

3 Dilute Solutions

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- 10/21: 1. (35 pts) Estimate, as a function of molecular weight, the characteristic diffusion time τ for a polymer in a solution of viscosity η , where τ 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 τ for polymer coils in a theta-solvent for...

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

Answer. Recall from class that in general,

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

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

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

Therefore,

$$\begin{aligned} \tau &= \frac{(N^{1/2}l_k)^2}{k_B T / N\xi^*} \\ \boxed{\tau = \frac{N^2 l_k^2 \xi^*}{k_B T}} \end{aligned}$$

□

- 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,

$$\begin{aligned} \tau &= \frac{R^2}{k_B T / (6\pi\eta\gamma R / \sqrt{6})} \\ \boxed{\tau = \frac{\sqrt{6}\pi N^{3/2} l_k^3 \eta\gamma}{k_B T}} \end{aligned}$$

□

- 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 τ 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,

$$\langle \Delta r^2 \rangle = 6D\tau$$

$$\tau = \frac{(5\text{ }\mu\text{m})^2}{6(0.01\text{ }\mu\text{m}^2\text{ s}^{-1})}$$

$\tau \approx 417\text{ s}$

□

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

$$F_s = m\omega^2 r \quad (\text{Sedimentation})$$

$$F_b = -m_0\omega^2 r \quad (\text{Buoyancy / Archimedes' Principle})$$

$$F_d = -\zeta U \quad (\text{Drag})$$

where m is the mass of a single polymer, ω 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, ρ is the solvent density, ζ 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

$$\begin{aligned} 0 &= F_s + F_b + F_d \\ &= m\omega^2 r - m_0\omega^2 r - \zeta U \\ &= \frac{M}{N_A} \cdot \omega^2 r - \frac{M}{N_A} \cdot \rho v \omega^2 r - \zeta U \\ U &= \frac{M\omega^2 r}{N_A \zeta} (1 - \rho v) \end{aligned}$$

□

- 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 γ 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 γ 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 η 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 mg/mL and in a water/methanol mixture to be 22.3 mg/mL. 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, ν must be higher for this solvent as well. Therefore, $\boxed{\text{water/methanol is a better solvent than water.}}$

□