Nanoparticle Surface Modification: Displacer Action of PEO

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ABSTRACT

From paints, to lubricants, to every industrial process imaginable, the stability of a dispersion and its interactions at the polymer-particle interface is critical to its function. Displacers are additives that interfere with these interactions, causing desorption of particle from polymer, and resulting in a destabilized dispersion. Displacer data can then be used to study environmental effects on molecular affinity. In the following study, we have observed the displacer action of PEO homopolymer on Pluronic P105, a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer, in the presence of silica nanoparticles. Our findings suggest that PEO is a weak displacer in the presence of P105. We conclude PEO that promotes a homogenous surface coating on the particles—containing both P105 micelles and PEO chains.

INTRODUCTION AND BACKGROUND

$$\Delta G = \Delta H - T\Delta S$$

The Alexandridis group studies molecular self-assembly and interfacial interactions at solid-liquid and liquid-liquid interfaces

Displacers like PEO control the stability of nanoparticles in solution. They are commonly found in lubrication and paints, and also aid in food formulation, nanoparticle syntheses, and pharmaceutical formulations.

Surfactants and amphiphilic block copolymers like P105 are detergents that lower surface tension and act as chemical dispersants. They form micelles in solution and can be used to clean up oil spills.

Critical displacer concentration (cdc) is the concentration of displacer where the displacer has completely taken the place of the target molecule (Pluronic P105)

Critical micelle concentration (cmc) is the concentration at which micelles form.

RESULTS & DISCUSSION

Effect of PEO Homopolymer on P105

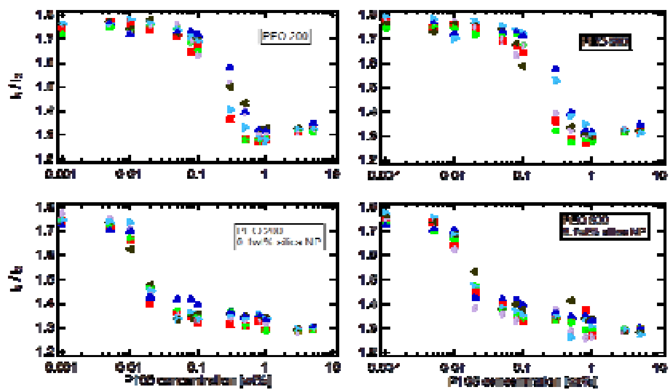


Figure 1. Pyrene fluorescence emission intensity I1/I3 ratio plotted against the Pluronic P105 block copolymer concentration in water for various PEO homopolymer concentrations added: (▲) 0 wt%, (■) 0.005 wt%, (●) 0.01 wt%, (♦) 0.05 wt%, (◄) 0.1 wt%, (►) 1 wt%. Left column: PEO 200. Right column: PEO 600. Top panels: no nanoparticles present in the solution. Bottom panels: 0.1 wt% 10.6 nm protonated silica. Temperature: 22°C. pH ~ 3.

Effect of Silica Nanoparticles on cmc/csmc

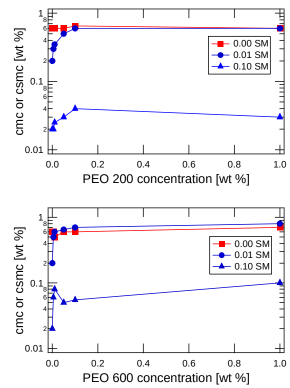


Figure 2. Values of cmc and csmc of Pluronic P105 in the presence of (■) 0 wt%, (●) 0.01 wt% and (▲) 0.1 wt% 10.6 nm SM protonated nanoparticles are plotted against the (top) PEO 200 or (bottom) PEO 600 concentration. Temperature: 22°C. pH ~3.

PEO is a Poor Displacer

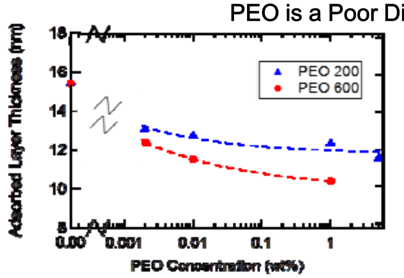


Figure 3. Adsorbed layer thickness observed for Pluronic P105-stabilized silica dispersions in the presence of (▲) PEO 200 or (●) PEO 600 plotted versus the logarithm of added PEO homopolymer concentration (wt%).

Final Effect of PEO Displacer

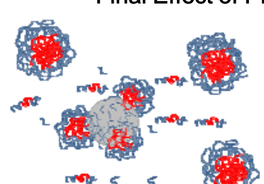


Figure 4. PEO promotes a homogenous surface coating on the particles—containing both P105 micelles (smaller than typical) and PEO chains.

METHODS & MATERIALS

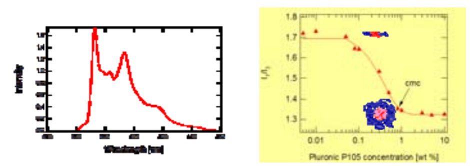
PEO Homopolymer Displacer is a common industrial stabilizer. In the medical industry, PEO is valued for its ability to resist electrical conductivity and anionic charge. Specifically, this study focuses on PEO 200 (MW 200Da) and PEO 600 (MW 600Da).

Pluronic P105 is the surfactant used in this study. It adsorbs onto the surface of silica nanoparticles in micellar aggregates in order to lower the Gibbs free energy of solution.

Silica Nanoparticles (Ludox® SM-type) 10.6 nm diameter particles were used. pH was lowered to 3 to ensure protonation of the silica surface.

Fluorescence Spectroscopy

- Measures cmc/csmc through microenvironment polarity
- Microenvironment polarity is measured through the vibrational peak ratio (I1/I3)
- Probe: hydrophobic Pyrene dye which emits five vibronic peaks when excited by light. Soluble in the hydrophobic centers of micelles



Capillary Viscometry

- Determines adsorbed layer thickness of silica nanoparticles.
- Calculated adsorbed thicknesses indicates how much PEO homopolymer can displace the P105 originally attached to the surface of the silica nanoparticles.

$$\emptyset_{eff} = \emptyset_c\left(1+\frac{\Delta}{R_{np}}\right)^3 = \emptyset_c k$$

$$n_r = \frac{n}{n_s} = 1 + 2.5\emptyset_{eff} = 1 + 2.5(k\emptyset_c)$$

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