3 Dilute Solutions

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Total grade: $\boxed{100/100}$

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,

$$R = N^\nu l_k \qquad\qquad D_t = \frac{k_{\mathrm{B}}T}{f}$$

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

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

Therefore,

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

$$\boxed{\tau = \frac{N^2 l_k^2 \xi^*}{k_{\mathrm{B}}T}}$$

$\square$

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,

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

$$\boxed{\tau = \frac{\sqrt{6}\pi N^{3/2} l_k^3 \eta\gamma}{k_{\mathrm{B}}T}}$$

$\square$

c) You are performing a GPC packed with beads with diameter $5\,\mu m$. Estimate the time for a DNA molecule with $D = 0.01\,\mu m^2/s$ 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 $D = 0.01\,\mu m^2/s$ by $\Delta r = 5\,\mu m$. Per class,

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

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

$$\boxed{\tau \approx 417\,s}$$

$\square$

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

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

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

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

$\square$

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

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

$\square$

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 $44.6\,\mathrm{mL/g}$. The MW of the polymer is $35\,000\,\mathrm{g/mol}$. 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,

   $$\langle R_g^2\rangle^{1/2} = \sqrt[3]{\frac{3M[\eta]}{10\pi N_\mathrm{A}\gamma^3}}$$

   $$= \sqrt[3]{\frac{3(35\,000\,\mathrm{g\,mol^{-1}})(44.6\,\mathrm{mL\,g^{-1}})}{10\pi(6.02\times10^{23}\,\mathrm{mol^{-1}})(1/1.5)^3}}$$

   $$\boxed{\langle R_g^2\rangle^{1/2} \approx 9.4\,\mathrm{nm}}$$

   $\square$

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

   Answer. From class, we have that

   $$c^* = \frac{2.5}{[\eta]}$$

   $$= \frac{2.5}{44.6\,\mathrm{mL\,g^{-1}}}$$

   $$\boxed{c^* \approx 5.6\times10^{-2}\,\mathrm{g/mL}}$$

   $\square$

   c) Assuming the solvent has a viscosity of $1.1\,\mathrm{Pa\,s}$, 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

   $$\eta = \eta_s\left(1 + c\cdot[\eta]\right)$$

   $$= (1.1\,\mathrm{Pa\,s})\left[1 + \frac{1}{2}(0.056\,\mathrm{g\,mL^{-1}})(44.6\,\mathrm{mL\,g^{-1}})\right]$$

   $$\boxed{\eta = 2.5\,\mathrm{Pa\,s}}$$

   $\square$

   d) The authors measured the intrinsic viscosity of the MW $= 10\,000\,\mathrm{g/mol}$ sample in water to be $11.9\,\mathrm{mg/mL}$ and in a water/methanol mixture to be $22.3\,\mathrm{mg/mL}$. 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, water/methanol is a better solvent than water. $\square$