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;

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

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

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 $\omega, r, v, \zeta, \rho, M, N_\text{A}$, where M is the molar mass of the polymer and N_A is Avogadro's number.

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.

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.

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

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

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?