University of Washington
Department of Chemistry
Chemistry 355
Spring Quarter 2005

Solutions for Homework Assignment 8: Due no later than 500 pm on 3 June
,8.19, 11.8, 11.6, 11.10

8.19)

a) $[\eta] = 0.069\left(130\times10^{6}\right)^{0.70} = 33{,}000 mL/gm$

b) The large value suggests a rod-like structure. Also, for a rod-like structure expect $[\eta] \propto M^{0.66}$

11.6) $\log\left(\frac{I_0}{I}\right) = \varepsilon c l \Rightarrow 0.88 = \varepsilon\left(3.4\times10^{-5} M\right)(0.1m)$

$\therefore \varepsilon = 2.6\times10^{5} M^{-1}m^{-1}$

11.10)

a) Using equations 11.12 and 11.19 we conclude the energy of a thin square box is

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2\right)$$

b) and c)

n_x , n_y	Energy (units of $h^2/8mL^2$)	Number of electrons (one pair per energy state)
1,1	2	2
1,2 and 2,1	5	4
2,2	8	2
1,3 and 3,1	10	4
3,2 and 2,3	13	4
4,1 and 1,4	17	4
3,3	18	2
4,2 and 2,4	20	4
4,3 and 3,4	25	0

The highest energy filled state is E=20. This has $(n_x,n_y)=(4,2)$ and (2,4).

d) Let $E_{nx,ny}$ be the energy corresponding to quantum numbers of n_x and n_y. Then

$$\Delta E = E_{4,3} - E_{4,2} = \frac{h^2}{8mL^2}(25-20) = \frac{5h^2}{8mL^2}$$

$$= \frac{(5)\left(6.62\times10^{-34}\,J\cdot s\right)^2}{(8)\left(9.11\times10^{-31}kg\right)\left(10^{-9}m\right)^2} = 3\times10^{-19}\,J$$

$$\therefore \nu = \frac{\Delta E}{h} = \frac{3\times10^{-19}\,J}{6.62\times10^{-34}\,J\cdot s} = 4.53\times10^{14}s^{-1}$$

$$and \quad \lambda = \frac{c}{\nu} = \frac{3\times10^{8}m/s}{4.53\times10^{14}s^{-1}} = 660\times10^{-9}m$$

Supplementary Problems

1) Suppose a rod has length L and diameter d. A prolate ellipsoid (i.e. a cigar) with major axis length 2a and minor axis length 2b has a volume equal to $\frac{4\pi}{3}ab^2$.

a) Prove the axial ratio of the rod L/d and the axial ratio of the prolate ellipsoid a/b are related by $\frac{a}{b} = \sqrt{\frac{2}{3}}\frac{L}{d}$ if the volumes of the rod and ellipsoid are equal.

$$V_{rod} = V_{cigar}$$

$$so\ldots\pi\left(\frac{d}{2}\right)^2 L = \frac{4\pi}{3}ab^2$$

$$\left(\frac{d}{2}\right)^2 = \left(\frac{4\pi}{3}ab^2\right)\left(\frac{1}{\pi L}\right) = \left(\frac{4}{3}ab^2\right)\left(\frac{1}{2a}\right) = \frac{2b^2}{3}$$

$$d = 2b\sqrt{\frac{2}{3}}$$

$$Then\ldots\frac{L}{d} = \frac{2a}{2b\sqrt{\frac{2}{3}}} \Rightarrow \frac{a}{b} = \sqrt{\frac{2}{3}}\frac{L}{d}$$

b) Assume a rod-like DNA 200 base pairs long has a length L=680 Angstroms and diameter d=20 Angstroms. Calculate the axial ratio a/b if the DNA is treated as a prolate ellipsoid with volume equal to the rod.

Solution: $P = \frac{a}{b} = \sqrt{\frac{2}{3}}\frac{L}{d} = (0.816)\left(\frac{680}{20}\right) = 27.8$

c) Calculate the shape factor ν of the DNA in part b where the DNA is treated as a prolate ellipsoid. See Lecture 29.

Solution:

$$\nu = \frac{\left(\frac{a}{b}\right)^2}{15\left(\ln\left(\frac{2a}{b}\right)-\frac{3}{2}\right)} + \frac{\left(\frac{a}{b}\right)^2}{5\left(\ln\left(\frac{2a}{b}\right)-\frac{1}{2}\right)} + \frac{14}{15} = \frac{(27.8)^2}{15\left(\ln(2\times 27.8)-\frac{3}{2}\right)} + \frac{(27.8)^2}{5\left(\ln(2\times 27.8)-\frac{1}{2}\right)} + \frac{14}{15}$$

$$= \frac{773}{15\left(4.02-\frac{3}{2}\right)} + \frac{773}{5\left(4.02-\frac{1}{2}\right)} + \frac{14}{15} = \frac{773}{37.8} + \frac{773}{17.6} + \frac{14}{15} = 20.45 + 43.92 + 0.93 \approx 65$$

I worked this one through the calculator several times and depending on how I round off I get between 63 and 65 for the shape factor.

d) Calculate the intrinsic viscosity of the DNA in part c assuming the gram specific volume of DNA is 0.51 mL/g and 0.30 grams of water hydrate each gram of DNA.

Solution: The easiest way to handle this calculation is given as equation 67 in Ch. 8.

$$[\eta] = \nu V_{eff} = \nu\left(\bar{V}_2 + \delta_1 \bar{V}_1\right)$$

$$= (62.5)\left(0.51 mL/gm + \left(\frac{0.30 gm\ water}{gm\ protein}\right)(1 mL/gm)\right) =$$

$$= 50.63 mL/gm$$

2) The flow of blood in the capillaries is regulated in part by constriction of small blood vessels, called arterioles.

a) Assume an arteriole has a radius 0.005 cm and a length of 0.05 cm. Assume the pressure drop across this arteriole is 50 mmHg. Calculate the flow Q in cubic meters per second through this arteriole. Assume the viscosity of blood is 0.04 poise. Assume flow of blood in the arterioles is governed by Poiseiulle's Law. Note 0.0075 mmHg=1 Nt/m^2= 1Pa.

Solution: This is just Poiseiulle's Law…Rate of Flow =Q where…

$$Q = \frac{V}{t} = \frac{\pi \Delta P R^4}{8L\eta} = \frac{(3.14)(50 mmHg)(1Pa/0.0075 mmHg)(0.00005m)^4}{(8)(0.004 Pa\cdot s)(0.0005m)}$$

$$= \frac{(3.14)(50 mmHg)(1Pa/0.0075 mmHg)(5.0\times 10^{-5} m)^4}{(8)(0.004 Pa\cdot s)(0.0005m)}$$

$$= \frac{(3.14)(6.67\times 10^3 Pa)(6.24\times 10^{-18} m^4)}{(8)(0.004 Pa\cdot s)(0.0005m)}$$

$$= 8.17\times 10^{-9} m^3/s = 8.17\times 10^{-6} L/s = 8.17\times 10^{-3} mL/s$$

b) By what fraction is the radius of the arteriole reduced if the flow is reduced by 40%?

Solution: If the flow is reduced by 40% then $Q_2 = (1-0.4)Q_1 = 0.6Q_1$. All other things being equal… $\frac{Q_2}{Q_1} = \left(\frac{R_2}{R_1}\right)^4 \Rightarrow \frac{R_2}{R_1} = \left(\frac{Q_2}{Q_1}\right)^{1/4} = (0.6)^{0.25} = 0.88$

?

3) Retinal is a visual pigment found inphotoreceptor cells . As shown in Figure 11.18 of your text retinal has a conjugated chain composed of 4 C-C double bonds. Each double bond contributes 2 electrons or 8 total "π" electrons are delocalized along the chain of retinal . Assume the conjugate chain of retinal is 1.0 nm long.

a) Suppose each π electron in the conjugated chain of retinal can be treated as a quantum mechanical particle in a one dimensional box. The energies for the particle in the box are $E_n = \frac{n^2h^2}{8mL^2}$ and the corresponding wave function are $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$, n=1,2,3,… Each energy level of the box can be occupied by at most two electrons. Calculate the energies of the levels that are occupied by electrons.

Solution: Four energy levels are occupied for eight electrons so n=1,2,3,4.

$$E_n = n^2\frac{h^2}{8mL^2} = n^2\frac{\left(6.62\times10^{-34}\,J\cdot s\right)^2}{(8)\left(9.1\times10^{-31}kg\right)\left(10^{-9}m\right)^2} = n^2\frac{43.82\times10^{-68}\,J^2\cdot s^2}{\left(72.8\times10^{-49}kg\cdot m^2\right)} = 6.02\times10^{-20}\times n^2 J$$

$$E_1 = 6.02\times10^{-20}J;\ E_2 = 24.08\times10^{-20}J;\ E_3 = 54.18\times10^{-20}J;\ E_4 = 96.32\times10^{-20}J$$

b) If retinal absorbs light it converts from the all-trans to the 11-cis conformation. For the light to be absorbed its frequency must be related to the change in energy of the electrons by $h\nu = E_{n+1} - E_n$ where ν is the frequency of the light, h is Planck's constant and E_n is the energy of the highest occupied energy state. Calculate the frequency of absorbed light for retinal which is treated as a particle in a box.

Solution: Highest unoccupied level is

$$E_5 = 150.5\times10^{-20}J \Rightarrow \Delta E = E_5 - E_4 = (150.5-96.32)\times10^{-20}J$$

$$\therefore \Delta E = 54.18\times10^{-20}J \Rightarrow \nu = \frac{54.18\times10^{-20}J}{6.62\times10^{-34}J\cdot s} = 8.18\times10^{14}s^{-1}$$

c) Sketch the wave functions for the highest occupied and the lowest unoccupied energy levels of retinal.

Solution: Plot $\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ for L=10^{-9} m and n=4 and 5.

c) Repeat the calculation in parts a and b for butadiene $CH_2 = CH - CH = CH_2$. How does the calculated frequency compare to the experimental wavelength of 220nm?

Solution: In the textbook β-carotene with 11 double bonds is about 2.5 nm. Retinal with four double bonds is about 1 nm. Approximate L for butadiene at around 0.5 nm. Then

$$\Delta E = E_3 - E_2 = (9-4)\frac{h^2}{8mL^2} = 5\times\frac{\left(6.62\times10^{-34}\,J\cdot s\right)^2}{(8)\left(9.1\times10^{-31}kg\right)\left(5\times10^{-10}m\right)^2} = \frac{219\times10^{-68}\,J}{1.82\times10^{-48}} = 1.20\times10^{-18}\,J$$

$$\nu = \frac{1.20\times10^{-18}\,J}{6.62\times10^{-34}\,J\cdot s} = 1.81\times10^{-15}s^{-1}$$

$$\therefore \lambda = \frac{c}{\nu} = \frac{3\times10^{8}m/s}{1.81\times10^{15}s^{-1}} = 1.66\times10^{-7}m = 166nm$$

This is about a 20% difference for the 220nm experimental number. If you use a value for L of 0.6 nm you get a closer result.