Lab 14B • 06/19/12

[test 2]

First problem: the Fischer projection of the aldaric acid of d-mannose, d-mannaric acid. You were also asked for the reagents that could have been used to synthesize it. [mannose: left, left, right, right] An aldaric acid means that both the aldehyde and the opposite end of the molecule have been oxidized, so you have a dicarboxylic acid. The reagent to synthesize it from its sugar is nitric acid.

Aldonic acid of d-xylose, d-xylonic acid. [xylose: right, left, right] Aldonic acid: the terminal -OH group remains unchanged, but the aldehyde gets oxidized. The reagent used for that is aqueous bromine.

Alditol of l-threose, l-threitol. [threose: right, left] Aditol means that the aldehyde has been reduced, so every carbon has an oxygen single bond. It's sodium borohydride, followed by acid work-up.

Fischer projection of alpha-l-ribofuranose. [l-ribose, left, left, left] The bottom -OH group is on the left; we're going to make a cyclic sugar, which means we're going to rotate it to be at the bottom of the sugar, so it's in the backbone. If we turn that bottom stereocenter, you rotate that down, the hydrogen that would be on the righthand side would end up right here; that means the CH2OH will move from the bottom to being on the righthand side, and then we have the oxygen that's now part of the ring. There is a new stereocenter that's created; since I want the alpha configuration, that's when you have the new stereocenter with the -OH group trans to the CH2OH group. [furanose: five-membered ring]

Haworth projection of beta-d-idopyranose. [structure]

Last one is a dash-wedge structure of l-talose. [structure] Writing this my normal, default way, carbonyl on the right, pointing up. That means the first stereocenter is pointing down, which means you have to visualize it from underneath. So, looking underneath with the carbonyl up towards the top of my vantage point, if you had something on the left of the Fischer projection, that's going to be out towards you, which means it's a wedge. The first group is on the right, which means it would be towards the board from the perspective I was in, so it's a dash. The next stereocenter, since I'm looking down, now with the -OH group on my right, it's pointing towards you, which makes sense, because if you have all of the -OH groups on the same side, as you go from one position to the next on a zig-zag, you're going to go from one apparent configuration to the other – in other words, you'll go from wedge to dash to wedge to dash. So first, we had a dash; next is a wedge; next one's still on the same side, so we're back to having a dash. If that last one was still on that same side, it would again be a wedge; it's now flipped over, though, so if I'm looking down with the carbonyl towards the front, then the -OH group being on the left is away from you, so that's why that last one ends up being a dash.

Question 2. Alpha-d-galactopyranose [structure] You're told that this compound has a specific rotation of +150.7°. That means that given a certain concentration of a certain distance, that's the angle change that'll happen with plane-polarized light. Can you predict anything about the specific rotation of beta-d-galactopyranose? The answer is no, because alpha and beta forms of the sugar are just epimers of each other; more specifically, they're anomers. Anomers are a class of epimers; epimers are a class of diastereomers; diastereomers don't necessarily have any physical properties in relationship to each other cause they're completely different structures. Because of that, no, you can't predict anything about specific rotation. If I asked about alpha-l-galactopyranose, d an l forms are enantiomers; enantiomers mean they have all the same physical properties except for opposite optical rotation [other]. So, if I asked you for the alpha-l-galactopyranose, then you can say it's -150.7°.

If you take alpha-d or beta-d-galactopyranose and put either one in solution, although they initially are going to have different specific rotations, give it time, they both end up having the same common optical rotation in solution. You're asked for an appropriate mechanism – not necessarily every single step of the mechanism, just enough to show the main point. Here's the main point: if we think about how this ring formed in the first place, we go in reverse. So, protonate not the anomeric position, but the oxygen in the ring itself. [drawing; breaking C-O bond] Here's the point: once you open that ring up, the anomeric position goes planar again, because you have sp2 hybridization. If the ring was to instantly reform again, now it can attack from either side of that plane, which means you can get either the alpha or the beta form. This is the process of mutarotation, [which] is exactly why you up with the same optical rotation. Since this is just an acid-catalyzed process, which means it's an equilibrium process, start with either of the two molecules, they'll establish an equilibrium, which means they'll always reach the same constant concentration.

Problem 3. Glucose, mannose, and fructose are all structurally related. In basic solution, [they] can be converted into each other. You're asked to write an appropriate mechanism [abbreviations]. Let's start with glucose [structure]. If we're in basic conditions, we effectively can have enolate chemistry. An alpha position, relative to the carbonyl, is deprotonated, which forms an enolate ion. Since the bottom three stereocenters are not involved in this mechanism, if we wish to, we can abbreviate all of it with R. [Spongebob]

This is a reversible mechanism, so once we reach this enolate intermediate, we could go right back to d-glucose, where we came from, but, because we made the enolate, we now again made a planar intermediate, so when the enolate collapses or re-attacks water to reprotonate that position, we're going to end up with two possible forms [including d-mannose]. [re-expanding R] From that enolate intermediate, instead of going just in reverse [blue], let's say we moved forward by having it attack water at this point. That makes an enediol; that means that either of the two oxygens at this point could be deprotonated. If we deprotonate the top one, we're still just going in the reverse direction; so, instead, if we show deprotonation of this bottom -OH group, then we made a different kind of enolate. Now, if it reacts to grab a proton through the carbon, you've now moved, effective, the position of where the carbonyl was. The bottom three stereocenter remain unaffected, which is the point of the problem. There's a way in solution for glucose, mannose, and this, d-fructose, to all interconvert; it's through the formation of these enolates.

Lactose. [structure – righthand, hemiacetal; lefthand, acetal] Lactose is a disaccharide. A disaccharide is when you have two individual sugar units joined through a glycoside, as we have here. What is a glycoside? It's any time you attach something through the anomeric position of a sugar – we have one sugar as a substituent to the other at this anomeric position, that's what make it a disaccharide. Unlike sucrose, lactose does form a silver mirror when reacted with Tollens' reagent. Why? Because hemiacetals in aqueous solution are in equilibrium with their open form; in other words, the sugar opens, closes, opens, closes constantly. When it opens, then the carbonyl has reformed. Any time you have an aldehyde, which is what you have in this case, or if you had an alpha-hydroxyketone, which is what we would have with other sugars potentially, both of those get oxidized by the Tollens' reagent, which is when you would see the silver mirror. Because you have this openable ring, that's why it reacts. The middle of the ring, though, the acetal part, does not open, at least not with hydrolyzing. If you had an acidic solution and you forced it, yes you could break the sugar apart and cause that ring to open. But, the sugar itself, if it remains intact, that middle part can't open; only the side can. Sucrose is in the same situation as this portion of the molecule, except from the perspective of both of the sugar units, because both of the sugar units are connected through their anomeric position. In this case, the galactose is attached just to one of the other -OH groups of glucose, not to it's anomeric position, which is why it's able to open up. The hemiacetal can open; it's in equilibrium with the linear form, which means it's oxidizable. That's why it reacts with the Tollens' reagent.

How could the size of the rings in lactose be determined by exhaustive methylation? [focus on lefthand ring] The process of exhaustive methylation would be to react this under basic conditions using silver oxide and then some kind of alkylating agent [such as dimethyl sulfate]. You then hydrolyze at this point, purposely breaking apart the ring. Focusing just on the galactose portion, here's what it would end up looking like. We see that we get the carbonyl back, which we expect upon hydrolysis, but notice that most of the rest of the oxygens have methyl groups on them. That's because when we did this exhaustive methylation, we made ethers. Ethers do not easily hydrolyze, so they survived hydrolysis conditions. Notice that one of the -OH groups dod not get methylated. Why? Since this methylation occurred under basic conditions, the rings are stable in basic conditions. The rings won't open, and the oxygen that ends up not methylated was the one part of the ring. If we can identify that it was part of the ring, we know that it was a six-membered ring. That's how exhaustive methylation can be used to tell us something about ring size.

Last problem. The Kiliani-Fischer synthesis. You're asked to make d-glucose – just like in the Fischer proof – which means we're going to use d-arabinose, which we can put through a three-step process: first, much like the first step of the Strecker synthesis, we react with sodium cyanide. Second, we reduce, but with a poisoned catalyst, because it'll take the nitrile down to an imine. The imine can then be hydrolyzed, which means it'll be converted into an aldehyde. Of course, since we added a new stereocenter, we don't get just glucose, we get mannose as well. Explain why this synthesis provided firm evidence that there's [a] structural relationship between glucose, mannose, and arabinose. Because, he made glucose and mannose from arabinose. That meant that there was some commonality in the three structures, because he knew also that we were adding just one stereocenter. Arabinose is converted into both glucose and mannose, and since they were made by just adding a stereocenter, they're epimeric. That's the topic of the last part of the question as well. What is an osazone? An osazone is a hydrazone, a phenylhydrazone. Normally, if you have a ketone, that would be an easy thing to draw. For sugars, there's a redox reaction that occurs after the initial hydrazone formation, which means there's a second carbon that ends up reacting with the reagent to make a double phenylhydrazone. If we use glucose or mannose – this is part of the point of the problem – either one, you're going to make the same product. The bottom three stereocenters survive, and both of the top two carbons, then, make the phenylhydrazones. Why were these useful in general carbohydrate research? Because they were crystalline, isolatable derivaties. At that point [in time] in chemistry, characterization depended heavily on melting point; these, you could get isolated and take the melting points of, so it greatly assisted research. Why is it important in [the] context of the glucose proof? Because it again shows there's an epimeric relationship between glucose and mannose, because if they both make the same osazone, and if it turns out it's because of the loss of just one stereocenter, the rest of the molecule of glucose and mannose are identical.

Exam 3

[amino acids]

Why does glycine not have the d or l designation? Cause it's not chiral; there's no stereocenter. You don't need d or l, cause there's no such thing on the molecule. How is the d or l determined? What's the definition of those? If you told me: it's when the amino group is on the left or the right – of what? An outside reader won't know what that means. If you say: left or right on the Fischer projection – I've gotta come back with this: I wrote my amino group on th left; is this correct for the l form? No, because it's not just that it's in a Fischer projection, it's a Fischer projection where the R group is written down. That is the full definition: l, when you write a Fischer projection so that the carboxylic acid's on the top, the R group's on the bottom, then if the amino group is on the left, it's l, if it's on the right, it's d.

Question 2. Draw all the structures possible of l-lysine. [not aspartic acid – double amine, not double acid] Both of the amino groups can get protonated, so you end up with a double cation form – which means you can have a single cation, which means you also have a neutral form, but the most basic you can get is to have a singly-negative charge form. Let's start with the zwitterionic form. For easier reading, I'll put the R group in the plane of the paper. I'll have that nitrogen protonated. The three pKa values involved were 2.18, 8.95, and 10.79; the third value correspond[s] to the side chain. Given that information, is this correct structure for the zwitterionic form of this compound? What if I had the alpha-amino group protonated instead and had the terminal group with NH2, would that be correct? It has the correct charge, there might be a little bit of it in solution, but look again at the pKa values. The fact that the side chain does have a pKa of 10.78 means it's a worse acid than the alpha-amino group. Turn it around the other way, that means that the amino group on the side chain is more basic than the alpha-amino group. So, in the zwitterionic form, this is the correct structure, not if you swap which one was NH2 and NH3. If I went more basic, then I'm going to lose that positive charge. Here is the anionic form. If I go more acidic, the amino group is more basic than the carboxylate is, so now both amino groups would be protonated. Then, even more acidic than that would be for the carboxylic acid to finally to be protonated.

[second part] What I was trying to get at: at the first pKa value, you are at 50/50% of these two forms, the double cation and the cation; the next pKa would be for the cationic and neutral; the next pKa, 50/50 of the neutral and the anionic.

[third part] Explain how pKa values can be determined experimentally. If you started to talk about how you looked at the crossover points on that ionization graph, what's the net charge in solution, no matter which one of these forms we have in solution? Neutral. You can't have a solution that's just cations or anions. If you have the double cation form of the amino acid, that's because you've got two chlorides, maybe, because you use HCl to get there. If you have the anionic version, it's cause you have a sodium in solution, so it's still going to be neutral. The only way we can determine these percentages is if we had spectroscopy, if each one of these was a different color, for example; otherwise, it's really difficult to determine. So, you had to do it through titration, and you had to mention titration. If all you said was half-equivalence point, how did you get there? [need to be able to identify equivalence point and half-equivalence point and their significance] The equivalence point, we use if we care about stoichiometry. There, we would talk about the concentration of acid and base, volume of the two, solving for moles. The three-sentence version of this answer is: titrate an amino acid with a strong base; find each equivalence point, then find the pH at each half equivalence point, because those pHs are the pKas.

[part of third part] The graph has four curves in it. Notice that the curves do not go back down to the bottom axis on either end, cause realize that this is a graph representing the percentage of an amino acid – how could you have 0% amino in a solution of an amino acid? If your curve came back down to zero, that meant that the solution is disappearing. [label axes; coloration][anions do not exist at ph 0; start with double cationic] The graph never trails off to zero completely; there's always something that's increasing in concentration as something else is decreasing. [using pKa values to construct the graph] The points where the graph crosses are the pKa values because those are the half-equivalence points; because there were three pKas, there were three crossover points. The pI does not occur at [a] junction; it occurs at the top of the neutral curve.

Question 4. [pI not point – x, y, z coordinates? – pH at which you reach the maximum percentage of an amino acid] Calculate the pI of lysine. The two values that matter are the one on either side of the neutral form of this, which are 8.95 and 10.79, so the pI was 9.87.

Imagine that you have both l-alanine and l-lysine in a buffer solution of pH 4.2. Explain how and why the two amino acids can be separated. The pH, the pI of alanine, and the pI of lysine have this relationship: the pH is lower than both pIs, there is no anionic form of either molecule around, not appreciable quantities. [can't automatically say one's cationic, one's anionic based on type of problem] Notice that the pH is much lower than lysine's pI, so lysine is going to be appreciably more in the cationic form than alanine is. They'll both move towards the negative terminal, but one will move further than the other. [hint: consider whether the amino acids really were 100% in their cationic or anionic forms] If there's a difference in that percentage, is that enough to separate them? The answer's yes. pH < pI: cationic; pH > pI: anionic. SInce the pH is lower than both pIs, they're both cationic. [On an electrophoresis plate], they'll both go to the negative side, but alanine, being the less cationic of the two at that pH, will move less than the lysine.

Column chromatography. Describe the conditions used to prepare the polypeptide chain for chromatography, and explain why [the conditions] make it where you can't do sequencing. You had to hydrolyze the polypeptide chain, which is why you couldn't sequence it [incomplete answer]. Hydrolyzing destroys the order, destroys the linkage between all the amino acids.

[why? hydrolyzed not enough of an answer] You hydrolyze under strongly acidic conditions. There is the matter of the disulfide bridges – there's an additional form of linkage that can occur if you have cysteine, which is that you can oxidize these thiols to make a disulfide bridge. [2-thioacetic acid? disproportionation?] Because [hydrolysis] breaks all of the amide bonds, it destroys any order that used to be in the polypeptide chain.

Draw a simplified structure of an example ion-exchange resin [and] describe how the resin is able to separate amino acids. A super-simplified resin looks something like this: polymer backbone, every once in a while benzene, every once in a while sulfonate, which is charged, but neutral. Sulfonic acids are extremely acidic; this is the conjugate base, which is not reactive, so it's neutral, but it's charged. Here's the three-sentence version: as amino acids pass through the resin, some of the amino acids will be in greater cationic form. The cations of the amino acid can interact with the anions of the resin, therefore as the amino acids pass through, they're separated on the basis of charge.

Explain the physical process. The physical process: you first fill the column with the resin and load this amino acid soup on the top. [soup!] After filling the column with the ion exchange resin, you add the amino acid soup to the top and flush it through with solvent. As the solvent passes through, the amino acids separate into bands. The elution time of those bands can be used to identify the amino acid. Once the amino acid passes off of the column, it can then be identified by elution time, and can be confirmed to be present by visualization using ninhydrin. Aside from visualization, why is it used? Because you can use Beer's law to get the concentration and the therefore the proportion of moles. Why can't you use it for sequencing? Because you destroy the structure of any amino acid you react with the ninhydrin. [structure of complex] The only thing that exists of the amino acid is that nitrogen.

Last question. You make these different phenylthiohydantoin derivatives. You can identity which of these derivatives you have, which, because you still have the R group on there, means you can identify which amino acid you had, which since you pull the amino acids off only one at a time from the chain, that's why you can sequence. You don't destroy the order all at one, you destroy it one at a time. [Aside from visualization, explain why ninhydrin is used in titration but is not used to identify an amino acid] Other than visualization, the reason it's used in titration is to determine concentration, through Beer's law. It's not used to identify the amino acid because the amino acid is not part of the complex formed, so you can't identify it. [When it turns purple] you know that an amino acid is coming off the column; that is visualization.

Liquid crystals

[historical example] It is this material that is able to flow; it has some of the physical properties of a liquid, and yet, there's some kind of internal structure, which is normally something that you would only see in solids, in things that are crystalline. Amphiphiles – amphi- meaning both, phile- means liking: a substance that can go both into the aqueous phase and the organic phase.

Let's start with a little bit of historical development. This is an [ester of a] carboxylic acid that has 14 carbons in it, including the carbonyl carbon; the other side of it is the molecule cholesterol. This molecule is cholesteryl myristate. [myristic acid, 14 carbons; chlosterol with -yl means substituent] Cholesteryl myristate was a biological sample that was determined to have really unusual behavior, from the perspective of these early researchers. It appeared that this compound melted twice; how could something melt twice? You start with a solid, add some energy to it, the molecules start moving around; that transition, that's melting. The next transition we're used to talking about is when those molecules start to totally pull apart from each other, turning into a gas. How can we see this experimentally? [There is a] kind of heating curve where, if we were to constantly, consistently add a certain amount of energy at a constant pace over time and observe the energy of the system, if we have a normal heating curve, we would start out with a solid, whose temperature would linearly increase with the amount of energy added (at least ideally). That would be proportional or based on the heat capacity of the object. At some point you start melting; you can either change the temperature or change the phase, but if you're doing so carefully, you can't do both at the same time, so the temperature will plateau as you go from solid to liquid. Once you've melted, the liquid will heat up until it then starts to change into a gas. That will keep heating up until you break down the difference between a gas and a liquid (with enough pressure) and reach the critical point. This is for a normal material. But, cholesteryl myristate, if we ignore the boiling of the material, had this behavior: it started out as a solid, which could be heated up. It then transitioned into something else. It had an observable change in phase, but things look different on either side of this temperature. But, it didn't properly melt and turn completely into a liquid. After heating this whatever-it-is, it eventually did go through another discreet, identifiable transition to become a real, true liquid. That liquid could then continue to heat up. The question is: what is this extra phase that was formed?

Polarized light microscopy

You have some kind of light source which releases incoherent light, which means there's multiple frequencies potentially involved, there's multiple directions the light could come out and radiate from all directions from the lightbulb, but not just in all directions – if you were travelling in just a straight line, what is the angle that the electric and magnetic components of that light make with the original light source?

You can light that wiggle straight up and down or side to side or it does so circularly – it's called circularly polarized light because as it travels in one direction. What you can do is pass this light through a polarizer. Let's say, for example, that the polarizer was designed so it only allows light that oscillated in the vertical direction to pass through. If you then pass that light through a polarizer that was at a 90° angle and observed what came out, no light would come through at all. If you first chopped out all light except that which oscillates in the vertical direction and you did that with a vertical polarizer, and then you tried to put it through a horizontal polarizer which will block anything except horizontal motion, vertical motion is exactly not horizontal motion, meaning that none of that light's going to make it through. [example of 3D movie glass put on top of each other]

There are some materials that if you put them in the middle of this – if you had some kind of container that had your sample in it, then if you had an original plane of polarization, maybe it would tilt that plane to rotate it, so you would get light out on the other side. With crossed polarizers, if no material is placed between the crossed polarizers, no light can make it through. If light is passed through orthogonal polarizers, with no sample between the polarizers, no light will reach the detector. If we did put some kind of sample in here – but it can't just be any sample, if we put just water between the polarizers, nothing changes. Why? Because when you pass light through water, it doesn't matter which direction that you pass it through, you get the same result. A chiral material, however, you pass light through and, irrespective of how you passed the light through, it's going to twist (it does matter how far it travels). [This is an example of optical anisotropy – or is it, since you get the same result in all directions?] Light passing through an object will somehow be altered by that object. Another form of it is how that object interacts with light depends on how light passes through it [real definition?][calcite – birefringence]. That is an object which its interaction with light depends on which angle the light makes with it; that's a form of optical anisotropy. [chirality also causes optical anisotropy – it's not which way it passes through the sample that changes the light, it's the structure of the material itself] Optical anisotropy would be [two things]: [altering of light due to interaction with a sample or] the property of a material that interacts with light differently depending on the way in which light passes through that material.

If we now imagine a slightly different situation. [diagram of microscopy] [The] light source [is] down at the bottom, [with the light] passing first through a polarizer, then passing through a sample of some sort; the light then passes through a second polarizer. This would be the set up for polarized light microscopy (PLM). If you have an optically isotropic material, which means it doesn't matter how light passes through it, it doesn't interact with that material [differently], then you won't seee anything remarkable coming through [the] microscope. You could set it to where the polarizers are parallel with each other, so the light simply passes through, which means you'd be looking at just the material itself, just magnified. Turn the polarizers, all you would see is the light going light and dark, light and dark, because nothing particularly special is going on. What kinds of materials are optically isotropic? Liquids. What kinds of materials are optically anisotropic? Lot's of different types of minerals. Back in the 1800s, this kind of microscopy was done on thin slices of minerals in order to try to characterize the structure of different minerals. You put a liquid crystal on this polarized light microscope and look at it, it generates all the same kinds of pretty color patterns that these thin rock samples generate. But it's a liquid crystal, which means it's squishy like a liquid, but liquids don't show anything remarkable under this microscope. So how can we have this stuff that looks like a liquid but acts like a crystal? That's where the term liquid crystal comes from.

True liquids are isotropic, because they have no internal structure (ignore chirality). Thus, liquids would not exhibit any remarkable patterns under polarized light microscopy. However, samples of structured solids, such as minerals, will display very colorful patterns under PLM. Here's the point: liquid crystals appear liquid, but exhibit the kinds of patterns under PLM as crystals, meaning liquid crystals are anisotropic.

[summary: double melting, PLM] You can take something that's a solid; you go through a phase transition where it does not completely melt. What the manifestation of this is is it's a liquid, meaning the molecules can move, but it retains order, which is why it appears to have some of the behavior of a crystal. You continue to add more heat, eventually the molecules do fully melt and separate from each other. Mesophase – meso- meaning in between, so it's a phase that has both the properties of a crystal – which means some kind of structural order – and a liquid – meaning that it's fluid. If you have a distinct mesophase, that's why it appears to have a melting point. Of course, you're in this odd, in-between phase that'll have another transition, which means another clear melting point. This mesophase explains the multiple melting points, as well as the crystalline behavior under polarized light microscopy.

[classes of LCs] Thermotropic liquid crystal – the type of phase that exists depends primarily on temperature; it's [normally a neat] phase, meaning you don't have a mixture. Lyotropic liquid crystals – [the] phase depends not just on temperature, but concentration, so you have solutions, interactions between polar and non-polar phases that cause mesophases to form. Under thermotropic, two broad classes are nematic and smectic; under lyotropic, lamellar and hexagonal phases.

Thermotropic liquid crystals

Cholesteryl myristate – let's say that I idealize it, take that pretty rigid structure of the cholesterol, and we'll think of it as some kind of disc. Then, we have this myristate, a carboxylic acid with a long, wiggly tail. You have contrasting behavior when you put a whole bunch of these together.

You could imagine that the discs, because they are rigid, have a lot of ability to pack really well with each other, easily forming crystalline materials. The tail, because they're long, they're easily formed, they can easily move about, and they don't, as easily, crystallize. Imagine that you had a solid that contained this kind of material and you slowly added heat to it. These tails, which are much more flexible, [are] harder to crystallize – they can start to melt. But these cores might have so much attraction with each other that, even while the rest of the molecule's melting, they try to keeps some semblance of order. That least to this split behavior – part of the system's melting, part of it's not – that's one way that this liquid crystal behavior is generated. That's the principle mode of self-assembly with thermotropic liquid crystals. In thermotropic liquid crystals, two contrasting effects occur: there's the tails, which are long, flexible, and harder to crystallize. If they're harder to crystallize, they're easier to melt than the rest of the structure. You then have the cores, which are usually very rigid and easily crystallize, which means they try to maintain order even as the rest of the molecule may melt.

Because of these two differing effects – you can get mobility from the tails, and you can get order from the cores... If you're going from low temperature to high temperature, you can have a number of liquid phases. Whether you might have just one phase or a dozen depends on the structure of the compound involved. If we do have this interaction between cores separate from the interaction with the tails, you could imagine that, if you change the structure of the core a little bit, you change what kind of order is possible; change the structure of the tails a little bit, you might change how broad of a temperature range you have for this split behavior. As an example of phase changes you can have: here are three different liquid crystal phases: smectic C, smectic A, and nematic. [nematic comes from word for thread, related to PLM patterns of these nematic LCs][smectic – related to soap, but would think lyotropic would be more appropriately named after soap]

What do these phases look like? In a solid, you'll have things very well lined up, but there's no movement. Jumping over to the liquid side, there's no order to a liquid. This nematic phase, the molecules are random in terms of position, but you can see that they're all pointed roughly the same; they won't all be identically parallel, but they'll be pointed roughly the same way. That way that they point is known as the director; that's some sense of directional order. Now imagine this: what if the core was sensitive to magnetic fields, [or] to electric fields? What if you put this [compound] between two glass plates that were charged and turn the current off and on and off and on? [those of you starting at your laptops right now, that's what you're looking at] Imagine that if the director was oriented one way, these crystals were opaque, meaning you can't see through them. What if, by twisting the director's direction, they become transparent? What if: one orientation, they're blue, and the other orientation, they're not? You take advantage of these special properties of these liquid crystals [leads to liquid crystal displays as an example]. Once you have order, you can play with that order; one you have directionality, using electric or magnetic fields, you can change that directionality, which means you change the property of the material. Since it's a crystal, you have a handle to grab onto, metaphorically; since it's a liquid, it has the ability to be manufactured.

The smectic A phase is where, instead of just some kind of directional order, you have positional. There's movement, so it's not like a solid. Molecules can move between these different rows or sheets, but the point is there are these rows or sheets, that is order, that's what the PLM sees. If you put on top of that some specific kind of tilt, which is an additional form of order – notice that's closer to the solid, low temperature, more order, high temperature, more disorder. We have positional order, but we have movement. Here, we have also directional order. From a solid that's ordered, to a smetic C that's got some order, to a smectic A that's got less order, to nematic that's even less order, to a liquid that finally has no order. Depending on how you tailor the structure of a liquid crystal, you might be able to generate all of these different phases – or even some others [not described]. Imagine that, just because of the way molecules self-assemble, that in one layer [of a smetic C phase the molecules] are pointed one direction; the next layer, they're pointed a little bit different; the next layer, a little different. You can have a helical arrangement of these directors as go from layer to layer to layer; that's called a chiral smectic C phase. Because there's directionality, that means you can exploit it in terms of its physical properties. That's thermotropic liquid crystals. [liquid – random orientation, random position; smectic – random position, some orientation of the orientation]

Lyotropic liquid crystals

Usually, thermotropic LCs are single-component systems, whereas in lyotropic liquid crystals, they are usually solutions or mixtures. The phase that a thermotropic liquid crystal forms is mainly based on temperature; the phase that a lyotropic liquid crystal forms is mainly dependent on concentration. Let's look at two different examples of lyotropic LCs. [leicithin – subclass of a phospholipid – phophatidyl choline derivative. [ammonium palmitate – shampoo bottles] Look at the structure of the compound: this is another split personality compound. Here, we have our very non-polar tail group, but we have an ionic head group [much smaller]. Hydrophilic/phobic – water-loving/-fearing; lipohobic/-philic. Lipophobic would be "fat-fearing" – other than our cultural fear of fat – and fat loving. Hydrophilic means compatible with a water phase; usually what makes something compatible in water make it incompatible with fat. Something that's hydrophilic is usually lipophobic. The opposite's true: if something won't dissolve in water, but it's organic, that means it's going to dissolve in the fat layer, which means it's hydrophobic but lipophilic. You have two different functionalities on these molecules; they are amphiphiles – molecules that are both hydrophilic and lipophilic. [amphi- both; phile- liking; amphitheater – indoor and outdoor use; amphibian – lives in both water and land]. An amphiphile straddles the two different kind of phases that you might encounter biologically.

Think of a cell: yes, it's got a lot of [organics it], but it's also heavily water-based [75%], so you have this dichotomy between organic and aqueous phases, that these amphiphiles end up participating, mediating. Surfactant – surface actant – which means active at the interface between the aqueous and the organic phases. [surfactants = soaps]

Soaps, in low concentrations, forms what's called a micelle.

The type of phase formed by a lyotropic liquid crystal does depend on concentration, but also on the relative geometric size of the head and tail groups. I can simplify the structure of a liquid crystal by this [little cartoon guy]: it's got an ionic headgroup and a very non-polar tail. [A] micelle forms when a lyoropic liquid crystal reaches what is called the CMC – the critical micelle concentration. Knowing the structure of the liquid crystal, how could you use its structure, the concentration of solution, and all the various intermolecular forces going on to predict what size shape is going to form from this liquid crystal? [scary math] There does come a minimum concentration that, based on the structure, it will self-assemble. Liquid crystals do these things without our intervention, so in terms of manufacturing, if we could have a liquid crystal make all our things down at the molecular level, and we just took advantage of it, doesn't that seem useful? [LCD screens] Micelle – one of these things that spontaneously forms because you're trying to minimize energy. Minimize energy in what way? Mixing oil and water is an endergonic process, because it's bad in terms of entropy. When you try to fat into water, you end up organizing water. Organizing water's not favorable, it doesn't want to do it, that's why things don't mix. Another way of saying all that is that it does whatever it does to minimize energy. You start getting enough of these amphiphiles in solution, at some point the organic bits start congregating together. Because there' s more water than the fat, those interactions get pushed to the inside of the structure. You think about the simplest symmetric structure there is – it's a sphere. These organic bits get pushed to the interior [burritose]; you have the hydrophilic exterior. When you add soap to your kitchen sink, little bubbles form, the fat's encapsulated in the middle, the outside's water compatible, so it all just gets washed away. That's how soap works.

Increase the concentration, what do you get? Increase it enough, and you start getting layers. You can get what's called a lamellar phase, which means sheet-like, a layer-like phase. Sometimes you might get just individual sheets of these molecules stacked one atop the other. Sometimes you end up with this kind of structure, which is kinda like a micelle that's been stretched out. Notice how there's two layers of the liquid crystals – in other words, you make a bilayer [make it out of leicethin –> phospholipid bilayers, parts of membranes] They're dynamic surfaces, though. There's nothing holding the molecules together, except self-assembly, so these can form and then decompose again. If we increase concentration further, then instead of just making layers, you can end up with these rods of liquid crystals in hexagonal shapes; this would extend in all directions. The inside would still contain the oily bits, the outside would contain the hydrophilic bits – this is what's known as a hexagonal phase. You can determine the spacing of these different columns by using x-ray diffraction, the same technique that would give us crystal structures – yet another physical demonstration of the quasi-crystalline nature of these liquid crystal materials – none of these are solid, but they have this diffraction ability. [utility – performing a different reaction in the organic and water phases] For example, in the water phase ... if you add water and heat to tetramethoxysilane, you first hydrate, and then you dehydrate. You can end up with a network of silicon-oxygen bonds – in other words, you end up with glass. You start off with a soluble substance, you end up with it gelling together, eventually forming a glass – this is what is known as a sol-gel process. [molecular sieves – industrially important] Hexagonal liquid crystal phases form specific sizes, depending on what molecule you use. Put a sol-gel in the water phase surrounding all of these hexagons, and you can crystallize this silicon honeycomb around all of the organics. Silicon and glass survive heat, organics don't, so once you do it, heat this whole thing up and burn the organic away, and you're left with this material that has pore sizes that are easily controlled, that are monodisperse – which means they're all roughly the same size – which makes it the perfect microscopic sieve.

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1a. d-mannaric acid b. d-xylonic acid c. l-threitol d. alpha-l-ribofuranose
e. beta-d-idopyranose f. l-talose 2. 3. 4. 5.
pKa1 = 2.18; pKa2 = 8.95; pKa3 = 10.79
pH < pI –> cationic; pH > pI –> anionic
PLM – polarized light microscopy – If light is passed through orthogonal polarizers with no sample between the polarizers, no light will reach the detector.

optical anisotropy – altering of light due to interaction with a sample (or) the property of a material that interacts differently with light depending on how light passes through that material.

True liquids are isotropic because they have no internal structure (ignore chirality). Thus, nothing remarkable will be observed in liquid using PLM. However, structured, crystalline solids will display colorful patterns under PLM.

Liquid crystals appear liquid, but exhibit the kinds of patterns under PLM as crystals, meaning liquid crystals are anisotropic.

mesophase – a phase that has some of the structural order of a solid but some of the fluidity of a liquid – explains multiple melting & anisotropic behavior

Thermotropic LCs – Single-component systems
In thermotropic LCs, two contrasting effects occur:
mobility (tails) : long, flexible, harder to crystallize; melt more easily than rest of structure
order (cores): very rigid and easily crystalize; try to maintain order as rest of molecule melts

The phase a thermotropic LC forms is mainly based on temperature.

Lyotropic LCs – Solutions/mixtures
The phase a lyotropic LC forms is mainly based on concentrations
hydrophilic/phobic – water-loving/fearing
lipophobic/philic – fat-fearing/loving
amphiphiles – molecules that are both hydrophilic & lipophilic

surfactant – active @ the interface between organic & aqueous phases

The type of phase formed by a lyotropic LC does depend on concentration, but also on the relative geometric size of the head & tail groups

Micelle – formed when LLC reaches CMC (critical micelle concentration)

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Structures *(remaining structures identical to lecture 13A and lab 13A)*

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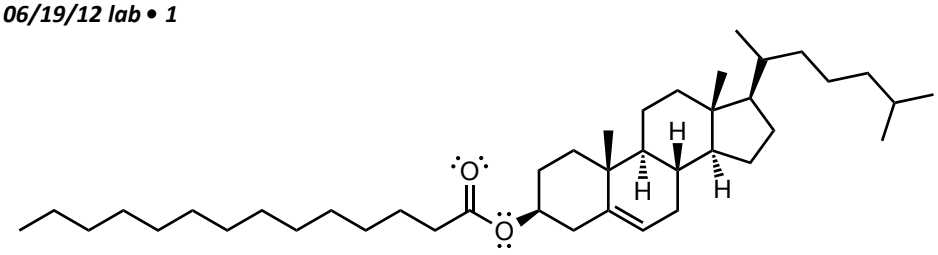

(14) cholesterol myristate

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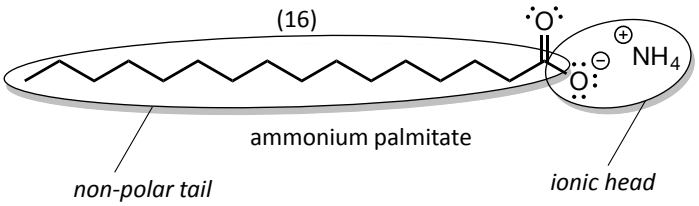

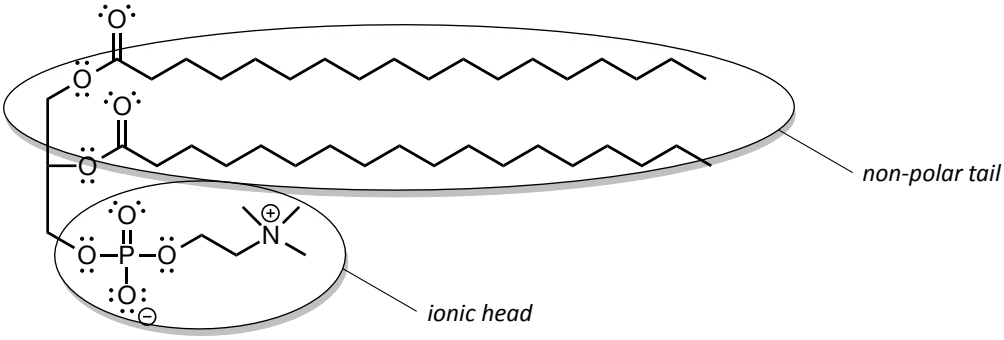

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