

### 3 Dilute Solutions

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- 10/21: 1. (35 pts) Estimate, as a function of molecular weight, the characteristic diffusion time  $\tau$  for a polymer in a solution of viscosity  $\eta$ , where  $\tau$  is defined as

$$\tau = \frac{R^2}{D}$$

where  $R$  is the size of the polymer (function of  $N$  and  $l_k$ ) and  $D$  is the diffusion coefficient (remember  $D$  is different for different coil models). Determine  $\tau$  for polymer coils in a theta-solvent for...

- a) Freely-draining (Rouse-like) model;

*Answer.* Recall from class that in general,

$$R = N^\nu l_k \qquad D_t = \frac{k_B T}{f}$$

Additionally, in the specific case of a theta solvent and free-draining model, we have respectively that

$$\nu = \frac{1}{2} \qquad f = N\xi^*$$

Therefore,

$$\tau = \frac{(N^{1/2} l_k)^2}{k_B T / N \xi^*}$$

$$\tau = \frac{N^2 l_k^2 \xi^*}{k_B T}$$

□

- b) Non-draining (Zimm-like) model.

*Answer.* Everything from Q1a holds except that we are now in a non-draining regime, so  $f \neq N\xi^*$  but rather

$$f = 6\pi\eta R_H$$

Additionally, we have in general that

$$R_H = \gamma R_g = \frac{\gamma R}{\sqrt{6}}$$

Therefore,

$$\tau = \frac{R^2}{k_B T / (6\pi\eta\gamma R / \sqrt{6})}$$

$$\tau = \frac{\sqrt{6}\pi N^{3/2} l_k^3 \eta \gamma}{k_B T}$$

□

- c) You are performing a GPC packed with beads with diameter  $5\text{ }\mu\text{m}$ . Estimate the time for a DNA molecule with  $D = 0.01\text{ }\mu\text{m}^2/\text{s}$  to diffuse a distance equal to a bead diameter.

*Answer.* We want to find the time  $\tau$  it takes for diffusion to displace a polymer with  $D = 0.01\text{ }\mu\text{m}^2/\text{s}$  by  $\Delta r = 5\text{ }\mu\text{m}$ . Per class,

$$\begin{aligned}\langle \Delta r^2 \rangle &= 6D\tau \\ \tau &= \frac{(5\text{ }\mu\text{m})^2}{6(0.01\text{ }\mu\text{m}^2\text{ s}^{-1})} \\ \tau &\approx 417\text{ s}\end{aligned}$$

□

2. (30 pts) Ultracentrifugation is a means to separate polymers. The same is placed in a tube and spun quickly to exert a centrifugal force on the solution. Three main forces on a polymer molecule are

$$\begin{aligned}F_s &= m\omega^2 r && \text{(Sedimentation)} \\ F_b &= -m_0\omega^2 r && \text{(Buoyancy / Archimedes' Principle)} \\ F_d &= -\zeta U && \text{(Drag)}\end{aligned}$$

where  $m$  is the mass of a single polymer,  $\omega$  is the angular speed of the centrifuge,  $r$  is the stator arm of the centrifuge,  $m_0$  is the mass of fluid displaced by the polymer (given by  $m_0 = m\rho v$ ),  $v$  is the partial specific volume of a polymer,  $\rho$  is the solvent density,  $\zeta$  is the drag on the polymer, and  $U$  is the speed at which the polymer moves.

- a) Assuming the polymer has reached its terminal velocity (constant velocity, sum of forces equal zero), calculate the velocity  $U$  as a function of  $\omega, r, v, \zeta, \rho, M, N_A$ , where  $M$  is the molar mass of the polymer and  $N_A$  is Avogadro's number.

*Answer.* By the definition of molar mass,

$$M = mN_A$$

Thus, since the polymer has no net force acting on it, we have by Newton's second law that

$$\begin{aligned}0 &= F_s + F_b + F_d \\ &= m\omega^2 r - m_0\omega^2 r - \zeta U \\ &= \frac{M}{N_A} \cdot \omega^2 r - \frac{M}{N_A} \cdot \rho v \omega^2 r - \zeta U\end{aligned}$$

$$U = \frac{M\omega^2 r}{N_A \zeta} (1 - \rho v)$$

□

- b) Calculate how  $U$  scales with  $M$  for a flexible polymer in a theta solvent. *Hint:* Don't forget that  $\zeta(M)$ ! Also,  $v$  is not a function of  $M$ .

*Answer.* For an impenetrable sphere (which is how a flexible polymer would behave in a theta solvent), we have from class that  $\zeta \propto R_H \propto R_g \propto R \propto N^\nu$ . Since  $N \propto M$  and  $\nu = 1/2$  in a theta solvent, it follows that  $\zeta \propto M^{1/2}$ . Thus, in the context of the above equation,  $U \propto M/M^{1/2}$ , or

$$U \propto M^{1/2}$$

□

3. (35 pts) This problem will explore viscometry of polymer solutions and data obtained from Lee and Tripathi (2005) in their microfluidic rheometer, discussed in Lecture 11.

- a) The authors measure an intrinsic viscosity of a polyethylene glycol solution to be 44.6 mL/g. The MW of the polymer is 35 000 g/mol. Estimate the radius of gyration of the molecule assuming a good solvent. Please use the experimental value of  $\gamma$  from the Lecture 10 slides.

*Answer.* From the Lecture 10 slides,  $\gamma = 1.5$  for a linear, monodisperse polymer in a good solvent. PEG tends to be linear, hence that selection, and there is no other provided experimental  $\gamma$  value for a linear polymer, so I believe I have to assume it's monodisperse?? Thus, based on our theory from class,

$$\begin{aligned}\langle R_g^2 \rangle^{1/2} &= \sqrt[3]{\frac{3M[\eta]}{10\pi N_A \gamma^3}} \\ &= \sqrt[3]{\frac{3(35\,000 \text{ g mol}^{-1})(44.6 \text{ mL g}^{-1})}{10\pi(6.02 \times 10^{23} \text{ mol}^{-1})(1/1.5)^3}} \\ \boxed{\langle R_g^2 \rangle^{1/2} \approx 9.4 \text{ nm}}\end{aligned}$$

□

- b) What is your estimate for the overlap concentration  $c^*$  for this polymer?

*Answer.* From class, we have that

$$\begin{aligned}c^* &= \frac{2.5}{[\eta]} \\ &= \frac{2.5}{44.6 \text{ mL g}^{-1}} \\ \boxed{c^* \approx 5.6 \times 10^{-2} \text{ g/mL}}\end{aligned}$$

□

- c) Assuming the solvent has a viscosity of 1.1 Pa s, calculate the viscosity of the polymer solution at  $c = c^*/2$ .

*Answer.* From class, the approximation of  $\eta$  in terms of  $[\eta]$  to one term is

$$\begin{aligned}\eta &= \eta_s (1 + c \cdot [\eta]) \\ &= (1.1 \text{ Pa s}) \left[ 1 + \frac{1}{2} (0.056 \text{ g mL}^{-1})(44.6 \text{ mL g}^{-1}) \right] \\ \boxed{\eta = 2.5 \text{ Pa s}}\end{aligned}$$

□

- d) The authors measured the intrinsic viscosity of the MW = 10 000 g/mol sample in water to be 11.9 mL/g and in a water/methanol mixture to be 22.3 mL/g. What can you conclude about the relative solvent quality of these solvents?

*Answer.* From class, intrinsic viscosity obeys the following proportionality.

$$[\eta] \propto M^{3\nu-1}$$

Thus, if the intrinsic viscosity is higher in the water/methanol mixture,  $\nu$  must be higher for this solvent as well. Therefore, water/methanol is a better solvent than water. □