

Chem 431A-L25-F'07

admin:

Last time: : soaps, DG's and phospholipids, sphingolipids and cholesterol.

We learned the structure of phospholipids:

Today we discuss: (know structures)

1. galactolipids (detailed structure)
2. sulfolipids (detailed structure)
3. ether-linked phospholipids: plasmalogen, platelet activating factor (detailed structure)
4. archeobacterial membrane lipids: GDGT = glycerol dialkylglycerol tetraethers (8 5-c isoprene groups) – traverse membranes, stable under harsh conditions (detailed structure)
5. globosides (detailed structure)
6. steroid hormones (no detailed structure)
7. vitamin A and D (no detailed structure)

Structure and properties of biomembranes:

-many varied functions.

-consider fatty acids: form micelles.

but phospholipids have very bulky  $H\phi$  chains but very ionic polar headgroups. so it forms bilayers. (2 molecules thick).

-bilayers spontaneously form when mixed with water and dispersed with a sonicator for instance. the bilayers eventually close up and form compartments. "bilayer vesicles".

Today: distinguish between various lipids specific lipids and their structures. Start discussion on lipid bilayer membranes.

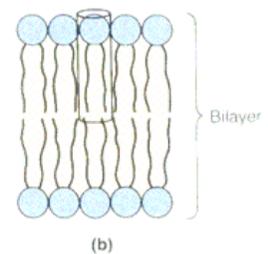
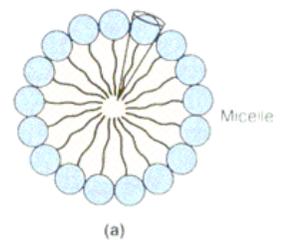
Reminders:

Wed: Nov 21 - Wednesday quiz is heavy on structures. Draw them. Be able to answer questions about structure.

Details about the molecules we have studied (Chapt 10 focus): TG, DG, PG, sphingolipids, ceramides, galactosides, sulfolipids, etc...

Wed: Nov 21 –deadline for online quiz for chapt7

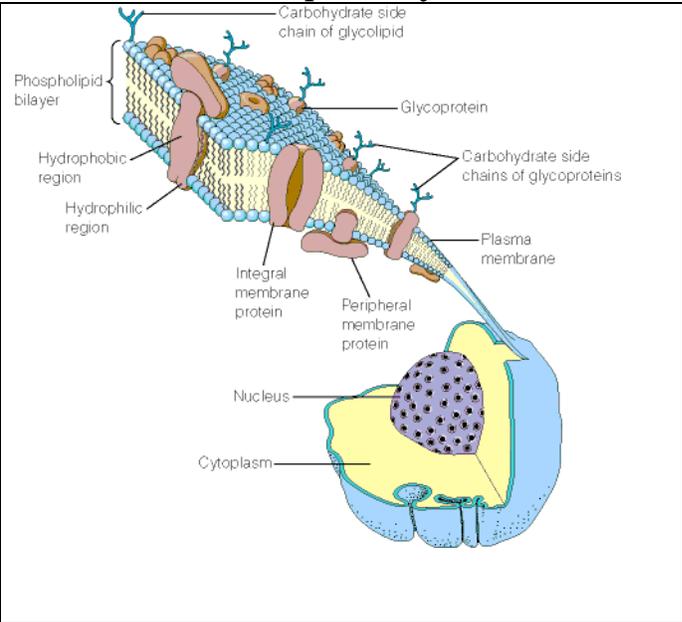
Monday Nov 26 deadline online quiz for chapt 10



Many basic properties of membranes can be viewed from the lipid bilayer model.

The basic model is the fluid mosaic model (Singer and Nicholson, 1972).

Draw the picture of a lipid bilayer showing also presence of proteins: transverse (integral) and peripheral membrane proteins. Note the hydrophilic and hydrophobic regions. It explains why for instance, water can pass thru the memb with some difficulty. In fact it is nearly impossible for anything else to pass thru.. nothing can really easily pass thru.



Let's consider the motion of the bilayer lipids:

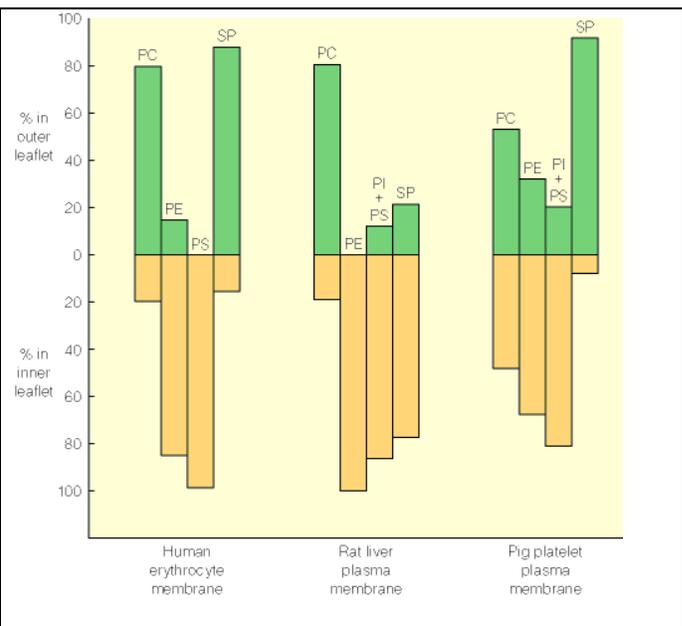
2 kinds of diffusion are possible in the membrane: flip-flop and 2-d diffusion.

Lateral diffusion or 2d diffusion may be demonstrated with the diffusion of the lipids from fused rat cells – in one of which the proteins are fluorescence-labelled. The fluorescence can be shown to spread over the fused cell. (draw this). Lipid lateral diffusion is rather rapid, about several sec to a minute to wander over the entire cell. Estimate is 1 sec to cover 1um length of a bacterial cell. Proteins also move laterally but many times more slowly. Because of this lateral mobility, lipid bilayer may be considered to be a 2-dimensional fluid.

-membrane asymmetry :

There is also transverse diffusion. “flip-flop”. Illustrate the process. It requires an unfavorable crossing of the polar headgroup thru the hydrophobic region. It is a very slow process. G is very high. Half life of many days or more. The rate is much slower for protein.

Slow flip flop accounts for membrane asymmetry. One side of the actual biomembranes has very diff properties than other side. The distribution of PLs is asymmetric.

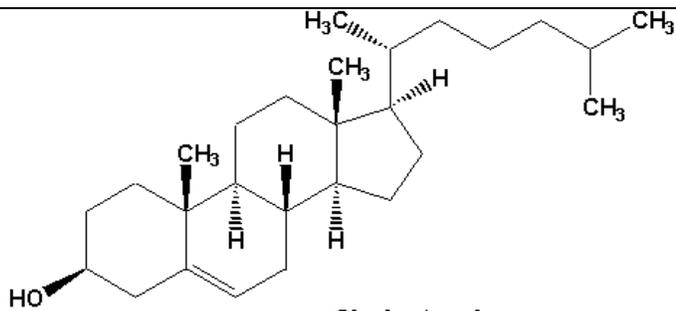


-melting transition of the membranes

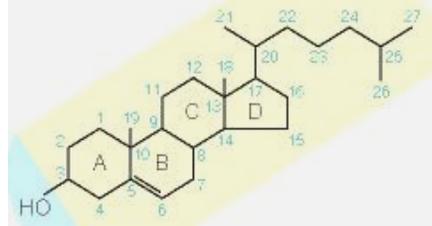
As expected, the fluidity of membranes is temperature dependent. There is a transition temperature for a lipid bilayer below which it takes on a gel like behavior and loses its fluidity.  $T_m$ . It becomes a liquid crystal. Thicker when it is "solidified" than when it is melted. Show picture. Explain why it is so: the HC tails line up or are disordered depending on the state. Recall the melting points of the various fa's. length of the fa's impt: the longer the higher the  $T_m$ . Unsaturation also impt: the unsatd fa's have

lower  $T_m$ 's due to the "disruptive" effect of the kinks to the ordered "interdigitation" of the tails. the cell membranes also adjust their unsaturated fa composition to lower their  $T_m$  and cope with cold conditions. If they didn't, it would seriously impede the role of the cell m.  $T_m$  for cell m. are about 19-40°C, Esp. cold blooded animals modify their cell m. fa composition. Bacteria don't have unsatd fa's. Instead, they adjust their fa's by increasing the "branching" of the tails.

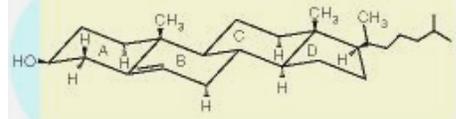
Role of cholesterol.

**Cholesterol**Role of

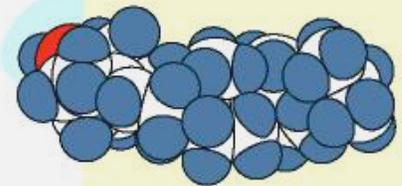
cholesterol. Give structure of cholesterol: 4 fused rings which are in the “chair config” and thus somewhat rigid and planar and definitely bulky. Slightly amphiphatic with –OH in the 3 position while the rest is very Hphobic. (it is found in animal cell m's and is much more rigid than other cell m lipids.). Cholesterol is a major example of the lipids called “steroids”. Steroids are mostly found in eukaryotic organisms. Based on 4 fused rings: A, B, C, D. cholesterol is most abundant steroid in animals. Plants have very little cholesterol in general.



(a)

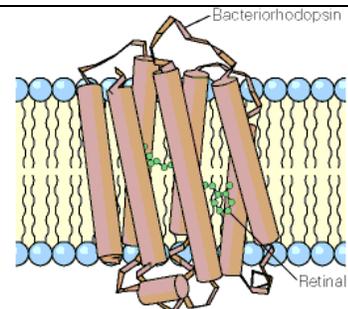


(b)



(c)

How does cholesterol act? By giving “plasticity” to the membrane. It blurs the  $T_m$ . Show graph of H vs T for a typical melting of a crystal. The H vs T for the melting of a membrane highly saturated vs highly unsaturated. Vs cholesterol rich m. - characteristics of membrane proteins.



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- melting transition of the membranes
- membrane asymmetry
- characteristics of membrane proteins.

<p>for instance. the bilayers eventually close up and form compartments. "bilayer vesicles". Many basic properties of membranes can be viewed from the lipid bilayer model.</p>	
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