

**Polymer Physics**  
**HW 8**  
**March 4, 2022 (Due March 8)**

Marina Tsianou at the University of Buffalo has studied polymer/micelle hybrid structures for a number of years. This year she published Kancharla S, Bedrov D, Tsianou M, Alexandrisdis P *Structure and composition of mixed micelles formed by nonionic block copolymers and ionic surfactants in water determined by small-angle neutron scattering with contrast variation* J. Coll. Inf. Sci. **609** 456-68 (2022). The paper investigates the structural self-assembly of a ternary system composed of aqueous colloidal suspensions of sodium dodecylsulfate (SDS) (also called sodium lauryl sulfate) and pluronic (or poloxamer) (PEO-PPO-PEO). The study is well summarized in the graphical abstract (top figure below) which shows PPO (red) chains embedded in the hydrophobic core of the SDS micelle with some water, and dangling hairy PEO chains.

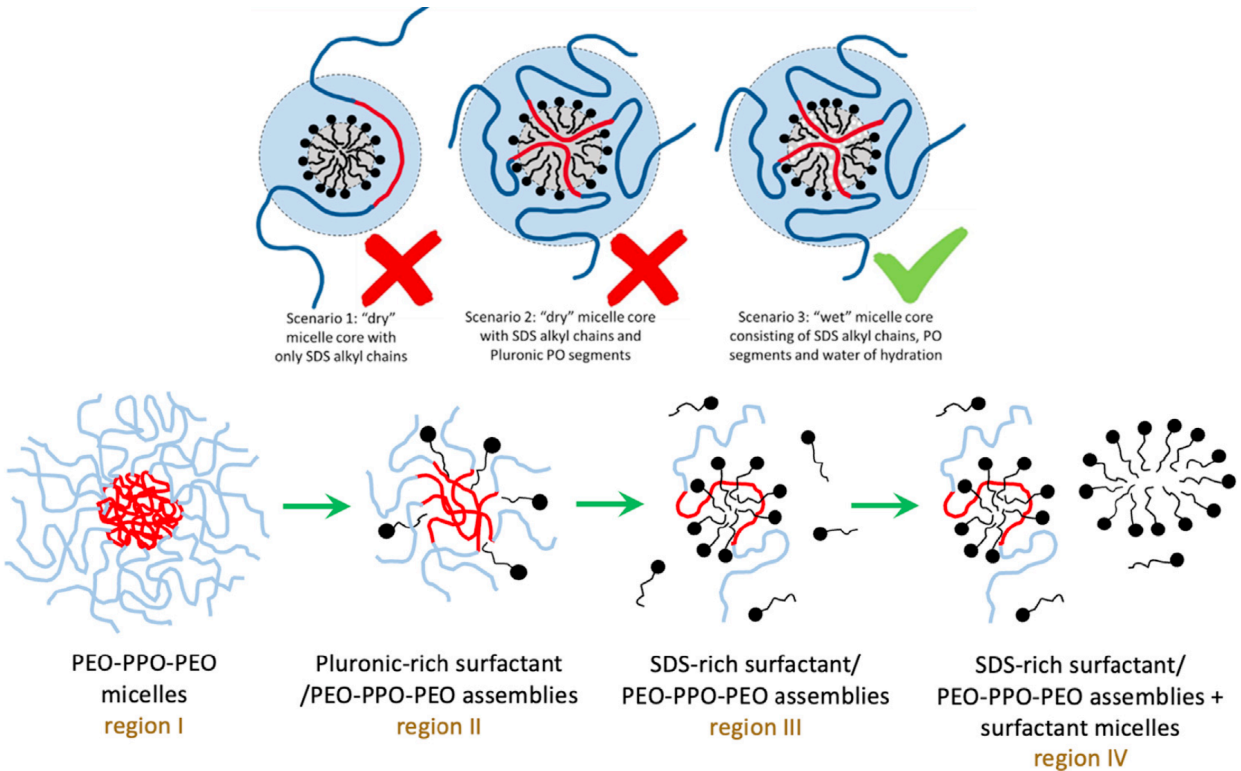
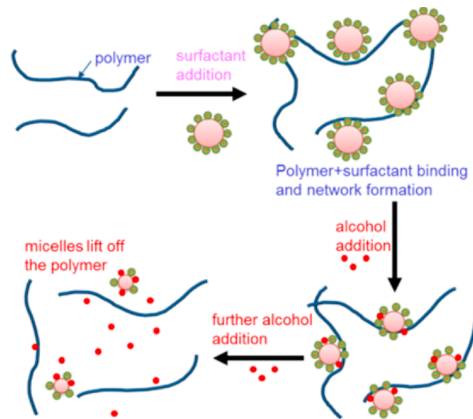


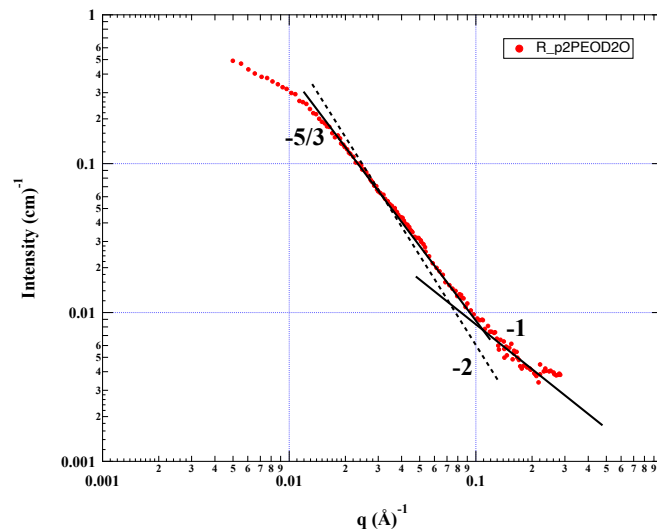
Figure 1 (bottom figure above) shows the impact of increasing SDS concentration on the self-assembled structure. A surfactant added to water at low concentrations has an equilibrium between surfactant at the air water interface and free surfactant molecules. More surfactant goes into water at higher temperature. At the critical micelle concentration (CMC) of about 0.2 wt% (0.008 mole/L) there are sufficient surfactant molecules in solution that some meet each other and form micelles. At this point there is a ternary equilibrium between surface molecules, free surfactant molecules and micellar surfactant molecules. The addition of oil or dirt shifts this equilibria since oil or dirt goes to the center of the micelles. For the addition of pluronics the PPO block acts as oil but has some water compatibility so it goes to the core but carries some water with it. Kancharla performed neutron scattering (SANS) on these ternary systems to study this structural emergence. The data was fit with equation (1) which contains three terms. The

summation of three terms indicates that the three components are independent of each other, as if you had three layers of material in separate containers in the neutron beam that do not interact with each other, first polymer chains, then micelles, then a flat background. Such a model wouldn't be appropriate if the components interacted since this would give rise to correlations between the structures which would lead to additional and modified scattering signals.

- a) Equation (2) has a familiar form where  $m$  is set to 2 by Kancharla and  $n$  has an arbitrary value between 1 and 3 for mass fractal “clusters” of “elusive origin”. The values used for  $n$  are not given. Explain the problems with the Ornstein-Zernike scattering function called the Lorentzian function by Kancharla. Kancharla indicates that this function “characterizes polymer-solvent interactions” and that  $\xi$  describes “the average distance between two polymer chains”. Critique this function. Is it appropriate to consider the first and second terms in equation (2) as being independent? Is  $m = 2$  appropriate for PEO-PPO-PEO block copolymer chains in water (PEO is soluble in water and PPO isn't)? Does  $\xi$  describe the distance between chains? Can the distance between chains be observed in the semi-dilute regime as indicated by Kancharla? Extrapolate the second term to low- $q$  and to high- $q$  to get an expression for  $R_g$  and for the power-law prefactor for the -2 power-law regime for this function as was done in the ppt slides for class.
- b) The scattering patterns in figures 2 and 3 display peaks that are associated with two distinct structural features, equation (3). First, the micelles are rather perfect structures so their form factor ( $P(q)$ ) contains peaks associated with the perfect distances in the structure where there is a discrete change in neutron contrast, such as the diameter of a sphere. Secondly, the micelles are charged so they repel each other leading to an organization of the micelles as reflected by the structure factor  $S(q)$ , with a repeat distance for this organization. These perfect distances of correlation also give rise to peaks. The summation in equation (1) indicates that the first two terms are independent of each other. Is equation (1) consistent with Figure 1, region III? (For instance, would the organization of the micelles impact the organization of the Pluronic chains?)
- c) For  $S(q)$  in equation (3) Kancharla refers to Fajalia AI, Tsianou M *Charging and Uncharging a Neutral Polymer in Solution: A Small-Angle Neutron Scattering Investigation* J. Phys. Chem. B **118** 10725-39 (2014) which deals with the interaction between SDS and PEO homopolymers in water/2-propanol mixtures where propanol modifies the micellar structure and interferes with the interaction between PEO and the micelles, as shown in the graphical abstract below. In this paper three scattering function are used. Equation (1) is the same as equation (2) in the 2022 paper. On page 10727 second column, Fajalia indicates that  $\xi = R_g/\sqrt{2}$ . Derive this expression.



- d) The second term for Fajalia's equation (2) is the Debye scattering function for a Gaussian polymer chain. Is this appropriate for PEO in water? What are the assumptions involved in the derivation of the Debye scattering function for polymers? The plot below is digitized data from 0.2 percent PEO in D2O from Figure 2 in Fajalia (2014). The dashed line is a Gaussian -2 slope. Explain the two scaling laws (power-laws) that are observed in the data. Are these consistent with the Debye polymer function?



- e) The third function used by Fajalia is equation (3). The second term is intended to describe a polyelectrolyte in water and involves the Debye screening length, the Bjerrum length, a contrast factor, an excluded volume term  $h$ , and a charge spacing term  $\alpha$ . Ignoring the details, consider the high- $q$  and low- $q$  limits of this function. What power-law is expected at high- $q$  and would this power-law be appropriate for a polyelectrolyte of almost rigid-rod structure? Is it possible to obtain Guinier's Law from this function at low- $q$ ? (These two features are essential for any function that hopes to be valid no matter how complicated the function or the number of terms (here 8 terms for just the second expression of equation (3)).)