [functional group] and we replace it with some other kind of carbon-containing group, we make a functional group called an ester. Naming-wise we do the same thing. If we were to cover up these two carbons over here, this looks like the molecule acetate. This two-carbon group, if you have a two-carbon chain all by itself, we call that ethane, -ane. But when we add it on to something else, it becomes a substituent, and the name changes a little bit. We drop the -ane ending and we add -yl instead. So, ethane becomes ethyl. So this compound is named ethyl acetate. Considerably more polar than hexane because it's got this oxygen in the middle and the carbon-oxygen bond sticking off the side. If we have a small enough molecule, a carbon-oxygen double bond can actually make a compound water-soluble, which the molecule acetone is. It is water-soluble.

How about some halogenated solvents? Solvents that have chlorine, iodine, bromine in them. One common one is CHCl3, chloroform. Then there's CH2CL2, which has two names. The systematic name is dichloromethane, but the common name is methylene chloride. The last one for now has a multitude of names. The common name, which is the most-used name, is diethyl ether. An ether is a functional group where you have carbons on either side of an oxygen. But because this is so commonly used, sometimes the "di" is left off and it's just called ethyl ether. In fact, it's even more-frequently referred to as just ether. In a lab, if someone says, "Could you go get the bottle of ether?", 99.99% of the time, it means diethyl ether. Chloroform is also a common name. The systematic name would be trichloromethane.

There is a common saying that oil and water don't mix. Why not? There's another way of saying it: like dissolves like. Polar dissolves polar; non-polar dissolves non-polar. But what's the underlying reason for that? It's too much energy for the molecules to be close. What it really is is entropy. When water is a liquid, the molecules are all randomly arranges. But what happens to water when it freezes? It expands. It's got this hole in it. This is why you don't put glass bottles filled with aqueous solutions in the freezer. At room temperature, the molecules all move past each other. But unlike most other substances on the planet, when water freeze the molecules pull apart from each other. It's because of the extreme polarity of water. They form (which I hate the term) hydrogen bonds (because it's not really a bond but are these attractions that occur in this kind of situation, where you have hydrogen attached to oxygen, nitrogen, or fluorine. Because of the strong interaction, the molecules pull each other apart and make this space. In terms of entropy, is this a favorable or an unfavorable process? Unfavorable, because any time you make order in a system, effectively it costs energy.

Think of two chalk erasers. Take two chalk erasers and clap them together, the chalk's not just going to sit there in a nice little pile. It's going to go every which way. To make the chalk come back together, you effectively have to add energy back in in order to organize. It's just like this lab. It takes hours to clean it, it takes seconds to make a mess of it. Something like that goes on when you try to force a non-polar substance into water, because water, at room temperature, would rather have its random arrangement. When you push another molecule in, it's making its own space and, therefore, in a way, organizing water. That's a negatie entropy change, which in terms of Gibbs free energy means a positive energy change. Positive energy is not favorable, and so it doesn't happen.

Like dissolves like is going to be a good enough reason for us most of the time.

Acid-base neutralization

Extraction does take advantage of differing solubilities in different solvents. We're going to stack on top of that a chemical reaction. Benzoic acid itself is not polar, so what if we ended up in a situation in which we have both benzoic acid and naphthalene together? They're both non-polar, so if you put them both into a non-polar solvent, it's going to be difficult to separate the two of them out from each other, unless we just happen to have the magic combination of solvents.

But there's another thing we could do. What we could do is to take advantage of the fact that benzoic acid is an acid. It is an acid, in fact, with a pKa value of 4.2. {guidance on pKa values} In this acid-base neutralization, hydroxide will give a pair of electrons to hydrogen. Hydrogen can only have one bond at a time, so the oxygen-hydrogen single bond on benzoic acid will break, and we'll end up with two compounds. We'll make a salt out of what used to be benzoic acid; we call that sodium benzoate. Just like acetic acid goes to acetate, benzoic acid goes to benzoate. We, of course, also have water a a byproduct.

What does having a pKa of 4.2 mean for benzoic acid? pKa is defined as the – log 10 of Ka. Ka, in turn, for a monoprotic acid, we show how many of the protons break off versus how much of the conjugate is left and compare that to the non-disassociated acid. If we want to make this conceptually this fraction, it's how much it dissociates versus how much of the acid does not dissociate. And yes, if you have a very large Ka, something that's much greater than 1, that means you're going to have a pKa that's less than zero, and that's for something that has extensive dissociation. We call those kinds of acids strong acids. If you have a Ka that's much, much less than 1, which means a pKa that's much greater than zero, that means you have minimal dissociation, which means that you have a weak acid.

Benzoic acid, in comparison to hydrochloric acid, is called a weak acid, because it doesn't dissociate all that much. In organic terms, benzoic acid is fairly strong, because it's somewhat unusual to have organic compounds with pKa's of 5 or under. The stronger an acid is, the weaker it's conjugate base is.

Let me rewrite this neutralization reaction but focusing not on mechanism, but on reactivity. Benzoic acid has a pKa of 4.2; water has a pKa of 15.7. So, out of the two compounds, benzoic acid and water, which one is the stronger acid? The one with the smaller pKa. Smaller pKa, because it's the negative log of Ka, means large Ka. So benzoic acid is the stronger acid, water is the weaker acid. The stronger the acid is, the weaker the conjugate is. So that means, the conjugate of benzoic acid – benzoate – is the weaker base; the conjugate of water is the stronger base. Stronger acid reacting with stronger base, making weaker acid and weaker base: that's the way that reactions want to happen because it'd be equivalent to an equilibrium constant greater than one. So this neutralization will occur.

What's the point of this neutralization? Benzoic acid is mostly non-polar. One point of interest: when you have boiling water, there's enough thermal energy that, somehow, it is able to dissolve benzoic acid; temperature can have an influence on solubility as well. Compare that to benzoate. Benzoate is a salt. Above any form of dipole is charge. When you have a real, full charge, that's going to have the strongest intermolecular effect, versus any dipoles that you might have. So, even though benzene is the larger portion of this molecule, even though it's incredibly non-polar, now you've got a full negative charge on the molecule: it becomes water-soluble. That's a great thing for us, because if we have naphthalene and benzoic acid that are together in solution and we want to be able to separate one from the other, we can target benzoic acid, change it's polarity, get it to bump out into the aqueous layer. Later on, since this is just an acid-base reaction which is a reversible reaction, we can react the benzoate with [a stronger] acid, make it benzoic acid, make it non-polar again, and it falls out of water. That's exactly the trick that we'll pulling in today's lab. So by neutralizing benzoic acid an forming an ion, we have now made it much more polar, we're able to accomplish the separation.

Hydrophilic, which means "water-loving", which means water-soluble. There's then hydrophobic, "water-fearing', which means not water-soluble. We also use a set of contrasting terms lipophlic and lipophobic, which mean "fat-loving" and "fat-hating", or "organic-loving" or "organic-hating". Instead of a relatively small molecule like benzoic acid, imagine that we have a really long molecule that's got a carboxylic acid group at the end. If you make a salt of that carboxylic acid group, you've now got a polar portion of the molecule with this long, stringy non-polar portion of the molecule – that's a soap. Detergent. Surfactant. The way that it works is: if you have grease, the long, stringy portions of the soap molecules end up combining with the grease and forms a little ball called a micelle. On the outside of the micelle, you have all these different polar groups that make that whole entity, that whole assembly, soluble in water. So you put soap into water, the grease bits all congregate together, but the outside makes it water-soluble, which is why you're able to wash away grease. You can reach a point in water, though, where if you get enough soap, it will start forming phases in water, it will self-assemble into liquid crystals. The you'll get this organic-water mixture. It'll hold the water, but it's got such a heavy organic component that it will start forming a biphasic material.

{separatory funnel demonstration}

When you need to drain the liquid, take the cap off, because if you're trying to drain liquid out without any air coming in, you're trying to form a vacuum.

How do I make sure that I get just that one layer and don't let any of the top layer come through? if some of that top layer came through it should still float, so you could get a pipette to transfer it backwards again. {part of point of lab is to learn to deal with liquids and separations}

{description of lab procedure}

For bottles of ether, we need to put the date down that it was opened. Ether, once it's exposed to oxygen, starts forming peroxides. Old, old ether bottles, because of a buildup of peroxides, explodes spontaneously on shock.

Most organic solvents are less dense than water – the notable exceptions, many of the halogenated solvents, such as methylene chloride.

{storage of chemicals}
{chemical pet peeves}

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polarity
solubility
acid-base neutralization
extraction
chemical safety

$H_3C – CH_3$ (ethane); MM = 30 g/mol; gas @ RT
H_2O; MM = 18 g/mol; liquid @ RT
why??
IMF – intermolecular forces – attractive electrostatic (involving + and – charges) forces between molecules
electronegativity – the tendency for an atom to pull electrons towards itself when part of a bond.
dipole – charge separation in space (has + and – end)
Bonds have dipoles when the atoms in the bond have different electronegativities.
polar – has a dipole – vector quantity

{sigma vs delta}

Although the bonds in CCl_4 are polar, because the dipoles exactly balance each other, the molecule as a whole is non-polar .
Molecules will have dipoles if they have some form of asymmetry.

Solubility

Benzoic acid is non-polar because the larger, very non-polar benzene portion outweighs the polarity of the carboxylic acid.

solution – homogenous mixture
solvent – major component of a solution {sol'n}
solute – minor component of solution
soluble – able to form a solution with a particular solvent
miscible – two solvents that form a solution regardless of the proportions used
immiscible – unable to mix regardless of the quantities used

hexanes (with an "s") – mixture of hexane isomers (molecules with the same formula but different structure)
ethyl – two-carbon substituent

The stronger an acid is, the weaker its conjugate its base is.

By neutralizing benzoic acid and forming an ion, the molecule is now water-soluble because it is now polar (the full – charge outweighs the non-polar benzene portion of the molecule).

hydrophilic – "water-loving" – water-soluble
hydrophobic – "water-fearing" – not soluble in water