P85 - Vital Statistics

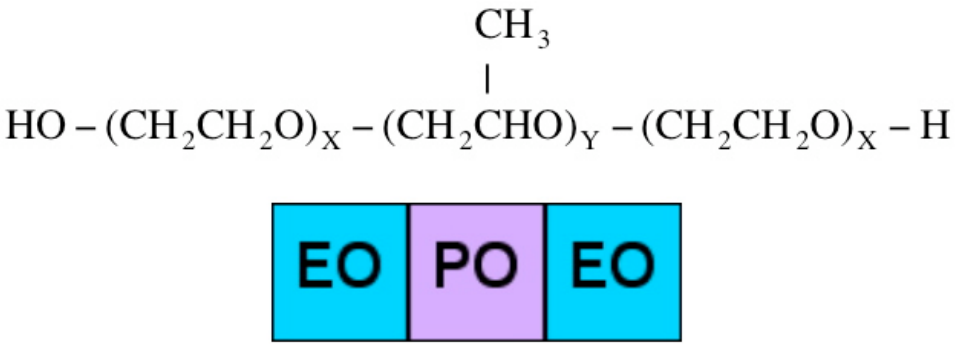

Figure 1: Structure of Pluronic copolymers

Pluronic P85 has an average structure of $EO_{26}PO_{40}EO_{26}$, giving it an overall molecular weight of 4600 g/mol. The polymer is very soluble in water, forming gels at high concentrations (> 20 wt %) and temperatures above room temperature.

The objectives of the experiment are to:

- **Determine the dimensions of the free polymer chain in solution.** Is the polymer chain in a Gaussian coil conformation, as it would be in a good solvent? This will be measured at low temperatures, where water is still a good solvent for both EO and PO blocks.

- **Determine the Critical Micelle Temperature.** At temperatures greater than room temperature, P85 molecules aggregate, as water becomes a poor solvent for the PO block. The transition temperature can be found by several methods.

- **Determine the size and shape of the micellar aggregates as a function of temperature.** This will be done by identifying trends in the q-dependence of the scattering and model fitting to a variety of structures.

From density measurements of Pluronic polymers in solution the molecular volume of each of the blocks can be calculated, and are found to be V_o = 69.5 Å^3 and V_o = 82.4 Å^3 for the EO and PO blocks, respectively.

Table 1. The scattering length densities (SLD's) for the average Pluronic, its component blocks, and water.

Material	Chemical Formula	Mass Density (g/ml)	SLD (Å^{-2})
Average P85	$EO_{26}PO_{40}EO_{26}$	1.106	0.50 x 10^{-6}
EO	CH_2CH_2O	(see V_o above)	0.59 x 10^{-6}
PO	$CH(CH_3)CH_2O$	(see V_o above)	0.40 x 10^{-6}
Light water	H_2O	1.00	-0.56 x 10^{-6}
Heavy water	D_2O	1.105	6.36 x 10^{-6}

The radius of gyration of a Gaussian polymer chain made of N monomer units is:

$$R_g^2 = \frac{N\ell^2}{6}$$

with the statistical segment length, l. The statistical segment length is the length for which the polymer chain follows a random walk. Typical values for l are 3.6 Å to 5 Å, depending on the chemical nature of the polymer. Using an estimated value of l = 4 Å, R_g ~ 16 Å.

5. Data Analysis

5.1 Guinier Approximation

The scattering from dilute objects, at small enough q-values, can be approximated by a simple exponential decay:

$$I(q) \approx I(0)\exp\left(-\frac{1}{3}q^2R_g^2\right)$$

So a plot of ln[I(q)] vs. q^2 will be linear, and the slope will be negative, and proportional to the radius of gyration of the object. This type of plot is called a

Guinier plot, and works for any shape object. It is valid in a q-range of approximately $qR_g \leq 1$.

To Do: Fit the data from a dilute solution to the Guinier approximation (1 % or 2 % by weight P85 in D_2O). Determine the R_g of the polymer in solution, and the R_g of the aggregate at a function of temperature. How does the R_g of the micelle change with temperature?

5.2 Gaussian chains in solution

The polymer chains in solution should behave like Gaussian coils, and their scattering should be well-described by a Debye function:

$$I(q) = \phi(\Delta\rho)^2 Z v_m \frac{2(e^{-x} + x - 1)}{x^2}$$

Z is the degree of polymerization, v_m is the specific volume of the monomer, and $x = (qR_g)^2$.

To Do: Fit the pre-micellar data (at low temperatures) with both the Debye function and a Guinier fit. Compare the results to our rough estimate of the polymer size. If there are differences, what could be the reasons? Does the fitted value of the scale factor make any sense?

5.3 Core – Shell Micelles

For a more detailed analysis of the scattering, we need to postulate a structure for the aggregate. The structure of the P85 micelles is expected to be like Figure 5, where the insoluble PPO blocks cluster together and are surrounded by a shell of the soluble PEO chains, much like a polymer brush. From a distance, the aggregate is simply a sphere. Closer up, it is a spherical core, with a shell on the surface. We will consider our solution to contain some concentration of these micellar structures, with a "dry" core that contains only polymer, and a shell that contains extended chains and some quantity of solvent.

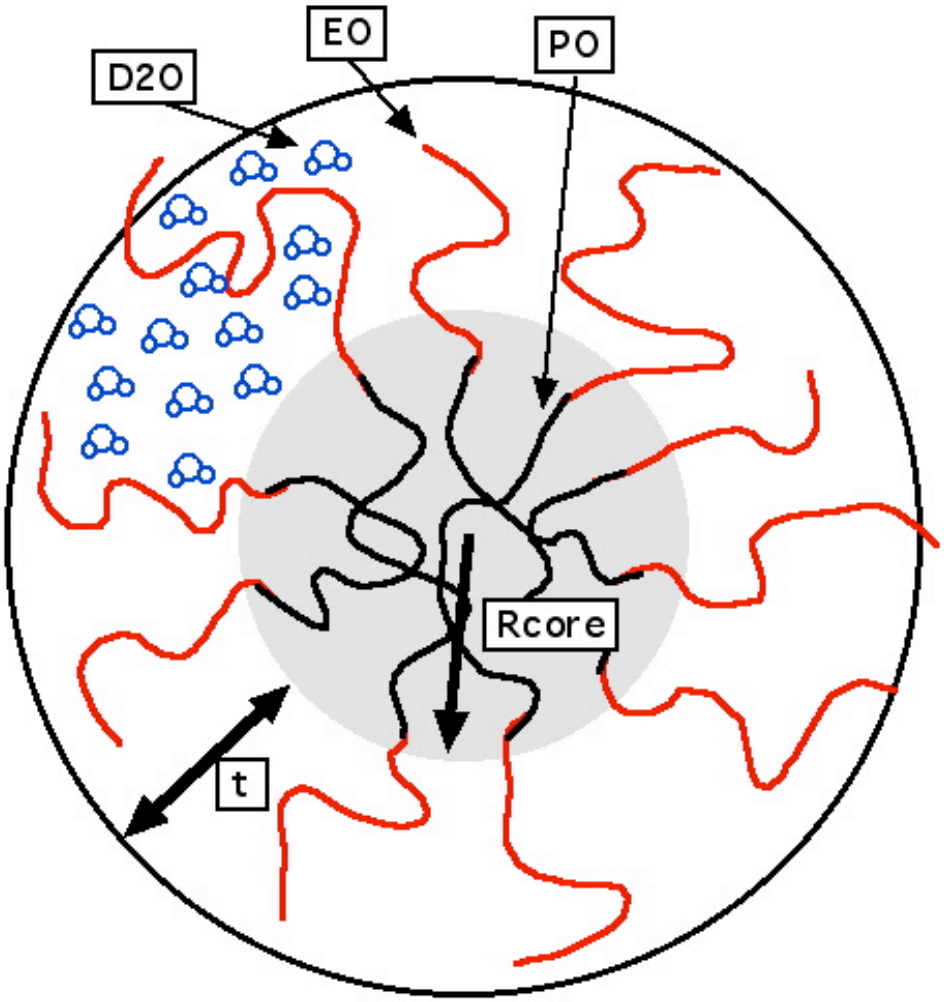

Figure 5: Schematic structure of a P85 micelle. The insoluble PPO blocks are expected to be in the core, surrounded by extended PEO chains that remain soluble in water.

The scattered intensity from a collection of monodisperse particles can be written as:

$$I(q) = n_p P(q) S(q)$$

where n_p is the number density of particles, P(q) is the form factor, and S(q) is the structure factor. We will assume that the solutions are dilute "enough" that the micelles do not interact, and S(q) = 1.

For the case of a core-shell sphere, the form factor can be expressed analytically:

$$P(q) = \left[\frac{3V_c(\rho_c - \rho_s)\, j_1(qR_c)}{qR_c} + \frac{3V_s(\rho_s - \rho_{solv})\, j_1(qR_s)}{qR_s} \right]^2$$

where R_c is the core radius, R_s is the outer radius of the shell (the total radius of the sphere), $j_1(x) = (\sin x - x\cos x)/x^2$, and $V_i = (4\pi/3)R_i^3$.

To Do: Fit the scattered intensity from 2 % P85 to a model of core-shell spheres. If the fit is not good at some temperatures, what part of the physical structure of the micelles has not been incorporated in the model? How would the model compare to the data if there were no interparticle interactions? If the fit is good, what do the parameters mean? Do they make any physical sense? How could the model be improved?