Chapter 44 - **SANS FROM A PLURONIC**

1. WHAT ARE PLURONICS?

Poly(ethylene oxide) (referred to as PEO) is the simplest water soluble polymer. Its structure –CH_2CH_2O- consists of a hydrophobic ethylene –CH_2CH_2– group and a hydrophilic –O– oxygen. Its neighbors in the homologous series poly(methylene oxide) (or PMO) and poly(propylene oxide) (or PPO) do not dissolve in water at ambient temperature. This behavior can be traced to the just-right balance between hydrophobic and hydrophilic interactions in PEO. For instance, the oxygen-oxygen inter-distance of 4.7 Å in PEO corresponds to the oxygen-oxygen next-nearest neighbor inter-distance in the structure of pure water.

Pluronics are triblock copolymers composed of one PPO block connected to two PEO blocks. The PEO blocks dissolve well in aqueous media because they are mostly hydrophilic while the PPO block does not dissolve because it is mostly hydrophobic at ambient temperature. This amphiphilic nature of Pluronics molecules makes them form micelles at ambient temperature. At low temperatures, this balance does not hold and both PEO and PPO blocks dissolve in water thereby inhibiting micelle formation. The Critical Micelle formation Temperature (CMT) is a temperature at which micelles form. The CMC is the Critical Micelle formation Concentration. CMT and CMC vary depending on the block composition of the various Pluronics.

Pluronics are commercially available materials used in the cosmetics and pharmaceutical industries. The P85 Pluronic considered here consists of 26 EO monomers in each of the outside blocks and 40 PO monomers in the middle block. P85 is referred to as $EO_{26}PO_{40}EO_{26}$. The molecular weight of P85 is around 4,600 g/mol (Slawecki et al, 1998).

2. SANS FROM P85 PLURONIC

SANS data were taken from 10 % P85 in d-water at various temperatures (from 20 ^{o}C to 60 ^{o}C). Two instrument configurations (one low-Q and one high-Q) were used. Micelles are well formed by 30 ^{o}C. When micelles are formed, the scattering is characterized by two features: a peak characteristic of inter-micelles interactions, and decay at high Q characterizing the tail of the single-particle form factor. In-between these two features, the hint of a second peak (shoulder around Q = 0.15 $Å^{-1}$) can be observed. This shoulder is also characteristic of the single particle form factor (oscillation of the spherical Bessel function) and is affected by polydispersity effects.

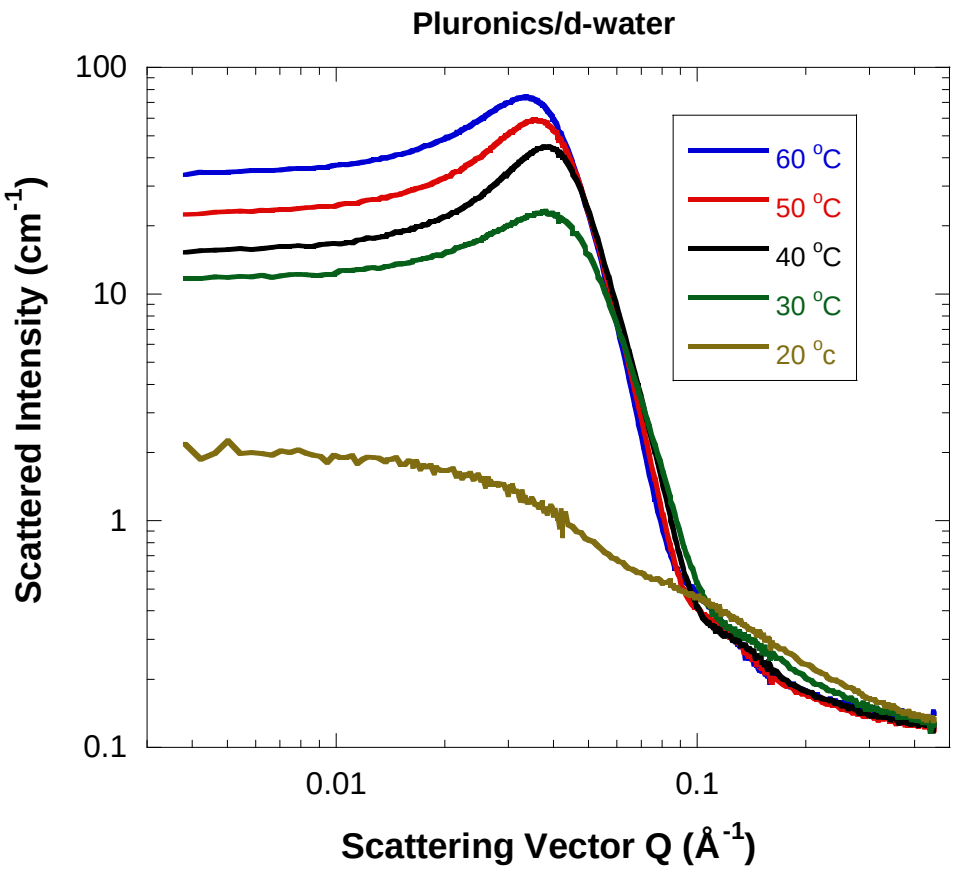

Figure 1: SANS data from the 10 % P85 in D_2O at various temperatures. Data statistics are different for the two instrument configurations. The overlap region for the two configurations is between 0.03 $Å^{-1}$ and 0.04 $Å^{-1}$.

3. THE CORE-SHELL PARTICLE MODEL

The P85 Pluronic forms micelles above the CMT and CMC. The simple core-shell model is used to analyze the SANS data from P85 in d-water (Kline-Hammouda, 2004). This model is reviewed here. Consider three regions: a core (region A) of radius R_A, a shell (region B) of thickness R_B-R_A and the solvent (region C).

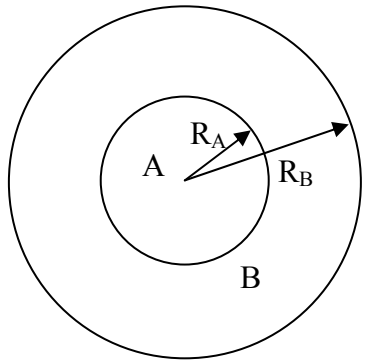

Figure 2: Schematic representation of the P85 micelle as a core-shell particle.

The following parameters are defined:

N: number of core-shell particles in the solution.
ρ_A: scattering length density for region A.
ρ_B: scattering length density for region B.
ρ_C: scattering length density for region C.
v_A: specific volume in region A (= density/molar mass).
v_B: specific volume in region B (= density/molar mass).
V_A: volume of region A. $V_A = (4\pi/3)R_A^3$.
V_{A+B}: volume of regions A and B. $V_{A+B} = (4\pi/3)R_B^3$.
V: total volume of the solution.

At first, assume that the particles do not interact, i.e., consider the infinite dilution case.

Assuming uniform densities in the core and shell regions, the macroscopic scattering cross section is given as the particle number density multiplied by the square of the single-particle form factor.

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ID} = \frac{N}{V}\left[(\rho_A-\rho_C)V_A\frac{3j_1(QR_A)}{QR_A}+(\rho_B-\rho_C)\left(V_{A+B}\frac{3j_1(QR_B)}{QR_B}-V_A\frac{3j_1(QR_A)}{QR_A}\right)\right]^2 \tag{1}$$

The VD subscript stands for infinite dilution. The first part is for the core contribution (integration between 0 and R_A) with the right scattering length density difference and the second part is for the shell contribution (integration between R_A and R_B). The single-particle form factor for a sphere (of radius R_A) is expressed in terms of the familiar spherical Bessel function

$$j_1(QR_A) = \left(\frac{\sin(QR_A)}{(QR_A)^2} - \frac{\cos(QR_A)}{QR_A}\right). \tag{2}$$

Another form for the same cross section is:

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ID} = \frac{N}{V}\left[(\rho_A - \rho_B)V_A \frac{3j_1(QR_A)}{QR_A} + (\rho_B - \rho_C)V_{A+B}\left(\frac{3j_1(QR_B)}{QR_B}\right)\right]^2 . \tag{3}$$

These forms reproduce the limit of the scattering cross section for uniform density spheres (of radius R_A) by assuming either $\rho_B = \rho_C$ or $R_B = R_A$.

4. CONCENTRATION EFFECTS

When the particle concentration is finite (i.e., non zero), the scattering cross section contains contributions from the inter-particle structure factor $S_I(Q)$. The simplest analytical form for expressing $S_I(Q)$ is through the Percus-Yevick approximation for spheres interacting through a hard sphere potential. The Percus-Yevick approximation was introduced as a "closure" relation to the Ornstein-Zernike equation. Within the Percus-Yevick approximation, $S_I(Q)$ for a finite concentration of spheres (of diameter D) is expressed as:

$$S_I(Q) = \frac{1}{1 - \overline{N}C(Q)} . \tag{4}$$

$\overline{N}C(Q)$ is the Fourier transform of the direct correlation function given by:

$$\overline{N}C(Q) = -24\phi\left\{\lambda_1\left[\frac{\sin(QD) - (QD)\cos(QD)}{(QD)^3}\right] - 6\phi\lambda_2\left[\frac{(QD)^2\cos(QD) - 2(QD)\sin(QD) - 2\cos(QD) + 2}{(QD)^4}\right]\right.$$

$$\left. - \phi\frac{\lambda_2}{2}\left[\frac{(QD)^4\cos(QD) - 4(QD)^3\sin(QD) - 12(QD)^2\cos(QD) + 24(QD)\sin(QD) + 24\cos(QD) - 24}{(QD)^6}\right]\right\} \tag{5}$$

The parameters λ_1 and λ_2 are given by:

$$\lambda_1 = \frac{(1+2\phi)^2}{(1-\phi)^4} \tag{6}$$

$$\lambda_2 = \frac{-(1+\phi/2)^2}{(1-\phi)^4} .$$

ϕ is the packing fraction which can be expressed in terms of the particle number density (N/V) and particle radius R (R = D/2) and is defined as $\phi = \left(\frac{N}{V}\right)\left(\frac{4\pi}{3}R^3\right)$. Note that in the core-shell particle model $R = R_B$.

The scattering cross section for a concentrated solution of hard spheres is obtained by multiplying the infinite dilution result by $S_I(Q)$:

$$\frac{d\Sigma(Q)}{d\Omega} = \left[\frac{d\Sigma(Q)}{d\Omega}\right]_{ID} S_I(Q). \qquad (7)$$

The single-particle form factor and the inter-particle structure factor are the main pieces of the scattering cross section for the P85 micelles.

5. FIT RESULTS

Fits of the P85 SANS data were performed using the non-dilute solution of core-shell particles. Results for the 10 % P85 in D_2O are presented here for the 40 ^oC temperature case where the micelles are well formed.

Packing volume fraction $\phi = 0.248$ (8)
Core radius $R_A = 43.96$ Å.
Polydispersity parameter $\sigma_A/R_A = 0.16$
Shell outer radius $R_B = 72.91$ Å.
$\rho_A = 7.563*10^{-7}$ Å^{-2}
$\rho_B = 5.940*10^{-6}$ Å^{-2}
$\rho_C = 6.40*10^{-6}$ Fixed.

These fit results are used to obtain detailed information about the P85 micelles using the material balance equations.

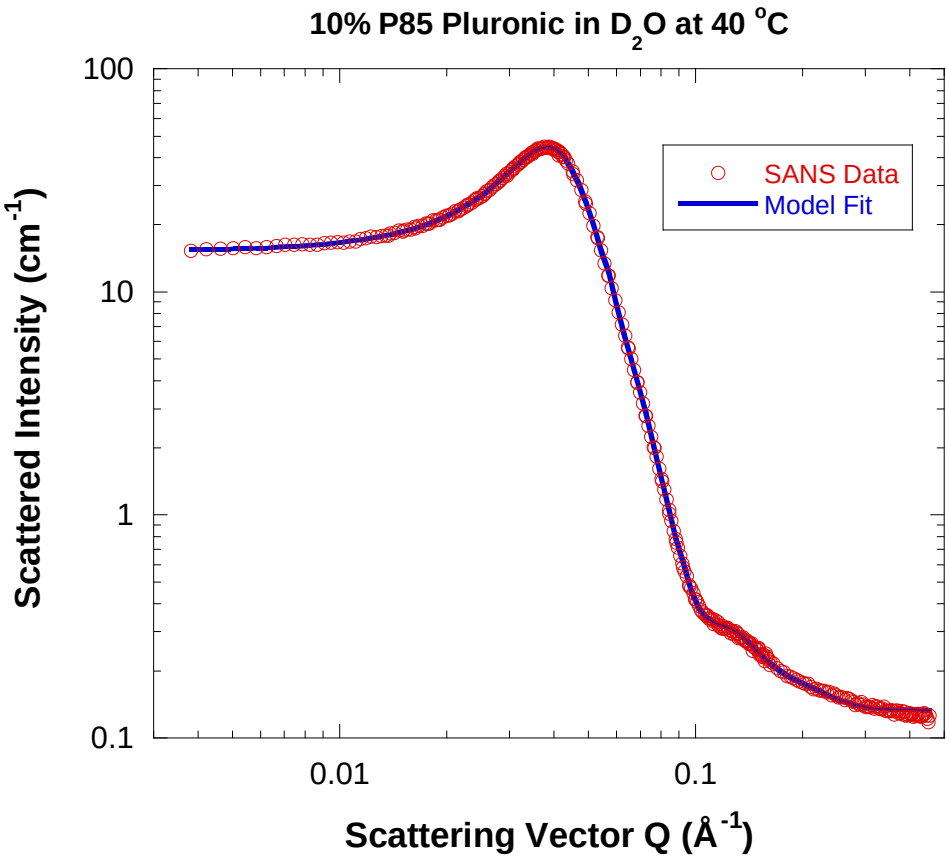

Figure 3: SANS data and model fit for the 10 % P85 in D_2O sample at 40 ^oC. The two curves are indistinguishable.

6. MATERIAL BALANCE EQUATIONS

Consider a model whereby the micelle core contains PO blocks and a fraction f of the EO blocks and the shell contains the remaining fraction (1-f) of the EO blocks. Moreover assume that D_2O exists in the core and in the shell to hydrate the EO blocks. Assume that there are y_A D_2O molecules per EO monomer in the core (region A) and y_B D_2O molecules per EO monomer in the shell (region B). Define N_{agg} as the aggregation number, i.e., the number of P85 molecules per micelle and recall that there are 40 PO monomers per block and 26*2 = 52 EO monomers per macromolecule.

The material balance equations are:

$$(1)\ \frac{4\pi}{3} R_A^3 = N_{ag}.[40.v_{PO} + 52.f.v_{EO} + 52.f.v_{D2O}.y_A] \qquad (9)$$

$$(2)\ \frac{4\pi}{3}(R_B^3 - R_A^3) = N_{ag}.[52.(1-f).v_{EO} + 52.(1-f).v_{D2O}.y_B]$$

$$(3)\quad \rho_A = \frac{N_{ag}[40b_{PO} + 52.b_{EO}.f + 52b_{D2O}.f.y_A]}{\frac{4\pi}{3}R_A{}^3}$$

$$(4)\quad \rho_B = \frac{N_{ag}[52.b_{EO}.(1-f) + 52.b_{D2O}.(1-f).y_B]}{\frac{4\pi}{3}\left(R_B{}^3 - R_A{}^3)\right)} \quad .$$

Specific volumes and scattering length densities have been defined for EO, PO and D_2O.

These four linear equations can be solved to obtain:

$$y_B = \frac{b_{EO} - v_{EO}\rho_B}{-b_{D2O} + v_{D2O}\rho_B} \qquad (10)$$

$$y_A = \frac{A + Bf}{f}$$

where:

$$A = \frac{[52v_{EO} + 52y_B v_{D2O}]\frac{R_A{}^3}{R_B{}^3 - R_A{}^3} - 40v_{PO}}{52v_{D2O}} \qquad (11)$$

$$B = \frac{[-v_{EO} - y_B v_{D2O}]\frac{R_A{}^3}{R_B{}^3 - R_A{}^3} - v_{EO}}{v_{D2O}}$$

$$f = \frac{E - C}{D - F}$$

And:

$$C = [40v_{PO} + 52.A.v_{D2O}]\rho_A \qquad (12)$$
$$D = [52v_{EO} + 52.B.v_{D2O}]\rho_A$$
$$E = [40b_{PO} + 52.A.b_{D2O}]$$
$$F = [52b_{EO} + 51.B.b_{D2O}]$$

The last parameter is given by:

$$N_{ag} = \frac{\frac{4\pi}{3}R_A{}^3}{40v_{PO} + 52v_{EO}.f + 52v_{D2O}.f.y_A} \; .$$

We have transformed the four fitting parameters R_A, R_B, ρ_A and ρ_B into four meaningful parameters N_{ag}, f, y_A and y_B. This set of solutions is unique.

7. RESULTS FOR THE 10 % P85 IN D_2O AT 40 ^oC

The following results are obtained for the 10 % P85 in D_2O at 40 ^oC.

Table 1: Scattering lengths and specific volumes for PO, EO and D_2O.

	Density g/cm^3		m_w g/mol	Molar volume cm^3/mol	Scattering Lengths cm	Scattering Length Densities (Å^{-2})
PO	1.004	C_3H_6O	58	$v_{PO} = 57.77$	$b_{PO} = 3.307*10^{-13}$	$\rho_{PO} = 3.44*10^{-7}$
EO	1.127	C_2H_4O	44	$v_{EO} = 39.04$	$b_{EO} = 4.139*10^{-13}$	$\rho_{EO} = 6.38*10^{-7}$
D_2O	1.11	D_2O	20	$v_{D2O} = 18.02$	$b_{D2O} = 19.145*10^{-13}$	$\rho_{D2O} = 6.39*10^{-6}$

Using the table of scattering lengths and specific volumes for the various components, and taking care of expressing everything consistently in units of Å or cm, the following results are obtained.

f = 0.53 (53 % of the EO monomers are in the core).
$y_A = 0.39$ (there is less than one D_2O molecule per EO monomer in the core).
$y_B = 26.44$ (there are 26.44 D_2O molecules per EO monomer in the shell).
$N_{agg} = 59.80$ (there are 59.80 P85 molecules per micelle).

The finding that 53 % of the EO monomers can be found in the micelle core is surprising. Not much D_2O makes it to the core region as expected even with the presence of a fraction of the EO monomers. The micellar shell region is swollen by quite a bit of D_2O as expected. Note that in this simple model we have assumed that the various specific volumes are constant with temperature.

The micelles number density $\left(\frac{N}{V}\right)$ (i.e., number of micelles per cm^3) can be obtained from the packing volume fraction ϕ as:

$$\left(\frac{N}{V}\right) = \frac{\phi}{\left(\frac{4\pi}{3} R_B^{\,3}\right)}. \qquad (13)$$

The estimated P85 volume fraction can be obtained as:

$$\phi_{P85} = \left(\frac{N}{V}\right) N_{agg}.(40.v_{PO}+52.v_{EO}). \qquad (14)$$

In the case considered here, one obtains $\left(\frac{N}{V}\right) = 1.53*10^{17}$ cm^{-3} and $\phi_{P85} = 0.066$ which is lower than the real mixing fraction $\phi_{Mix} = 0.1$.

With a rather simple (core-shell) model, one can obtain quite a bit of information from the SANS data. The purpose of this exercise is not to prove that the core-shell model used is correct, but to show an example of the mass balance equations that relate the fitted parameters to more meaningful properties.

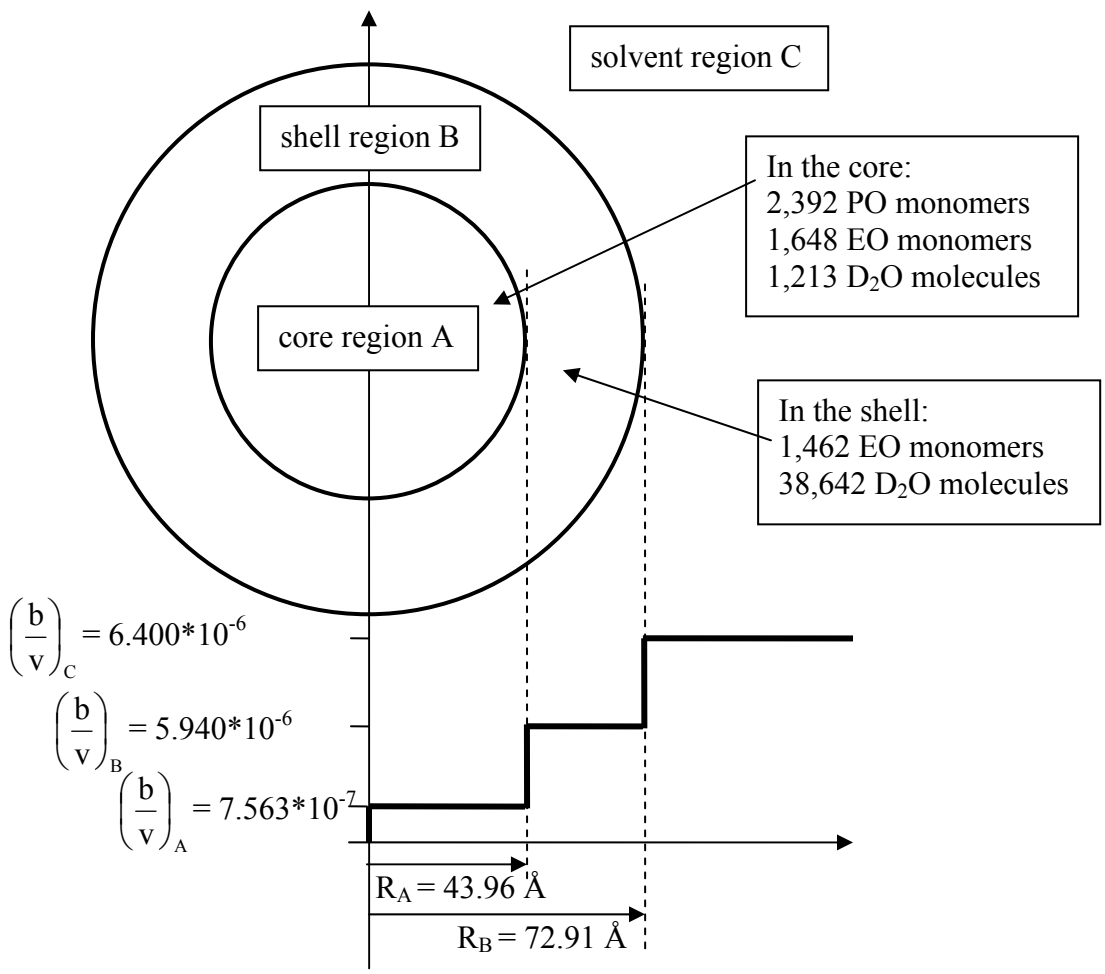

Figure 4: Schematic representation of a micelle with sizes, scattering length densities and contents.

8. POLYDISPERSITY EFFECTS

The polydispersity parameter obtained from the fit to the SANS data for the 10 % P85 sample at 40 ^{o}C was $\sigma_A/R_A = 0.16$, where σ_A is the standard deviation of the core radius size distribution. This distribution was assumed to correspond to the Schulz distribution.

$$f(R) = (z+1)^{z+1}\left(\frac{R}{R_A}\right)^{z}\frac{\exp\left[-(z+1)\frac{R}{R_A}\right]}{R_A\Gamma(z+1)}. \qquad (15)$$

R_A is the average value for the peaked distribution and the standard deviation σ_A is related to z as:

$$\frac{\sigma_A}{R_A} = \frac{1}{\sqrt{(z+1)}}. \qquad (16)$$

The integration over the Schulz distribution is performed over the macroscopic cross section for the core-shell particle model.

$$\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{polydisperse} = \int_0^{\infty} dR\, f(R)\left[\frac{d\Sigma(Q)}{d\Omega}\right]_{monodisperse}. \qquad (17)$$

This integration can be performed numerically and is available analytically. Due to the lengthy expression, the analytical form is not reproduced here.

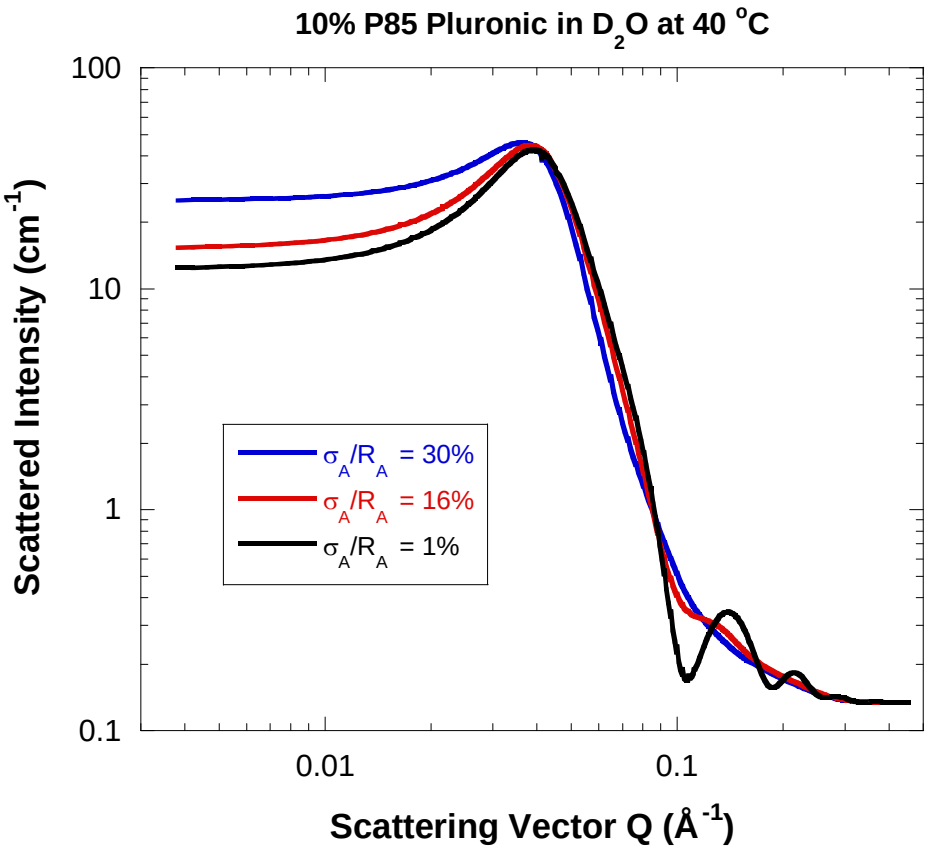

Figure 5: Simulated data corresponding to parameters for the 10 % P85 sample at 40 °C. The polydispersity parameter has been varied to see its effect. All other parameters were kept the same. The effect of polydispersity is seen to broaden peaked features.

Note that the particle core volume averaged over the polydisperse size distribution is given by:

$$V_A = \frac{4\pi}{3}\langle R^3 \rangle = \frac{4\pi}{3} R_A{}^3 \frac{(z+2)(z+3)}{(z+1)^2}$$

In practice the average volume ($4\pi R_A{}^3/3$) is often used for low polydispersity.

9. TEMPERATURE EFFECTS

SANS data were taken from the 10 % P85 in D_2O at various temperatures going from the partly dissolved copolymer phase at 20 °C to the fully formed micelles at temperatures of 30°C and above. The above described model was applied to the SANS data for 40 °C, 45 °C, 50 °C, 55 °C, and 60 °C. For simplicity, the specific molar volumes were assumed to be independent of temperature. The results are presented in a series of figures.

When temperature is increased both R_A and R_B increase while the micelle packing volume fraction decreases. This is due to the fact that the aggregation number increases because the driving force for micelle formation gets stronger. As this happens, D_2O gets squeezed out of the shell region. As temperature increases, the micelles packing volume fraction decreases because there are fewer larger micelles.

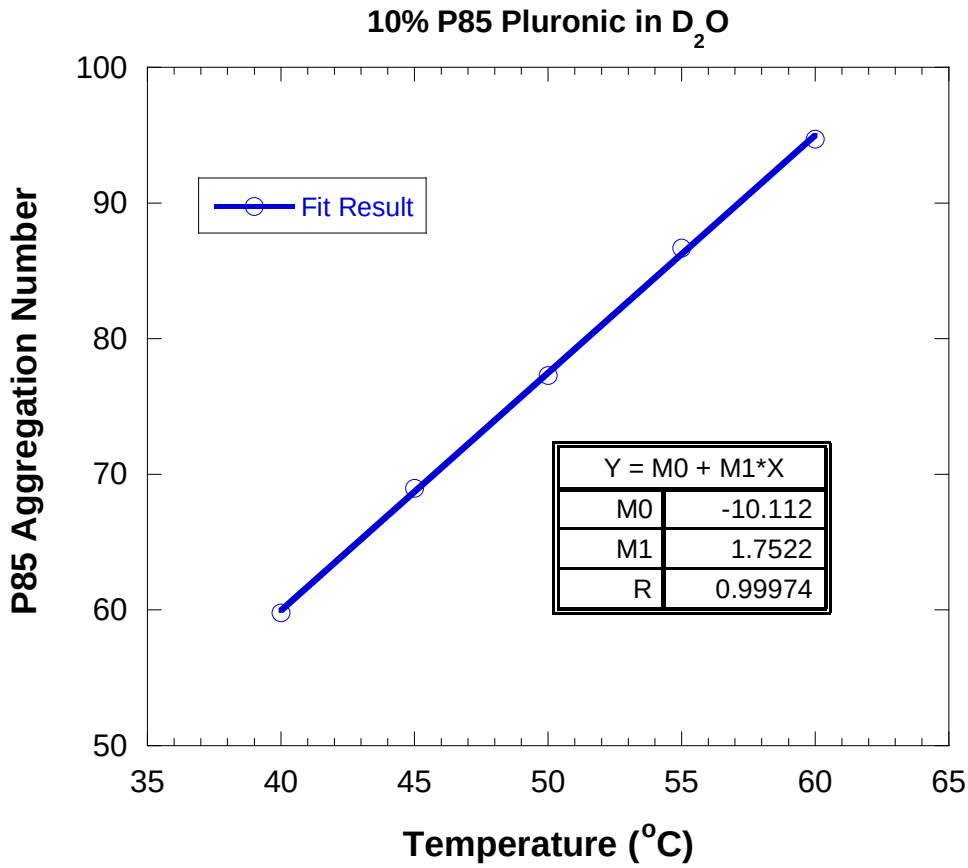

Figure 6: Variation of the aggregation number with temperature.

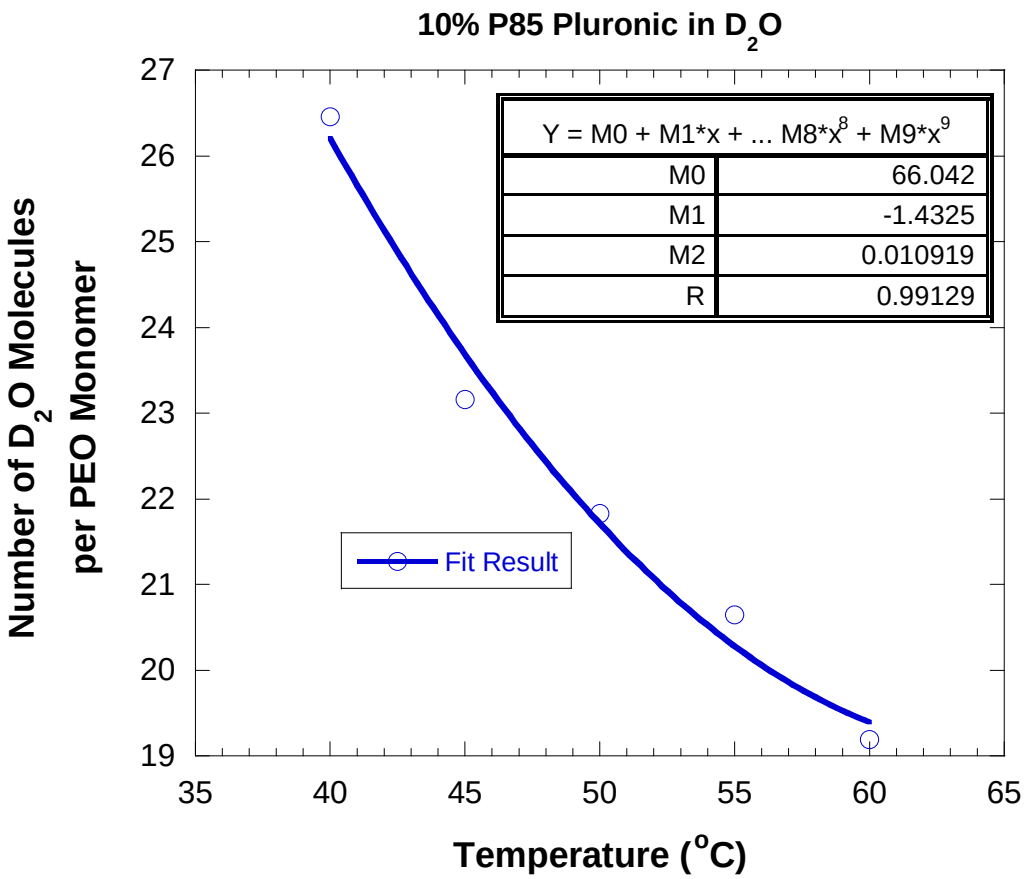

Figure 7: Variation of the number of D_2O molecules per EO monomer in the shell region with increasing temperature.

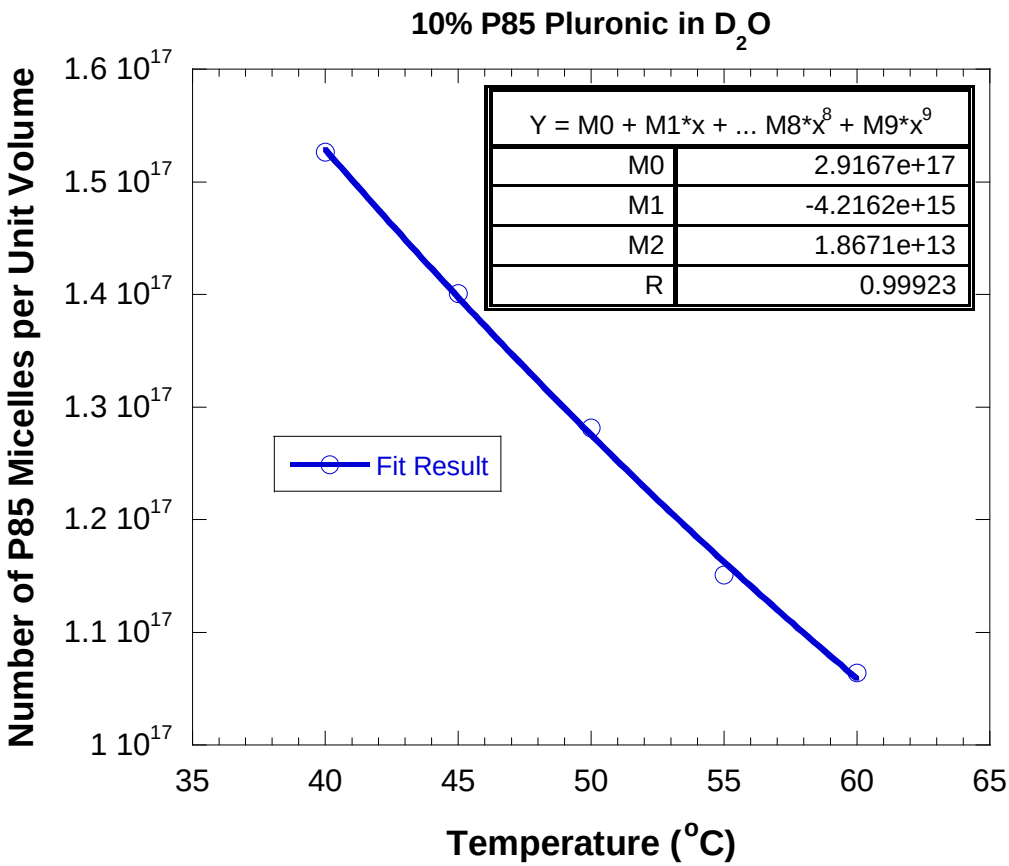

Figure 8: Variation of the micelles number density with temperature.

10. DISCUSSION

P85 is a typical nonionic micellar system comprising hydrophilic EO blocks and hydrophobic PO blocks. SANS data from P85 micelles were fitted to a core-shell model in order to obtain core sizes and shell thicknesses, scattering length densities of these two regions, fitted volume fractions and core polydispersity characteristics. Using a materials balance equation, useful information such as the fraction of EO blocks in the core, the aggregation number, and the number of D_2O molecules per EO monomer in the two regions. The purpose of this last exercise was not to prove the correctness of the core-shell model but to show how useful material balance equations could be.

REFERENCES

T. Slawecki, C. Glinka and B. Hammouda, "Shear-Induced Micellar Crystal Structures in an Aqueous Triblock Copolymer Solution", Phys Rev E 58, R4084-4086 (1998).

S. Kline and B. Hammouda "Free Chains and Micelles of a Triblock Copolymer in Water", NCNR Summer School (2004).

QUESTIONS

1. Do Pluronics form ionic or nonionic micelles?
2. What is the CMC? How about the CMT?
3. Are micelles always spherical?
4. What is the Percus-Yevick approximation?

ANSWERS

1. Pluronics are not charged. They form nonionic micelles.
2. The CMC is the Critical Micelles (formation) Concentration. The CMT is the Critical Micelles (formation) Temperature. These are conditions at which micelles form.
3. No, micelles are not necessarily spherical. Micelles come in many shapes including elongated wormlike micelles.
4. The Percus-Yevick approximation is a closure relation that allows the analytical solution of the Ornstein-Zernike equation for hard sphere interaction potential.