Amphiphiles at Interfaces: Fundamentals and Applications in Dispersions

by

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Self-Assembly of Polyethylene Glycol Ether Surfactants in Aqueous Solutions: Effect of Linker between Alkyl and Ethoxylate

(Bodratti A.M., Cheng J., Kong S.M., Chow M.R., Trianou M., Alexandridis P. To appear in Journal of Surfactants and Detergents)

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ABSTRACT

The nanoscale organization of nonionic amphiphilic molecules in bulk aqueous solution and on interfaces leads to unique micro- and macroscopic material properties beneficial to a variety of applications and industries. A brief list includes fields/topics such as printing inks, mineral flotation, enhanced oil recovery, cleaning detergents, and drug delivery. The use of amphiphilic molecules is wide-spread but gaps in fundamental knowledge of their self-assembly and adsorption properties remain. In particular, the development of generalized guidelines for controlling the equilibrium amphiphile adsorbed amount and layer configuration is needed. These properties are driven by physical interactions between amphiphile, interface, and solvent. However, prediction of the self-assembly and adsorption behavior is not always straightforward. The nature of the interactions is specific to the class (structure and composition) of the amphiphile being considered. The adsorbing surface and solvent quality also dictate adsorption and self-assembly behavior.

We present here an approach to control the aqueous adsorption and self-assembly behavior of nonionic amphiphiles by modulating the surface and solvent properties. A commercially available nonionic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer (PEO-PPO-PEO, Pluronic®) served as the adsorbing amphiphile, while spherical silica nanoparticles were used for a solid-liquid interface. We observed that the PEO-PPO-PEO block copolymer adsorbed onto the silica nanoparticles and formed micelle-like surface assemblies. The block copolymer concentration required for surface self-assembly (critical surface micelle concentration, csmc) was lower than that for self-assembly in the bulk. The csmc could be shifted by changing the amount of available nanoparticle surface area. The addition of
short (200 and 600 Da) PEO homopolymers to aqueous silica nanoparticle dispersions increased the csmc and suppressed the adsorbed layer thickness of PEO-PPO-PEO on the surface by a few nm, possibly resulting in a heterogeneous mixed adsorbed layer of micelle-like block copolymer assemblies and adsorbed PEO homopolymers. Mono- and divalent salts were also found to increase the csmc. Divalent salts were more effective, requiring a lower amount in order to reach the maximum observed csmc. Beyond this point of maximum effectiveness, the salts affect micellization in the bulk.

The aqueous micellization behavior of two homologous series of poly(ethylene oxide)-containing surfactants based on a C_{10}-Guerbet hydrophobe was also investigated. The surfactants are described as alkyl ethoxylates and alkyl alkoxlyates and are commercially available under the trade name Lutensol® XP and XL, respectively. The latter incorporate propylene oxide (PO) units in the surfactant chain. Relationships between the surfactant composition/structure and micellization thermodynamics were drawn and compared with compositionally similar C_iEO_j surfactants with linear alkyl chains. Conclusions drawn from these data may enhance understanding of surfactant structure-property relationships required for industrial formulation.
Chapter 1

Overview of Dissertation: Fundamental Contributions and Future Prospects
1.1. Amphiphiles on Interfaces: Introduction and Open Questions

Amphiphilic molecules comprised of hydrophilic and hydrophobic moieties are capable of spontaneously self-assembling in solution into a variety of thermodynamically stable nanostructures [1]. The dual nature of amphiphiles also causes them to physically adsorb on solid-liquid, liquid-liquid, and air-liquid interfaces, often resulting in useful phenomena such as reduced surface tension and enhanced stability of dispersed phases [2]. This behavior has been leveraged for the development of important technologies, including waste water treatment [3, 4], oil-spill dispersion [5, 6], nanoparticle synthesis [7, 8], and drug delivery [9-13].

Poly(ethylene oxide) (PEO)-containing surfactants and block copolymers represent a diverse and ubiquitous class of amphiphilic molecules capable of self-assembly and adsorption on various interfaces in aqueous solution. The industrial importance of such amphiphiles motivates the study of mechanisms underlying their interfacial behavior.

An important class of nonionic amphiphiles are poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers, available commercially as Pluronics® or Poloxamers [14-17]. PPO is relatively hydrophobic and tends to separate out of water. PEO-PPO-PEO block copolymers are available in a broad range of molecular weights and PEO/PPO ratios, making them a flexible choice for formulators. The micellization properties of PEO-PPO-PEO block copolymers have been extensively studied in water [18], in aqueous solution with additives such as salts, glucose, and organic solvents [19-23], and in water-oil mixtures [24-26]. Their spontaneous self-assembly in aqueous solution at a given temperature occurs at a block copolymer concentration known as the critical micellization concentration (cmc). The process is
endothermic (several hundred kJ/mol) and is compensated for by an increase in entropy when the PEO-PPO-PEO chains assemble into micelles. The cmc is lower when the block copolymer molecular weight or PPO fraction is high [18].

The physical adsorption of nonionic amphiphiles on interfaces has been theoretically investigated [27, 28] and experimental results reviewed [29-32]. In polymer-particle dispersions, the adsorbed amount and adsorbed layer structure depend on enthalpic (polymer-surface contacts) and entropic (polymer configuration, liberation of solvent) contributions. Spontaneous physical adsorption of nonionic amphiphiles from water onto particles occurs when the Gibbs free energy of adsorption is negative. Nonionic block copolymers and surfactants adsorb as individual molecules and can also form self-assembled micelle-like aggregates on the interface. The influence of surface type (chemistry, curvature) and block copolymer molecular characteristics (molecular weight, PPO/PEO ratio) has been investigated for PEO-PPO-PEO block copolymer adsorption from water onto a variety of surfaces including latex [33-35], hydrophobized gold [36], silica [37-40], carbon nanotubes [41], perfluorocarbon emulsions [42], and silicone oils [43]. These studies have helped define important features including adsorbed amount and adsorbed layer configuration, while giving insight into the free energy change associated with confining polymer chains and micelle-like assemblies to the interface.

The nanoscale structure of the adsorbed layer is critical in controlling properties such as viscosity, flow under shear, emulsion stability, and wettability. However, in order to maximize the benefit of nonionic amphiphiles such as PEO-PPO-PEO block copolymers for industrial use, formulators must be equipped with knowledge of how to influence the adsorbed amount and
nanostructure [44-46]. Despite recent advances, further understanding of how to tune the self-assembly and adsorption properties is required.

A methodology we explore here is the ability of so-called displacer molecules [47-49] to modulate equilibrium adsorption properties. A variety of displacers can be employed, the effectiveness of which depends on their adsorption energy with the interface compared with solvent and amphiphile. At high concentrations, these additives can behave as cosolvents which alter the bulk self-assembly behavior of amphiphiles [50].

Related open questions in the field of amphiphile adsorption addressed in this dissertation are: (i) how does the adsorbing surface nature influence adsorption, (ii) how can the free energy of adsorption and adsorbed layer structure be controlled by the use of common processing additives, and (iii) how do novel amphiphile molecular characteristics influence aqueous solution self-assembly properties which are also important along interfaces.

Our research group has had a long-standing interest in the aqueous solution self-assembly and interfacial activity of nonionic amphiphiles. Recent work has focused on how the curvature, chemical composition, and surface area of silica nanoparticles changed the free energy of PEO-PPO-PEO block copolymer adsorption and adsorbed layer configuration [51]. This work was extended to assess the effect of polar organic solvents on PEO-PPO-PEO adsorption onto silica nanoparticles dispersed in water [52]. Glycerol, dimethyl formamide, and dimethyl sulfoxide were found to preferentially adsorb in PEO-PPO-PEO-containing dispersions, as reflected in an increase in the concentration of PEO-PPO-PEO required to form self-assembled hydrophobic domains on the particle surface. Strong reductions in the adsorbed layer thickness were also
observed in the presence of the additives [52]. At high concentrations, the added polar solvents strengthened the hydrogen bond network of the bulk water, dehydrating the PEO-PPO-PEO block copolymers and leading to a decrease in the cmc for self-assembly in the bulk solution. The work presented in this dissertation (Chapters 3 and 4) continues to explore the theme of additives as an approach to tuning the self-assembly and adsorption behavior of nonionic amphiphiles.

Recent work in our group has been focused on the relationship between chemical composition and micellization properties of linear C_iPO_nEO_j surfactants in water [53] and in the presence of added polar solvents [54]. PPO was found to behave in a hydrophilic manner (opposite to its character in PEO-PPO-PEO block copolymers) on the basis of its free energy contribution to micellization. However, the contribution changed depending on the PEO block length of the surfactant. This work highlighted the importance of developing information on the role that each amphiphile moiety plays in driving self-assembly behavior, an approach useful to formulators. Chapter 5 of this dissertation presents findings of how branching and chemical composition affect the micellization thermodynamics of a homologous series of C_{10}-Guerbet alcohol-based ethoxylated surfactants. The commercially available surfactants contain added propylene oxide units which may act as molecular “linkers” to improve solubilization capacity [55].

1.1.1. Chapter 2: Literature Review of PEO-Containing Amphiphile Adsorption

Chapter 2 serves as an introduction and literature review to the topic of amphiphile adsorption on solid-liquid interfaces. An emphasis is made on nonionic, poly(ethylene oxide) (PEO)-based amphiphilic molecules, and in particular, PEO-PPO-PEO block copolymers. The chapter begins
with an overview of general features of polymer adsorption, including a section for PEO homopolymers adsorbing on various interfaces. The remainder of the chapter discusses the adsorption and surface self-assembly of PEO-PPO-PEO block copolymers on hydrophilic, hydrophobic, and carbon surfaces. The use of additives to modulate the block copolymer adsorbed amount and layer nanostructure is presented in detail. This approach is emphasized for its ability to tune formulation properties and to uncover the details of molecular interactions between block copolymers and interfaces.

1.1.2. Chapter 3: Influence of Short PEO Homopolymers on Amphiphile Adsorption

We present findings on the influence of added short PEO homopolymers on the adsorption of PEO-PPO-PEO block copolymers on silica. Compared with surfactants or solvents, there is less guidance in the literature on the impact of additives which have a similar affinity to the adsorbing surface as the amphiphile of interest. Using pyrene fluorescence spectroscopy we found that in the absence of added PEO homopolymer, the free energy of surface self-assembly (critical surface micellization concentration, csmc) on silica for PEO-PPO-PEO is lower than the cmc of the block copolymer in plain water. However, the csmc increases as the concentration of
added short PEO homopolymers increases. The csmc reaches a plateau, defined as the point of maximum effectiveness of PEO in disrupting the surface self-assembly of the block copolymer. A capillary viscometry technique was utilized to monitor the polymer adsorbed layer thickness on silica as a function of the added short PEO homopolymer concentration. The effect of added PEO was to slightly suppress the adsorbed layer thickness. The ability of PEO homopolymer to change the adsorption behavior of PEO-PPO-PEO on silica is compared with other displacers studied by our group and is found to be very effective on a molar basis. These results are interpreted in a possible mechanism. Open questions addressed in this chapter include the effect of nanoparticles on the surface self-assembly of PEO-PPO-PEO and the manner in which competitive adsorption by an additive with similar affinity to the particle surface modulates the free energy of adsorption.

1.1.3. Chapter 4: Modification of Amphiphile Adsorption and Self-Assembly by Salts

Chapter 4 continues to explore the possibility of using common processing additives to influence amphiphile adsorption. Findings in this chapter relate more specifically to on-going work in the field of oceanic oil spill cleanup, where dispersants are commonly employed in attempts at
remediation. The formation of oil-mineral-aggregates, where finely divided oil droplets are emulsified by particulate such as clay, are of particular interest. While potentially useful in dispersing oil, in some cases applied dispersants will adhere to the aggregates and aid in proliferation. It is therefore important to develop information on the conditions and mechanism(s) under which this occurs. We evaluated the influence of \( \text{CaCl}_2 \), \( \text{MgCl}_2 \), and \( \text{NaCl} \) on the micellization and adsorption behavior of PEO-PPO-PEO in the absence and presence of silica nanoparticles. A dye solubilization fluorescence technique allowed us to monitor the cmc (absence of particles) and csmc (presence of particles), which in turn gives insight into how each salt impacts the bulk self-assembly and surface self-assembly behavior of PEO-PPO-PEO, respectively. Each salt was found to decrease the cmc. Surface self-assembly was increasingly suppressed as the salt concentration in aqueous silica dispersions increased, up to a maximum. Beyond the maximum, the added salts are believed to act as a cosolvent. We conclude by comparing the efficacy of salt as a displacer with other additives studied by our group, including organic solvents and short PEO homopolymers. The results are explained in the context of an electrostatic mechanism. Similarly to Chapter 3, the open question addressed is how to modulate the free energy of surface self-assembly using simple additives in order to achieve a desired adsorbed amount and configuration.
1.1.4. Chapter 5: Structure-Property Relationships in Amphiphile Self-Assembly

In Chapter 5 we present findings on the relationship between structure, composition, and aqueous micellization behavior for a novel homologous series of single-branch, PEO-containing surfactants based on a C_{10}-Guerbet hydrophobe. Two surfactant subfamilies were studied: alkyl ethoxylates and alkyl alkoxylates, both commercially available from BASF. The latter family incorporates propylene oxide (PO) units in the surfactant chain. Pyrene fluorescence spectroscopy was used to measure the cmc of each surfactant at two temperatures. We found that the PO-containing surfactant family has lower cmc values which were also more temperature sensitive. The cmc data obtained from fluorescence were utilized to calculate the Gibbs free energy, enthalpy, and entropy of micellization. These in turn were used to estimate the contribution of each surfactant moiety (alkyl chain, PO unit, poly(ethylene oxide) (PEO) block) in controlling the cmc. The effect of the single-branch Guerbet alkyl chain on micellization was ascertained by comparison of this data with compositionally similar but linear surfactants. The cmc and enthalpy of micellization were also measured with isothermal titration calorimetry, and showed good agreement with results from fluorescence. Cloud point data revealed non-monotonic relationships for the surfactants with respect to composition, an interesting difference in comparison to linear surfactants. Dilute solution viscosity measurements of some of the branched surfactants show changes in slope of relative viscosity at surfactant concentrations near the cmc. This indicated structural change is more dramatic for surfactants with long PEO blocks. The information developed in this chapter addresses the role of propylene oxide in branched, low molecular weight surfactants, which has not been previously investigated. More broadly, it
provides structure-property information for an important class of amphiphiles which could be useful for formulation.
1.2. Fundamental Contributions and Novelty of Present Work

The contents of this dissertation are concerned with open questions in (i) the adsorption and surface self-assembly of nonionic amphiphiles on interfaces and (ii) their aqueous self-assembly behavior. Each chapter aims to develop fundamental information about interactions between broad classes of materials which can be leveraged to formulate products with well-defined nanoscale organization and desirable properties. The phenomena described are responsible for the nanostructure of colloidal systems whose properties are important to a wide range of commercial applications including personal care products, drug delivery, oil spill remediation, specialty inks and coatings, and many others.

Chapter 2 serves as a comprehensive review of the adsorption properties of PEO-containing amphiphiles, and in particular PEO-PPO-PEO block copolymers. Several reviews exist which address in a general way observations of how interface and amphiphile characteristics influence adsorption behavior. Most of these reviews were published a decade or more ago. In this chapter we interpret recently published findings with a focus on how the adsorbed layer nanostructure can be controlled by judicious choice of surface, amphiphile, and formulation additives (solvent quality). This perspective could be informative to formulators seeking unique and customizable system properties. Chapters 3 and 4 present findings of studies aimed at controlling the free energy of adsorption of PEO-PPO-PEO block copolymers through the use of common formulation additives. The methodology utilized demonstrated that the free energy of adsorption can be increased by raising the additive concentration (short PEO homopolymers and salts) as manifested by measurement of the csmc. While PEO homopolymer does not appear disruptive to PEO-PPO-PEO micellization in the bulk, added salts decrease the concentration required for
self-assembly of PEO-PPO-PEO by altering the solvent structure and changing the hydration state of the block copolymer. The use of simple and common additives to tune the adsorption behavior of PEO-PPO-PEO is beneficial to formulators. This approach stands in contrast to many studies which describe desorption approaches through the use of additional surfactants or large (100,000 + Da), which may unfavorably impact desorption timescales or other interfacial properties. The findings show that the nanoscale organization of amphiphiles on the solid-liquid interface can be controlled by modulating the enthalpy and entropy of adsorption via small changes to the dispersion composition. The control mechanism depends on the type of additive. Applications include stabilization of colloidal particles and so-called oil-mineral-aggregates (OMAs), of interest in oil-spill remediation [56].

Chapter 5 addresses the question of structure-property relationships in surfactant micellization in aqueous environments. Trends are well-understood for industrially important ethoxylated surfactants of the linear alkyl chain \( C_i \text{EO}_j \) type, where the alkyl chain contributes to the hydrophobic effect responsible for self-assembly in water. This chapter explores the role of the less-studied \( C_{10} \)-Guerbet alcohol chain on micellization thermodynamics. Guerbet alcohols contain a branch and display lower melting points than linear fatty acids with a similar number of carbon atoms, making them of interest to personal care products such as cosmetics. Some of the surfactants studied in Chapter 5 incorporate PO units. Our group previously determined the role of PPO to be hydrophilic in a different surfactant system, on the basis of its free energy contribution to micellization. In the current study we see that the PO units act in a hydrophobic manner. The roles that the Guerbet hydrophobe and PO play in the self-assembly of the low molecular weight surfactants were elucidated and add new information regarding self-assembly of nonionic amphiphiles.
1.3. Future Directions

The knowledge developed in Chapters 3 and 4 (mechanistic understanding of adsorption behavior and its tunability with common formulation additives), and in Chapter 5 (how amphiphile structure determines the properties of self-assembled solutions), are topics integral to the function of numerous industrial products and processes. Drug delivery is a rapidly expanding field where the benefits of amphiphiles are being applied to solve longstanding challenges such as solubilization of hydrophobic therapeutics, transport through selective and diverse physiological barriers, and controlled release.

Two of our publications not included in this dissertation detail the use of PEO-PPO-PEO block copolymers as versatile excipients which have shown promise in addressing these needs in drug delivery. The *Journal of Functional Biomaterials* article [12] describes formulation techniques for drug encapsulation enabled by the broad compositional range and solution behavior of PEO-PPO-PEO block copolymers (Poloxamers). This touches on aspects including drug-amphiphile compatibility, how PEO-PPO-PEO molecular characteristics impact the formulation properties (structure in particular), and how different formulation techniques can access equilibrium and kinetically-frozen structures of interest. The *Expert Opinion on Drug Delivery* publication [13] reports on how self-assembled PEO-PPO-PEO block copolymer formulations, including equilibrium micelles, hydrogels, and lyotropic liquid crystals, and some nonequilibrium structures, have been successfully employed to deliver drugs through a multitude of pathways (nasal, oral, subcutaneous, transdermal, and ophthalmic). The underlying mechanisms of drug delivery discussed in these papers include how amphiphile composition and processing relate to
self-assembly behavior, and how adsorption behavior of the self-assembled amphiphile impacts drug delivery performance in administration routes.

Technological advancement in fields including drug delivery will require further elucidation of molecular interactions which influence amphiphile self-assembly and adsorption. We have addressed in this dissertation the role that additives play in tuning the adsorption behavior of amphiphilic molecules on solid-liquid interfaces and how structure-property relationships relate to the micellization behavior of a family of surfactants with unique molecular composition and structure. While we have demonstrated that short PEO homopolymers and salts can modulate the free energy of adsorption and adsorbed layer composition and thickness, this work should be expanded to include additives of rapidly growing industrial importance, such as ionic liquids [57]. These are known to influence self-assembly behavior of PEO-PPO-PEO block copolymers [58] and may also influence adsorption behavior. Clarification of the adsorbed layer configuration in the presence of additives should also be a priority. The configuration (e.g., monolayer, micelle-like assembly, brush) relates directly to the macroscopic properties of dispersions.

The aqueous micellization of the Guerbet alcohol-based surfactants has been described in Chapter 5, including the relative viscosity of micellar solutions for surfactants of differing PEO block length. However it would be useful to obtain more detailed structural information about the micelle, particularly as it relates to the single-branch Guerbet hydrophobe and incorporated PO units. The micelle shape impacts micro- and macroscopic solution properties, while the PO units may have potential benefit to solubilization. Small-angle neutron scattering (SANS) has proven to be a useful tool for studying the nanostructure of ethoxylated block copolymers [20,
SANS has recently been used to identify micelle-shape transitions and changes in core volume in C$_i$EO$_j$ surfactants with different compositions [60]. The hydrophilic-lipophilic balance (HLB) of the surfactant was strongly linked to the micelle shape and core volume. Complimentary 2-dimensional nuclear Overhauser effect spectroscopy revealed that the alkyl chain in C$_i$EO$_j$ surfactants protrudes into the hydrophilic PEO shell [60]. Applying these techniques to the Guerbet-based surfactants discussed in Chapter 5 may lead to useful and interesting information on the role that the mildly hydrophobic PO moiety and branched alkyl chain play in the micelle structure. These features may also influence the organization of surfactants on solid-liquid and liquid-liquid interfaces, which should be also be investigated. Linear alkyl chain C$_i$EOj surfactant adsorption has been well-characterized and serve as an important comparison. Quartz Crystal Microbalance with Dissipation (QCM-D) can be used to study equilibrium and kinetic aspects of amphiphile adsorption on model surfaces [61]. Adsorbed amount can be measured directly, while information about the adsorbed layer configuration may be inferred from frequency dissipation data and an appropriate model. Linear alkyl chain surfactants have been previously studied [62-65], with some uncertainty remaining about how molecular characteristics such as PEO block length influence the adsorbed amount and configuration. Applying this technique to the Guerbet-based surfactants may help clarify the effect of PEO block length, and provide novel information on how incorporated PO units and the single-branched alkyl chain influence adsorption on various interfaces.
1.4. Publications by A.M. Bodratti Not Included in This Dissertation


References for Chapter 1


Chapter 2

Adsorption of Poly(ethylene oxide)-Containing Amphiphilic Polymers on Solid-Liquid Interfaces: Fundamentals and Applications

Chapter 2 Abstract

The adsorption of amphiphilic molecules of varying size on solid-liquid interfaces modulates the properties of colloidal systems. Nonionic, poly(ethylene oxide) (PEO)-based amphiphilic molecules are particularly useful because of their graded hydrophobic-hydrophilic nature, which allows for adsorption on a wide array of solid surfaces. Their adsorption also results in other useful properties, such as responsiveness to external stimuli and solubilization of hydrophobic compounds. This review focuses on the adsorption properties of PEO-based amphiphiles, beginning with a discussion of fundamental concepts pertaining to the adsorption of macromolecules on solid-liquid interfaces, and more specifically the adsorption of PEO homopolymers. The main portion of the review highlights studies on factors affecting the adsorption and surface self-assembly of PEO-PPO-PEO block copolymers, where PPO is poly(propylene oxide). Block copolymers of this type are commercially available and of interest in several fields, due to their low toxicity and compatibility in aqueous systems. Examples of applications relevant to the interfacial behavior of PEO-PPO-PEO block copolymers are paints and coatings, detergents, filtration, and drug delivery. The methods discussed herein for manipulating the adsorption properties of PEO-PPO-PEO are emphasized for their ability to shed light on molecular interactions at interfaces. Knowledge of these interactions guides the formulation of novel materials with useful mesoscale organization and micro- and macrophase properties.
2.1. Introduction to Chapter 2

Academic and industrial research has long been engaged in the study of new materials to address societal, economic, and environmental needs. However, emerging technologies frequently involve unique and challenging conditions which traditional engineered materials can no longer meet. Such materials were typically processed at the micrometer length scale and higher. Today, however, the capability exists for precise manipulation of matter at the nanometer scale, meaning that materials can be built from the ground up. This change in methodology and mindset allows for tailoring of materials to better suit their end use. The formulated materials derive often unique (and therefore valuable) properties from their internal organization at the sub-micron length scale [1-3]. Due to effects such as quantum confinement, for example, previously unrealized optical and electronic properties can be achieved [4, 5]. Nanoparticle–polymer composites, a broad and ubiquitous class of materials, represent a significant thrust in composite materials research with a rich diversity of applications [6-18]. They rely on the uniform dispersion of sub-micron particles into a continuous phase to elicit enhanced and novel properties. Composites also break the common formulation rule that when one property is improved, a related property suffers (e.g., increasing tensile strength also increases brittleness). This means that property-tradeoffs can be minimized or fully avoided, allowing greater flexibility for engineers in choosing their raw materials [19]. These engineered colloidal systems contribute toward a large fraction of goods which we interact with on a daily basis (coatings, detergents, biomedical devices, electronics, and foodstuffs) and appear in many different forms (e.g., structured liquids, foams, semi-solids). They are also driving innovation in emerging fields
such as nanoparticle synthesis [20, 21] and targeted drug delivery [22-25]. The promise of nanoparticle-polymer composite materials motivates the study of their underlying fundamentals.

The hallmark of these colloidal systems is their interfaces, which are typically high in energy and abundant in surface area. These interfaces enable interaction amongst many different types of dispersed colloids and solvents [26-29]. The interactions are dictated in turn by a variety of forces, including van der Waals, hydrogen bonding, hydrophobic, depletion, and electrostatic [26]. The multitude of forces at play renders the design of nanostructured materials complex and their behavior in various environments difficult to predict. Even small changes to the environment can cause aggregation of the dispersed phases, typically to the detriment of performance. However, their sensitivity to environmental variables also creates the opportunity to build systems that are responsive to stimuli (e.g., to change in pH or temperature).

The aggregation of dispersed liquids or particles occurs as the system free energy is minimized. Some examples of destabilization mechanisms include: Ostwald ripening (inclusion of smaller particles into larger particles), coalescence (combination of dispersed liquid droplets), and flocculation (combination of dispersed solid particles). Aggregation can be mitigated by the introduction of amphiphilic macromolecules which spontaneously adsorb on the interfaces between the continuous and dispersed phases. The adsorbing molecules provide steric or electrostatic repulsion between the dispersed particles or liquids, thereby kinetically stabilizing the system [30-34]. In many cases these amphiphiles are synthetic, however there are many natural amphiphiles which are being investigated for use as sustainable alternatives [35-37]. Colloidal particles with adsorbed polymers can be used in turn to prepare stable liquid-liquid emulsions [38-40]. Liquid-liquid microemulsions are characterized by droplets which are
typically a few nanometers in diameter (smaller than a typical emulsion) and are thermodynamically stabilized (in contrast to common emulsions) by adsorbed amphiphiles. The amphiphilic polymers we describe in this review are either homopolymers or block copolymers. We focus mainly on block copolymers, which comprise two or more chemically different monomers in a single chain. This characteristic allows block copolymers to be designed with wide ranging hydrophobic-lipophilic balance (HLB) values and other special functionalization. Block copolymers can be synthesized in a variety of architectures, including diblock, triblock, graft, and star [41, 42]. Their amphiphilic nature allows them to self-assemble into well-defined nanostructures in different solvents and solvent mixtures [43]. They can also self-assemble on solid-liquid and liquid-liquid interfaces. The solvent and/or surface type dictates the properties of these supramolecular structures. Surfactants, typically having a lower molecular weight and comprising a hydrophilic head group and a hydrophobic alkyl chain, can also spontaneously self-assemble into nanostructures in solvents and on interfaces [44, 45].

The manner in which amphiphiles adsorb on an interface dictates how well the system is dispersed and the subsequent microscopic and macroscopic properties. The interaction between particle and amphiphile is affected by solvent quality (pH, ionic strength, and temperature) [46-49], molecular characteristics (architecture, moiety affinities) [50-52], and surface properties (geometry, chemistry) [53-55]. One can imagine that, based on all of the available combinations of the aforementioned attributes, an enormous number of tunable and responsive systems exist. Their design will require improved understanding of fundamental mechanisms of interaction between amphiphiles, solvents, and particles, such that predictive models and guidelines may be constructed which are applicable to broad classes of materials.
Reviews have been published in the previous three decades which cover theoretical treatments and experimental results for nonionic and ionic amphiphile adsorption [56-63]. In particular the roles of surface type and molecular architecture have been investigated. This has led to improved understanding of the various physical and chemical mechanisms which govern adsorption kinetics and adsorbed layer structures. Recent reviews have covered complex fluids such as surfactant-polymer mixtures [31, 64]. The adsorption of surface active block copolymers on biological interfaces (e.g., proteins) is another rapidly growing field, which is related to drug delivery [65-67]. However, the need exists to present recent findings in block copolymer adsorption behavior with a focus on how system components (e.g., solvents and particle type) can be used to purposefully modulate the nanoscale adsorbed structure. Interpretation of fresh data with a focus on the underpinning thermodynamics allows for common trends to be extracted, which can be easily applied across diverse and nascent fields. In particular this review focuses on the adsorption properties of PEO-based amphiphilic polymers, which have become popular because of their sensitivity to environmental changes and rich phase behavior. Several reviews exist which describe the adsorption of low molecular weight PEO-containing surfactants such as alkyl ethoxylates [56, 60-63, 68]. On the other hand, a similar review on block copolymer adsorption on solid-liquid and liquid-liquid interfaces has not been undertaken recently [69-72].

Poly(ethylene oxide) (PEO) is a nonionic polymer that is compatible with a variety of solvents, including water, chloroform, and dimethyl formamide [73]. These properties have made PEO suitable for a wide range of industrial applications. PEO has also received attention in the bioengineering community because of its high interfacial activity, benign interaction with
proteins and cells, and potential use as a drug release agent [74, 75]. PEO homopolymers are also known to associate with ionic surfactant micelles, such as those formed by anionic sodium dodecyl sulfate (SDS); such association can be reversed by the introduction of simple alcohols, indicating the potential use of PEO as a tunable additive [76]. Structurally, PEO homopolymer is represented by H-(O-CH2-CH2)n-OH, and has a mildly amphiphilic character. PEO is available in a broad range of molecular weights (100s to many million Da) spanning physical states from a viscous liquid (low molecular weight) to a durable thermoplastic (high molecular weight) [73]. PEO-containing nonionic amphiphilic polymers, especially symmetric A-B-A triblock copolymers of PEO and poly(propylene oxide) (PPO), have been well-studied [77-79]. Due to their low toxicity, wide range of PEO and PPO composition, and varying molecular weights, they are suited for many applications which require fine control and tunability [80]. PEO-PPO-PEO block copolymers will spontaneously self-assemble into a wide array of microphase-separated structures in mixed solvent systems and non-aqueous solvents [81-84].

This review is structured in the following manner. First, we introduce general characteristics of homopolymer and block copolymer adsorption on solid-liquid interfaces. Secondly, we highlight key features of adsorption of PEO homopolymers on various interfaces. PEO homopolymer serves as both a foundation, and contrast, for discussion of the adsorption properties of more complex, larger PEO-containing block copolymers. Next, we focus on the topic of amphiphile adsorption, and in particular, that of PEO-PPO-PEO block copolymers. Here we cover factors influencing PEO-PPO-PEO adsorption, including particle size and solution conditions. We also discuss recent results from our research group and others on various methods for elucidating polymer-particle-solvent interactions towards better control of the adsorbed amount, ad-layer
thicknesses, and macromolecular organization on the solid-liquid interface. Finally, we draw connections between fundamental adsorption properties discussed throughout the text and practical applications. We conclude with a summary and outlook on the state of the art.
2.2. Fundamentals of Polymer Adsorption

The variety of forces and interactions at play, electrostatic, hydrogen bonding, hydrophobic, and van der Waals, among others, can be a complicating factor in the study of colloidal systems. The summation of these forces dictates whether the net interaction between two components of a mixture will be repulsive or attractive [85]. Determining which behavior will be displayed is not straightforward, but the DLVO theory (not described here) provides general guidelines for aqueous dispersions by taking into account interparticle separation, attractive van der Waals forces, and repulsive electrostatic interactions [26]. In the following sections, we briefly discuss general adsorption characteristics of neutral homo- and block copolymers on surfaces as predicted from theory and modeling.

2.2.1. Nonionic Homopolymer Adsorption

The conformation of an adsorbed homopolymer can be portrayed in terms of trains, loops, and tails [86]. Trains are defined as a series of points of attachment (anchors) between chain segments and the surface, while loops are segments of the polymer chain residing between the anchors and which extend into solution. The tails, or chain ends, also extend into solution. Several models have sought to predict the volume fraction profile, layer thickness, and configuration of adsorbing nonionic homopolymers on surfaces of varying geometry under different solvent conditions [46, 52, 87-90].

The “train-loop-tail” model is useful for explaining the thermodynamic concepts which govern adsorption. The requirement for spontaneous adsorption of a polymer chain on an interface is that the free energy of adsorption is negative \( \Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \). In order to meet this
requirement, the heat of interaction (enthalpy) between the monomer and surface must be more favorable in comparison to that between monomer and solvent. Secondly, the reduction in possible polymer chain configurations upon adsorption (entropy) must not outweigh the enthalpic benefit of attachment. If the physical attraction is strong, more polymer segments will attach to the surface, thereby improving the enthalpy term but simultaneously reducing the configurational entropy term. However, these configurational entropy losses can be offset by the liberation of solvent molecules from the particle surface as the chains preferentially adsorb. In order to predict the extent of adsorption, free energy changes must be analyzed between polymer-solvent, polymer-particle, and solvent-particle [61].

In a polymer-solvent mixture, the interaction energy per solvent molecule is captured by the Flory-Huggins parameter, $\chi$ [91, 92]. The parameter is calculated from a lattice model, and takes into account the system change in internal energy when polymer-solvent interactions occur [93]. Quantitatively, $\chi$ is defined as $\chi = (z*r_1*\Delta\omega_{12})/kT$, where $z$ is the lattice coordination number (number of nearest neighbors), $r_1$ is the number of solvent segments, $\omega_{12}$ is the internal energy change due to the pairing of a solvent molecule and a polymer segment, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature.

Three regimes exist for $\chi$, where $\chi < 0.5$ (complete solubility, good solvent); $\chi > 0.5$ (low solubility, poor solvent); and $\chi > 2$ (zero solubility, complete demixing). The value of $\chi$ tells whether the polymer chain is expanded (prefers interaction with the solvent if “good solvent”) or is contracted (prefers polymer segment-segment interaction if “poor solvent”). It is generally taken that a poor solvent (with respect to the polymer) promotes adsorption. In the special case of a theta-solvent ($\chi = 0.5$), the polymer chains are assumed to be ideal and can be appropriately
modeled by a random walk process. This is in contrast to the three previously stated regimes, where excluded volume effects constrain the number of possible chain conformations. For very short, uncharged chains, Monte Carlo simulations show that adsorption onto planar surfaces will increase when shifting from a good to a theta solvent [46]. As described earlier, the adsorption of a polymer to a surface depends upon the strength of interactions between polymer-solvent, polymer-particle, and solvent-particle. Specific polymer-particle and solvent-particle interactions can be estimated by the theory of Silberberg: the tendency for adsorption is defined by the interaction parameter $\chi_s$, which is calculated from a lattice-based derivation of the partition function for the configurational energy of a polymer chain [94]. For adsorption to take place, the value of $\chi_s$ must exceed the critical energy of adsorption, $\chi_{sc}$. Both $\chi$ and $\chi_s$ are useful for theoretical predictions of polymer adsorption.

Theories of homopolymer adsorption have been presented by Jenkel and Rumbach [86], Silberberg [94-96], Hoeve [97, 98], Roe [99], and de Gennes [87]. Another well-known theory is the quasi-crystalline lattice model for homopolymer adsorption proposed by Scheutjens and Fleer (“SF Theory”) [90, 100], which considers a mixture of solvent molecules and polymer segments occupying a lattice framework. The model can be used to calculate adsorbed amount, surface coverage, bound fraction, and train, loop, and tail fractions by making use of $\chi$, $\chi_s$, polymer chain segment length, and the equilibrium bulk volume fraction of polymer. Important trends that the SF Theory identifies include: homopolymer adsorption increases as solvent quality decreases; adsorption increases as chain length increases; and that the bound fraction of segments from adsorbed chains decreases as the polymer molecular weight, bulk polymer volume fraction, and/or solvent quality increases [100]. The SF Theory emphasizes the
contribution of tails to the adsorbed layer thickness and adsorbed amount; tails were neglected in earlier theories. This resulted in underestimation of adsorbed layer thickness, to which tails contribute substantially (the root-mean-square layer thickness due to tails varies proportionally with the square root of the chain length) [90].

2.2.2. Block Copolymer Adsorption

Nonionic block copolymers adsorb on surfaces under the same thermodynamic principles described for homopolymers. However, differences in adsorption behavior arise because block copolymers comprise blocks with varying affinity for the solvent and surface. For example, block A of an ABA triblock copolymer may be attracted to a surface while block B is highly soluble in the solvent. This property often manifests in complex three-dimensional adsorbed structures, such as micelle-like aggregates [101]. Thus the block copolymer composition is an integral factor when modeling adsorption. The self-consistent field theory of Scheutjens and Fleer has been modified to describe the adsorption of surfactants [102] and block copolymers [103-105] by taking into account the increased number of interactions between polymer blocks, solvent, and surface.

Adaptation of the SF Theory to non-self-associating, multicomponent block copolymer systems demonstrates how segment density profiles for block copolymers differ from those of homopolymers [104, 105]. For instance, for an AB diblock copolymer where A is strongly attracted to a surface and B strongly attracted to the solvent, the A blocks adsorb while the B blocks extend outward into solution. As the solvent quality for B decreases, a less extended chain is obtained. In the case that the A segments weakly adsorb, and the solvent is poor with respect
to B segments, a higher density layer accrues on the surface. However, total layer collapse (i.e., an even higher surface segment density) is avoided because the enthalpy gained via adsorption outweighs the entropic loss associated with restricted and compacted surface layers [104].

Since the block copolymer block affinity contributes significantly to the adsorption profile of the polymer, block copolymer chain composition also becomes an important aspect. The modified SF model demonstrates that AB diblock copolymer adsorbed amounts vary linearly with the block length ratio (A:B) [105]. This is related to the interplay between enthalpy (from favorable surface-segment interactions) and entropy (from configurational changes) towards the overall free energy of adsorption. For instance, if A blocks are strongly adsorbing, then a longer A block compared to the B block will lead to a higher adsorbed amount. Due to space constraints caused by dangling tails, a BAB triblock copolymer would be found to have lower adsorbed amounts and also decreased hydrodynamic thicknesses compared to an AB diblock copolymer of the same number of A and B segments [105].

2.2.3. Adsorption Isotherm

The adsorption isotherm relates the equilibrium adsorbed amount of a molecule on an interface to the bulk solution concentration of this molecule at a given temperature [26, 27]. An example of an adsorption isotherm for PEO homopolymers of various molecular weights adsorbing on silica from water at 25°C is given in Figure 2.1. The key features of the adsorption isotherm include an increasing adsorbed amount at low bulk solution concentrations, which gives way to a plateau at higher concentrations. This plateau is considered to be the maximum adsorbed amount. Further information may be discerned from the shape of the isotherm. For example, the
steepness of the rise in adsorbed amount can indicate the affinity of the molecule (or portions of the molecule) to the surface. The solution concentration corresponding to the maximum adsorbed amount is also telling in this regard [44]. The adsorbed amount of polymer is useful knowledge in its own right, for example in the role it plays in stabilization of titania pigment in paints to achieve desirable properties like opacity and gloss [106]. The Langmuir isotherm [107], \[ \theta = \frac{k_{ad} * A}{k_{ad} * A + 1} \], where \( \theta \) is the equilibrium surface coverage fraction, \( k_{ad} \) is the adsorption equilibrium constant, and \( A \) is the adsorbate concentration, is often used to describe the adsorption of surfactants and amphiphilic polymers [60, 108]. The isotherm assumes one-to-one binding of molecule segments to surface sites, and monolayer coverage at the maximum adsorbed amount (though this is not often observed in practice). Ultimately, the adsorption isotherm can lead to inferences about the adsorbed layer structure. However in order to probe these features directly, other methods must be used, such as light scattering (ellipsometry [109], photon correlation spectroscopy [PCS] [110]), capillary viscometry [111], NMR solvent proton relaxation [112], and small-angle neutron scattering (SANS) [113]. In the case of amphiphilic polymers, discussed later, the adsorption isotherm can reveal self-assembly processes on the solid-liquid interface.

2.2.4. Molecular Displacers

Competitive adsorption between two molecules of different size or functional affinity to a common surface is a simple method for determining the interaction parameters and segmental adsorption energy for polymers [114, 115]. This information is in turn useful for determining adsorption mechanisms and how these can be manipulated by changing solution properties. A polymer segment will adsorb if the interaction energy parameter \( \chi_s \) is greater than \( \chi_{sc} \), the critical
adsorption energy. The use of so-called displacer molecules to cause desorption of pre-adsorbed polymer from a surface is a technique that can reveal the value of \( \chi_s \) and indicate a polymer’s preference to adsorb at a given surface. A typical experimental protocol is to measure the change in surface coverage with displacer concentration, with the point of zero surface excess (i.e., no remaining adsorbed polymer) identified as the critical displacer concentration (cdc) \([115, 116]\). As an example, the displacer effects of various added solvents, including dioxane, acetone, benzene, and methyl cellosolve, on polystyrene \([116]\) and PEO homopolymer \([117]\) adsorbed on Aerosil 130 silica in carbon tetrachloride (CCl\(_4\)) have been compared, showing that PEO preferentially adsorbs to silica in comparison to polystyrene. This was deduced by comparing calculated values of \( x_{s,PD} \) (the adsorption energy per polymer segment adsorbing from a displacer) for both PS and PEO for the same displacers in CCl\(_4\), which were higher for PEO than PS.
2.3. Adsorption of PEO Homopolymers

2.3.1. Solid-Liquid Interfaces

The adsorption of PEO homopolymers on the solid-liquid interface is straightforward compared to that of PEO-containing block copolymers. However, a brief discussion of the PEO homopolymer interfacial behavior is instructive, as PEO is a common constituent in several useful nonionic surfactants and polymers. The hydrophilic PEO blocks in amphiphiles play an integral role in their microphase separation properties in the bulk. PEO also contributes significantly to the thickness and structure of adsorbed layers comprised of block copolymers. We review here factors influencing the adsorption of PEO homopolymers on hydrophobic and hydrophilic surfaces as a foundation for the discourse on PEO-PPO-PEO block copolymer adsorption.

The lack of side groups and a flexible back-bone allow for rapid adsorption kinetics for PEO homopolymers. Their adsorption onto substrates can be considered as a three-stage process including transport to the surface, adsorption, and then relaxation to equilibrium conditions as trains, loops, and tails [118]. Adsorption onto silica and silicate glasses has been characterized as mass transport-limited over a wide range of PEO molecular weights (20 – 963 kDa) in aqueous [119] and buffered saline solutions [118]. The timescale of adsorption for PEO homopolymers is on the order of minutes, but is influenced by both the molecular weight and solution concentration of homopolymer. Generally, higher molecular weight chains will adsorb more slowly due to their size [119]. Adsorption kinetics also slow down as the solution concentration of PEO increases. This is caused by a more congested pathway to the particle surface and
increased difficulty in finding vacant anchoring sites. For example, adsorption kinetics have been shown to slow down above 20 ppm homopolymer concentration for 32.6 kDa PEO [119]. Another cause for slowed kinetics at high concentrations is that the polymers may arrive to the surface as clusters rather than chains, and the rate of chain-particle collisions is higher than the rate of attachment [118].

2.3.1.1. Adsorption Isotherm

PEO homopolymer molecular weight, surface concentration, surface coverage, and particle type all influence the adsorption isotherm. Longer PEO chains will preferentially adsorb on a surface over shorter chains, as predicted by adsorption models for neutral polymers. However, the equilibrium adsorption configuration can take time (on the order of minutes to hours) to be realized. Co-adsorption experiments of PEO 33 kDa (coumarin-labeled) and 120 kDa (unlabeled) from water on acid-treated silica glass revealed that long and short chains simultaneously adsorb on the glass surface initially [120]. While the equilibrium surface coverage of the mixed PEO system was achieved after ten minutes, desorption of the 33 kDa homopolymer began after about three minutes [120], indicating the thermodynamic preference of longer chains to adsorb rather than shorter ones [120, 121]. Molecular weight plays at least a minor role in determining the rate of PEO self-exchange at a surface. In co-adsorption experiments of PEO 120K / 460K and PEO 120K / 963K from water on silica glass, total internal reflectance fluorescence (TIRF) measurements indicated that desorption of short chains from the surface became slower as the higher molecular weight PEO chain increased in size. For example, the remaining adsorbed amounts of labeled PEO 120K after 50 minutes of co-adsorption were 0.15 and 0.22 mg/m² when the longer pair PEO chain was 460K or 963K Da, respectively [120]. Surface coverage has
a more pronounced effect on the time-scale for achieving equilibrium adsorption, however. Self-
exchange studies for PEO adsorbing on silica glass in aqueous buffer revealed that the exchange
rates were approximately the same for a given surface coverage for PEO 10K, 32K, and 112K
Da. Above 0.2 mg/m² (large fraction of polymer segments in train formation [122]), the
exchange rates slowed from about 10-15 minutes for PEO 32K and 112K to about 7 hours and 9
hours, respectively, at 0.4 mg/m². This is demonstrated in Figure 2.2, which shows the time (τ-
50) required to remove half of the labeled pre-adsorbed PEO chains from silica glass upon
addition of un-tagged, competing PEO [123]. This can be counter-intuitive, since at low surface
coverages more of the adsorbed polymer would be in train conformation, with a greater number
of energetically favorable surface-segment contacts to be overcome during desorption. The
development of an osmotic pressure barrier on the solid-liquid interface by adsorbed chains at a
crowded surface has been argued to cause the slowed dynamics [123].

2.3.1.2. Role of Surface Type and Curvature

The adsorption mechanism, isotherm, and the adsorbed layer structure of PEO homopolymers on
a surface depend on the surface type and chemistry. The molecular architecture of PEO
comprises hydrophobic (CH₂-CH₂ backbone) and hydrophilic (ether oxygen) segments. As such,
PEO is mildly amphiphilic and capable of adsorbing on both hydrophilic and hydrophobic
surfaces.

The PEO homopolymer adsorption isotherm on common, hydrophilic oxide surfaces, including
silica and alumina, tends to be of the high-affinity type. The two leading mechanisms of
adsorption on these surfaces are (i) hydrogen bond formation between ether oxygen groups in
PEO chains and particle surface hydroxyls (silanols) and (ii) Lewis Acid-Base interactions [124].
The strength of the hydrogen bond can vary based on the silanol type and quantity. Isolated silanols (as opposed to vicinal, germinal, and bonded configurations) have been shown to attain larger adsorbed amounts of PEO [53]. Oxide surfaces with strong Brønsted acidity, an indicator of silanol group strength, also display higher adsorbed amounts [124]. PEO can also adsorb on Lewis Acid sites on metal particles such as alumina, though the adsorption energy tends to be higher for hydroxyl groups (adsorption energies of 5.1 and 4.1 kT have been measured for PEO on silica and alumina relative to carbon tetrachloride, respectively) [114].

Surfaces that are hydrophobic in nature, such as polystyrene latices, interact with PEO differently. Rather, the attraction occurs between the CH$_2$–CH$_2$ PEO back-bone and the particle, resulting in a high-affinity adsorption profile, similar to hydrophilic surfaces [125]. Higher adsorbed amounts have been measured in cases where hydrophobic interactions are dominant, in comparison to those where hydrogen bonding is prevalent. For example, the peak adsorbed amounts of PEO 1,000,000 Da adsorbing from water on hydrophobic latex (222 nm diameter), hydrophobic octyl-modified silica (164 nm diameter), and hydrophilic silica (146 nm diameter), were 1.5, 1.2, and 0.8 mg/m$^2$, respectively [126]. The plateau adsorbed amounts increased with PEO homopolymer molecular weight for both hydrophobic surfaces. There was no apparent increase in adsorbed amount with increasing PEO molecular weight on the hydrophilic silica surface. This behavior presents because polymer loops (rather than trains) develop on hydrophobic surfaces, allowing more mass to accrue and organize on the particle surface [126]. By comparison, the formation of hydrogen bonds on hydrophilic surfaces will force the polymer into a flat conformation, saturating more binding sites per polymer chain.
The substrate geometry also plays some role in the adsorbed amount and layer thickness of adsorbed polymers [54, 127]. Self-Consistent Mean Field Theory (SCF) has been used to predict simple (neutral) polymer adsorption in good solvent on cylinders and spheres of varying radius [128]. Segment density profiles generated from SF theory show that the segment density on the surface increases quickly as the radius decreases. At the same time, the layer thickness decreases with decreasing radius, likely due to the increased conformational freedom that the polymers have to adsorb on the surface (as opposed to being crowded into a standing brush on a flat surface). As an example, evaluation of the plateau hydrodynamic adsorbed layer thickness (by PCS) of PEO homopolymers of various molecular weights on different diameter latices found that the layer thickness was roughly halved as the latex radius decreased from 500 to 29 nm. Fourier transform infrared spectroscopy (FTIR) measurements of dried PEO-silica samples showed that the number of surface silanol groups involved in PEO adsorption was lower for 15 nm diameter as opposed to 100 nm diameter silica, leading to the conclusion that the adsorbed layer comprised relatively more loops and tails on the surface of the smaller diameter silica [127].

2.3.1.3. Role of Polymer Molecular Weight and Concentration

Polymer molecular weight and solution concentration also determine the adsorption isotherm and adsorbed layer structure. PEO homopolymers adsorb in a train-loop-tail fashion, with the fraction of trains and loops increasing as either the solution concentration of polymer or polymer molecular weight increases. The loops and tails grow because of increased competition amongst polymer segments for attachment points. The adsorbed amount of PEO on hydrophobic and hydrophilic substrates in water increases rapidly, beginning at low polymer solution
concentrations. The adsorption of PEO homopolymers (ranging from several thousand to one million Da) from water at room temperature on hydrophobic smectite [129] and hydrophilic silica nanoparticles [130] commenced at polymer solution concentrations of less than 100 mg/L. At lower polymer solution concentrations, the surface coverage is also low. In this case, PEO homopolymers will tend to lay flat on the surface, forming a higher fraction of trains resulting in favorable (negative) contributions to the adsorption enthalpy and also lower adsorbed amounts [131]. As the bulk concentration of PEO increases and the adsorbed amount increases, the layer structure begins to change from flat trains, to loops and tails. Infrared spectroscopy analysis of PEO 600 kDa adsorbing on fumed silica showed that, as the solution concentration of PEO increased, the fraction of PEO ether oxygen atoms interacting with silanols decreased from 0.8 (10% of monolayer coverage) to 0.2, indicating the formation of loops and tails [132]. Finally, the rearrangement of the adsorbed layer reaches equilibrium and the plateau adsorbed amount is obtained. Osmotic pressure measurements on aqueous PEO-silica systems revealed minima in the reduced chemical potential (\(\mu^*\), defined as \(\mu * MW/RT\), where \(\mu\) is the chemical potential, \(MW\) is the polymer molecular weight, \(R\) is the ideal gas constant, and \(T\) is the absolute temperature) when \(\mu^*\) was plotted versus the dosed volume fraction of PEO homopolymer for a given silica loading [133]. The minima were suspected to occur at the point of surface saturation of polymer, and represent a thermodynamically stable state of balanced entropy (polymer configuration and excluded volume effects) and enthalpy (exothermic, arising from favorable polymer-silica binding sites).

The hydrodynamic layer thickness of adsorbed PEO increases with surface coverage [134]. Thus, the hydrodynamic thickness increases (to a plateau) as the polymer solution concentration and
adsorption time increase, in concert with the adsorbed amount profile. At low polymer concentrations, there is little competition for adsorption sites, leading to flat adsorbed conformations on the given surface. As more polymer chains are introduced and adsorbed, steric repulsion causes the polymers to “stand” on the surface. This occurs so long as the enthalpic benefit of attachment is not outweighed by steric interactions and entropic constraint. The growth in hydrodynamic layer thickness has been observed for PEO homopolymers of various molecular weights adsorbing from water on cellulose ester filters [135] and on polystyrene latices [136]. The plateau adsorbed amounts of PEO homopolymers are typically quite low for a given molecular weight in comparison to amphiphiles, but depend on the adsorption mechanism. Plateau hydrodynamic layer thicknesses (obtained from quasielastic light scattering, QELS) of about 14 to 156 nm for PEO homopolymers ranging in molecular weight from 21 to 1300 kDa were found on 113 nm polystyrene latex [136]. On the other hand, a volumetric flowrate technique found plateau adsorbed layer thicknesses of about 4.5 to 20 nm on hydrophilic cellulose ester filters for PEO of molecular weight ranging from 40 – 1200 kDa [135]. The significant difference in layer thicknesses can be attributed to surface-specific interactions. At the hydrophobic interface, larger loops and tails form as the CH$_2$-CH$_2$ polymer back-bone adsorbs on the surface. On the polar (hydrophilic) cellulose surface, hydrogen bonds form which bound the ether oxygens along the PEO chain to the surface.

Generally, adsorbed amounts are larger for higher molecular weight PEO homopolymers [119, 126]. For example, the adsorbed amounts of PEO 20 kDa and 900 kDa on octyl-modified silica in water at room temperature were approximately 0.71 and 1.15 mg/m$^2$, respectively [126]. As longer chains adsorb, a larger fraction of the chain is accumulated on the substrate surface in the
form of loops and tails, versus trains. Considering the interplay of enthalpy and entropy, the adsorption of longer chains is favored over shorter chains. As more segment-particle bonds are made, the enthalpy of adsorption becomes more negative. At the same time, removing long chains from the solvent increases the entropy of mixing. Longer chains also have more options for rearrangement on the particle surface, owing to a greater number of bonds around which to rotate. This means that the reduction in entropy upon confinement of the polymer on the surface will be less for longer chains than for shorter chains. A preference for the adsorption of longer chains has been demonstrated previously [118, 137]. However, molecular weight effects on the plateau adsorbed amount are not always straightforward; the plateau adsorbed amount does not necessarily increase with molecular weight. For example, it was reported that PEO 1,000,000 Da achieved a lower plateau adsorbed amount on spherical silica at room temperature than PEO of molecular weight 50K, 150K, and 500K Da (Figure 2.3) [130]. This was attributed to the formation of more loops and tails for the high molecular weight polymer, rather than train configuration segments, at the surface. SANS studies of PEO adsorption on laponite clay revealed a weak power law relationship between adsorbed amount and molecular weight, owing to the disk-like shape of the particles [138]. Different adsorbed amounts for the same molecular weight PEO can occur because of subtle differences in the PEO chain chemistry as well. Adsorption studies of short PEO homopolymers (~ 400 Da) with a hydroxyl group either on one chain end or both chain ends revealed that the singly hydroxylated PEO achieved a greater adsorbed amount at elevated solution concentrations (> 0.7 g/kg), owing to its ability to “stand” on the particle surface and leave more adsorption sites free for other chains to adsorb [131]. Short, di-hydroxylated PEO chains adsorbed with both chain ends occupying surface sites.
2.3.1.4. Role of Solvent Quality

The solution properties of PEO homopolymers have been studied in water and various organic solvents including benzene [139] and methanol [140]. In room temperature water, PEO homopolymers will adopt an extended coil conformation at sufficiently large molecular weights (greater than 7-8 kDa) [139]. Solvent type, in addition to impacting the bulk solution conformation of PEO, can also influence adsorption by altering the chemistry of the adsorbing surface. For example, the silanol groups of silica gel [141] and colloidal silica particles [142] can participate in ion-exchange with various metals, thereby altering their surface chemistry. The dependence of the adsorption isotherm on surface chemistry allows for the use of external controls (e.g., pH, additives) to modulate adsorbed amounts and ad-layer thicknesses. An example is the modulation of the adsorbed amount of PEO on colloidal silica dispersed in water by variation of the system pH. At low pH (~ 4 and lower), the silica surface is protonated, allowing for hydrogen bond formation to occur and adsorption to take place. At neutral pH, however, the surface is less protonated and slightly less PEO adsorption occurs [143].

Displacer studies are useful because they can reveal information about the adsorption energy of a polymer on a surface relative to a competing solvent. The adsorption energies of polymers including PEO, polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(tetrahydrofuran) (PTHF), among others, on silica and alumina in binary mixtures of carbon tetrachloride (CCl₄) and one of over a dozen different organic displacers (e.g., THF, acetone, toluene) were calculated from desorption studies [114]. Interestingly, the order of displacer strength on both silica and alumina was very similar for PS (the most comprehensively studied polymer of the study), highlighting the importance of surface-specific interactions with
molecules in determining adsorption behavior. Ethylbenzene, which was the weakest displacer, also has a near identical affinity as PS to each surface, meaning that there is no advantage to either molecule to adsorb, leading to weak displacement. Acetone and acetonitrile, on the other hand, were the two strongest displacers, requiring the least added amount (volume fraction basis) to cause desorption. These two additives were the most acidic, and as such interacted with the surface more strongly, preferentially occupying sites that the polymers would adsorb on [114].

2.3.2. Air-Liquid Interfaces

The adsorption properties of PEO on the air-liquid interface and solid-liquid interface have some commonalities. PEO homopolymers will adsorb at soft interfaces (air-liquid, liquid-liquid), due to their mild amphiphilic character [73]. The surface activity of polymers on soft interfaces is measured in numerous ways, including ellipsometry [144], neutron reflection [145], and, most commonly, surface tension measurements [146]. Similarly to the solid-liquid interface, adsorption at soft interfaces is the result of a balance of surface energies. Surface pressure, \( \pi \), represents the difference in surface tension of an interface with and without adsorbed amphiphiles, or equivalently, the change in free energy with change in surface area. Plotting surface pressure versus area per monomer for a given amphiphile reveals information about the adsorption isotherm and hints at layer structure. On the air-liquid interface, PEO homopolymer displays an isotherm profile which is marked by a positive slope and an eventual plateau in surface pressure with increasing surface excess [147]. The plateau in surface pressure occurs due to a balance of the entropy and enthalpy changes associated with PEO homopolymer chains aligning along the air-water interface [148]. Entropy is gained during adsorption up to a critical adsorbed amount (near 0.35 mg/m\(^2\)), beyond which entropy gains are reversed due to
configurational restrictions at the crowded interface. This condition eventually leads to collapse of the surface PEO monolayer, where entropy can be re-gained [148]. In the collapsed state, the PEO homopolymer chains transition from a flat, 2-D configuration, to loops which protrude further into the water phase.

Interpretation of the flat layer that PEO adopts on soft interfaces has been discussed at length [149-151]. One study on PEO 90,000 on the air-water interface concluded that, as long as the surface concentration was low, PEO would lay flat on the surface [152]. It has also been shown that with increasing concentration PEO homopolymers form an inverted “U” shape on the interface, with at least one ethylene oxide unit lying parallel to the surface at the apex [153]. The adsorption of PEO homopolymer (425 up to 8,000,000 Da across two studies) on hydrophobic oily surfaces (i.e., emulsions) was found to be driven by CH$_2$-CH$_2$ segment adsorption [154, 155].
2.4. Adsorption of PEO-Containing Amphiphiles

Nonionic surfactants and block copolymers commonly incorporate PEO groups as a hydrophilic component. Examples include linear C\textsubscript{i}EO\textsubscript{j} and C\textsubscript{i}PO\textsubscript{4}EO\textsubscript{j} surfactants, PEO-PPO di- and triblock copolymers, and siloxane graft-PEO amphiphiles. The most significant difference between PEO homopolymers and nonionic, PEO-containing amphiphiles, is the latter’s ability to self-assemble into various three dimensional structures in solvents and mixtures of solvents. In the case of PEO-PPO-PEO block copolymers, wide ranging polymorphism is observed in selective solvents, leading to ordered structures from spherical micelles to liquid crystals (with micellar cubic, hexagonal, lamellar, and other types of geometries) \cite{81, 83}. Our main focus is on the spherical micelles which form in dilute solution during a process called micellization. This spontaneous process commences at a solution amphiphile concentration known as the critical micellization concentration (cmc) at fixed temperature. The micellization process can also be initiated by changes in temperature (critical micellization temperature, cmt) at fixed amphiphile concentration \cite{77}.

Nonionic amphiphiles are thought to self-assemble in aqueous solution because of the hydrophobic effect \cite{27}. This effect originates from the differences in hydrophobicity of the covalently bonded chemical groups which comprise the molecule. In short, the solvent (water) structure is interrupted by the oily hydrophobic portions of the dissolved amphiphiles. As the bulk amphiphile concentration is increased, and the water structure becomes more highly ordered (entropically constrained), it becomes thermodynamically favorable for the amphiphiles to associate together in such a way as to reduce the interaction of their oily portions with the water \cite{27}. The net effect is a rebalancing of enthalpic and entropic interactions which minimizes the
Gibbs free energy. Micelles, which vary in their size and shape based on solvent conditions and amphiphile molecular architecture, are useful for their ability to solubilize hydrophobic compounds [156, 157].

The cooperative association behavior of PEO-containing amphiphiles can be observed on solid-liquid interfaces. Near the cmc of the amphiphile in pure solvent, large steps in the adsorption isotherm have been observed, as shown in Figure 2.4 [158, 159]. Increases in the adsorbed layer thickness occur simultaneously, providing further evidence of self-assembly into supramolecular structures at the interface. Similarly to PEO homopolymers, the solvent quality, surface type, and molecular architecture influence the adsorption isotherm and resulting surface structure. These serve as levers which can be manipulated to achieve desirable / useful micro- and macroscopic properties via fine-tuning of the system molecular structure. Below, we outline recent advances in the adsorption of nonionic PEO-based amphiphiles, with particular attention to factors influencing the adsorption of PEO-PPO-PEO block copolymers. As noted earlier, block copolymers offer added functionality versus homopolymers due to the incorporation of different covalently bonded chemical groups into single chains.

### 2.4.1. PEO-PPO-PEO Block Copolymer Adsorption Characteristics

Block copolymers of the PEO-PPO-PEO type, known commercially as Pluronics and Poloxamers, will spontaneously self-assemble into micelles in dilute aqueous solution [79]. Throughout this manuscript, we identify specific PEO-PPO-PEO block copolymers with the notation used by BASF (the manufacturer of Pluronics) [160] and also by denoting the chemical structure as \( EO_xPO_yEO_x \), where \( x \) and \( y \) are the average degrees of polymerization of the PEO
and PPO blocks, respectively (e.g., Pluronic F127 [EO_{100}PO_{65}EO_{100}]). Systematic dye-solubilization studies of a large range of Pluronics® revealed that the micellization process follows the closed association model, and is driven by a favorable (positive) change in entropy upon association [79]. PEO-PPO-PEO block copolymers with a larger hydrophobic fraction (PPO block) were observed to have lower cmc values. For example, the cmc values of P103 (EO_{17}PO_{60}EO_{17}) and F108 (EO_{132}PO_{50}EO_{132}) (nearly constant PPO block size but differing PEO block length) in water at 25 °C were 0.07 and 4.5 w/v%, respectively [79]. The cmc in water is influenced more per PO unit than per EO unit on a free energy basis, highlighting the importance of the hydrophobic PPO block in the micellization process. The structure of PEO-PPO-PEO micelles in water is described as spherical, with the PPO blocks forming the micelle core and the PEO blocks forming a hydrated corona [79, 82, 161, 162]. The micelle structure can change, and even “reverse” micelles can form, solubilizing water in organic solvents [163, 164]. Similarly to alkyl ethoxylate surfactants, PEO-PPO-PEO block copolymers cause a decrease in the surface tension of aqueous-block copolymer solutions [78].

The adsorption isotherm of PEO-PPO-PEO block copolymers is similar to that of PEO homopolymers at low concentrations [165]. However, as the bulk solution concentration of the block copolymer increases, there is a step change increase in both the adsorbed amount and layer thickness. The concentration of block copolymer at which this occurs is known as the critical surface micelle concentration (csmc) [70, 101, 166]. Analogously to the cmc, the csmc represents a thermodynamic condition where the association of amphiphiles on solid-liquid interfaces results in favorable enthalpic and entropic interactions such that the system free energy is minimized. Throughout this document, the use of “csmc” will indicate that an adsorbing
surface (e.g., nanoparticles) is present in the system of study. The use of “cmc” will refer to systems without an adsorbing surface present (i.e., micellization in bulk solution). In the following sections, we discuss how the factors of surface chemistry and geometry, and molecular properties (i.e., molecular weight and PEO/PPO ratio) influence the adsorption isotherm and layer structure of PEO-PPO-PEO block copolymers.

2.4.1.1. Hydrophobic Surfaces

PEO-PPO-PEO block copolymers adsorb strongly on hydrophobic surfaces via hydrophobic interactions which occur between the PPO blocks and the substrate [167, 168]. Early adsorption studies of different PEO-PPO-PEO block copolymers in aqueous dispersions of latex particles suggested that PPO blocks formed trains and thin loops on the particle surface while the PEO blocks formed well hydrated and brush-like tails. [167, 168]. The isotherms displayed for the hydrophobic latices in these studies were of Langmuir type, and exhibited peak adsorbed amounts near the cmc of each block copolymer. They also showed that the highest plateau adsorbed amounts occurred for PEO-PPO-PEO with longer PPO blocks and high block copolymer molecular weight [168]. For example, the peak adsorption of F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}, Mw = 14,400 Da) on polystyrene latex (900 nm diameter) was about 13 mg/m\textsuperscript{2} while the peak adsorbed amount measured for P75 (EO\textsubscript{23}PO\textsubscript{35}EO\textsubscript{23}, Mw = 4150 Da) was about 7 mg/m\textsuperscript{2} [168]. These data, combined with a positive correlation between the hydrodynamic thicknesses (determined by PCS) of the adsorbed layer and the PEO block size, indicated that PEO-PPO-PEO adsorbed via PPO anchors and with a thick PEO brush. Similar scaling factors for the adsorbed layer thickness in the plateau adsorption region were obtained between PEO-PPO-PEO
block copolymers and PEO homopolymers of similar PEO molecular weight: $M_w^{0.43}$ and $M_w^{0.55}$ for PEO homopolymer and Pluronics, respectively [168].

In the case of the hydrophobic polystyrene particles described above, the adsorbed amounts and layer thicknesses of the PEO-PPO-PEO block copolymers increased rapidly near the cmc of the block copolymers in plain solvent. [167, 168]. This behavior has also been observed in adsorbed amount measurements (obtained using quartz crystal microbalance with dissipation, QCM-D) of PEO-PPO-PEO block copolymers and butylated EO$_x$PO$_y$ diblock copolymers adsorbing on flat polypropylene surfaces (Figure 2.5) [169]. In Figure 2.5, the adsorbed amount before and after (to remove loosely bound polymers) rinsing is plotted versus the cmc of each block copolymer. Surface plasmon resonance (SPR) investigation of a homologous range of Pluronics including P103 (EO$_{17}$PO$_{60}$EO$_{17}$), P104 (EO$_{27}$PO$_{61}$EO$_{27}$), P105 (EO$_{37}$PO$_{56}$EO$_{37}$), and F108 (EO$_{132}$PO$_{50}$EO$_{132}$), adsorbing on gold slides coated with a hydrophobic, self-assembled alkanethiol layer showed somewhat different behavior [170]. While maxima in the adsorbed amounts still occurred in the vicinity of the block copolymer cmc, Langmuir-type isotherms were not obtained. Rather, a decrease in the adsorbed amounts was observed beyond concentrations corresponding to the cmc (beyond the plateau adsorption region), possibly attributable to polydispersity [171]. The peak adsorbed amount for this series of PEO-PPO-PEO was greatest for P103 (EO$_{17}$PO$_{60}$EO$_{17}$) (highest PPO/PEO ratio by weight) at 4.83 mg/m$^2$. On the other hand, for the significantly larger molecular weight F108 (EO$_{132}$PO$_{50}$EO$_{132}$) the maximum adsorbed amount was lower, 4.20 mg/m$^2$. Adsorption isotherms of P105 (EO$_{37}$PO$_{56}$EO$_{37}$) on surfaces of varying hydrophobicity (from most to least according to water contact angle: polypropylene [PP], poly(ethylene terephthalate) [PET], nylon, and cellulose) in water at 25 °C obtained using
QCM-D revealed that hydrophobic surfaces resulted in sharper increases in the adsorbed amount versus more hydrophilic ones. This indicated strong, long-range interactions between the PPO portion of the block copolymer and hydrophobic surface. The adsorbed amounts decreased in order of decreasing hydrophobicity of the substrate: 2.49, 1.69, 1.08, and 0.37 mg/m² for PP, PET, nylon, and cellulose, respectively [171]. Adsorption measurements carried out with QCM-D must be interpreted with the understanding that the total weight adsorbed is a sum of both polymer and any adsorbed water. In the case of reference [171], the results agreed closely with side-by-side SPR measurements, except for the cellulose substrate, which is strongly hydrated and thus overestimates the adsorbed amount to a greater degree. Dynamic light scattering (DLS) data collected for F127 (EO₁₀₀PO₆₅EO₁₀₀) adsorbing on carbon black (CB) in water at two different fixed block copolymer concentrations and fixed CB concentration (3.75 x 10⁻⁴%) showed sizeable increases in the adsorbed layer thickness as the temperature was increased above the cmt [113]. For 0.01 and 1.0 wt% F127 concentrations the layer thicknesses grew from 7.1 to 13.3 nm and from 19.6 to 22 nm as the temperature increased from 20 to 50 °C and from 20 to 40 °C, respectively. The larger thicknesses at high concentration were considered to be possibly caused by multilayer formation or bridging between particles.

The slope of QCM-D “dissipation – frequency” plots (ΔD – Δf) reveals information about the viscoelasticity of the adsorbed polymer layer. This technique, in concert with atomic force microscopy (AFM) images and data, showed that P105 (EO₃₇PO₅₆EO₃₇) adsorbed from water on PP, PET, nylon, and cellulose, in tightly bound, smooth layers below the cmc [171]. However, above the cmc, steeper slopes in the ΔD – Δf plots were observed, especially for the hydrophobic PP substrate, indicating that thicker, softer adsorbed layers had formed. The steeper slope
observed above the cmc for P105 on the PP surface may indicate that the outer regions of adsorbed PEO-PPO-PEO are not as tightly bound as those closer to the substrate [171]. AFM images showed a similar configuration for PEO-PPO-PEO block copolymers adsorbing from water on hydrophobic interfaces, including F127 (EO$_{100}$PO$_{65}$EO$_{100}$) on petcoke above the cmc [172], P105 (EO$_{37}$PO$_{56}$EO$_{37}$) on gold substrates coated with a hydrophobic self-assembled alkanethiol layer [170], and P105 on graphite below and above the cmc [171]. Interestingly, AFM images for P103 (EO$_{17}$PO$_{60}$EO$_{17}$) adsorbed on the alkanethiol-coated gold substrates showed the formation of aggregates as opposed to smooth layers [170]. Small angle neutron scattering (SANS) studies of Pluronic F127 (EO$_{100}$PO$_{65}$EO$_{100}$) adsorbing on hydrophobic carbon black (CB) in water above the cmt revealed a similar aggregate layer structure [113, 173]. The hydrodynamic thickness of these adsorbed F127 aggregates was found by DLS to be about 23 nm, which was the same diameter obtained for F127 micelles formed in the bulk solution (water) above the cmt.

2.4.1.2. Hydrophilic Surfaces

In contrast to hydrophobic surfaces, the adsorption isotherm of PEO-PPO-PEO block copolymers on hydrophilic surfaces, like silica [174, 175], is considered to be lower affinity. Early, comprehensive studies of ten different PEO-PPO-PEO block copolymers adsorbing on polystyrene latex and hydrophilic silica nanoparticles found adsorbed amounts that were about five to six times lower on silica compared to latex [110, 174]. For example, F108 (EO$_{132}$PO$_{50}$EO$_{132}$) peak adsorbed amounts were found to be 1.4 [110] and 0.23 [174] mg/m$^2$ on polystyrene latex (450-540 nm diameter) and silica nanoparticles (50-80 nm diameter), respectively. The underlying reason for the difference in adsorption behavior stems from the
adsorption mechanism. At hydrophilic surfaces, hydrogen bond formation occurs between silanol groups on substrates and the ether oxygens of the PEO blocks, in a fashion similar to PEO homopolymers [124, 176]. An analysis of the free energy of interfacial interactions between PPO-water-silica and PEO-water-silica using the van Oss method [177] indicates that PEO binds to silica more strongly than both PPO and water [166]. However, these hydrogen bonds are weaker than the hydrophobic interactions which anchor the block copolymers to hydrophobic substrates via the PPO block. Surface-specific interactions which facilitate physisorption can be manipulated by simple means in order to influence polymer adsorption. For example, the capacity of silica to form hydrogen bonds with polymers can be modulated by the system pH, since the dissociation and association of hydrogen with silanol groups is highly pH sensitive [178]. This was demonstrated for Pluronic® P105 (EO$_{37}$PO$_{56}$EO$_{37}$) on silica nanoparticles (10.6 nm diameter) using capillary viscometry to monitor changes in the block copolymer adsorbed layer thickness [166]. Capillary viscometry operates on the principle that the viscosity of polymer-particle dispersions increases as the effective volume fraction of nanoparticles increases due to the growth of an adsorbed layer [111]. At a concentration well above the cmc (where surface aggregate formation is expected to occur) the P105 (EO$_{37}$PO$_{56}$EO$_{37}$) adsorbed layer thicknesses in dispersions prepared at pH 10 and 3 were measured to be 1.5 and 15.7 nm, respectively (Figure 2.6). Similarly, the hydrodynamic thickness of F127 (EO$_{100}$PO$_{65}$EO$_{100}$) adsorbing on the water-silica interface measured by PCS showed pH sensitivity [175]. In this case, the adsorbed layer thickness increased from around 0.5 nm to between 3-4 nm as the pH was decreased below 10.5. In both cases, the lack of protonated silanol groups on the silica surface at elevated pH reduced the adsorption of PEO-PPO-PEO molecules on the surface.
A slightly positive correlation between the PEO-PPO-PEO block copolymer adsorbed amount and PEO block length was observed for adsorption on hydrophilic silica in water [174, 175]. For example, the adsorbed amounts of L62 (EO₆PO₃₄EO₆), L64 (EO₁₃PO₃₀EO₁₃), and F68 (EO₇₆PO₂₉EO₇₆) on silica nanoparticles (50-80 nm diameter) at 25 °C were found to be 0.06, 0.07, and 0.175 mg/m² by solution depletion, respectively [174]. The hydrodynamic layer thicknesses on the silica nanoparticles (obtained by PCS) were low at block copolymer concentrations below the cmc or cmt: about 3 and 8 nm for F108 (EO₁₃₂PO₅₀EO₁₃₂) and F127 (EO₁₀₀PO₆₅EO₁₀₀), respectively [174, 175]. This is indicative of a rather flat PEO-PPO-PEO conformation. The hydrodynamic thicknesses were also found to correlate positively with the PEO block length of the PEO-PPO-PEO block copolymers [174].

An abrupt increase in the adsorbed amount of PEO-PPO-PEO block copolymers on hydrophilic surfaces is observed in the vicinity of the cmc, similar to the behavior on hydrophobic surfaces [179]. Ellipsometry studies of Pluronic F127 (EO₁₀₀PO₆₅EO₁₀₀) adsorbing from water on hydrophilic silica slides demonstrated a three-fold increase in the adsorbed amount as the PEO-PPO-PEO solution concentration reached the cmc at 25 °C [165]. This was coupled with an increase in the adsorbed layer thickness from about 4 to 12-14 nm, which is smaller than the diameter of F127 micelles in water (23 nm, by DLS [113]). However, a separate study of Pluronic F127 adsorption on hydrophilic silica wafers as a function of temperature (constant concentration, 6000 ppm) found a jump in the adsorbed amount but no change in the adsorbed layer thickness, which remained constant around 8 nm [175]. The adsorbed layer thickness of P105 (EO₃₇PO₅₆EO₃₇) adsorbing from water on silica nanoparticles (10.6 nm diameter) was found to increase from 2.6 to 15.7 nm as the block copolymer concentration was raised from
0.01 to 2 wt% (from below to above the csmc) at 20 °C. The adsorbed layer thickness of 15.7 nm is smaller than the diameter of Pluronic P105 micelles in plain water at a similar temperature (about 28 nm). The aggregates were considered to be micelle-like on the basis of their dimensions and the fact that the adsorbed layers exhibited a hydrophobic microenvironment similar to that of P105 micelles in water, as assessed by dye-solubilization [166]. The csmc for the aqueous Pluronic P105-dispersed protonated silica system (0.10 wt% silica) [166] is significantly lower than the cmc of P105 in water at room temperature: 0.02 versus 0.6 wt% respectively.

QCM-D measurements on the adsorption of Pluronic F127 (two concentrations evaluated, 0.0005 and 0.5 g/L) from water on various flat surfaces including hydrophobic gold, titanium oxide, and hydrophilic gold, showed that the polymer adsorbed layer thicknesses were reduced on hydrophilic surfaces (those which demonstrated lower water contact angles, Figure 2.7) [180]. At contact angles well below 80°, the adsorbed layers were described as a pancake structure, with the PEO blocks anchoring the PEO-PPO-PEO chains to the high energy, hydrophilic surface. As the contact angle became higher and surpassed 80°, the PPO blocks became the anchor, allowing mushroom-like and eventually brush-like structures to form as the adsorbed amounts increased and the PEO blocks were pushed outward into solution (illustrated in Figure 2.8) [180]. QCM-D has recently been used to evaluate the free energy of association of various PEO-PPO-PEO block copolymers on different surfaces [169]. This was done by fitting adsorption and rinsing data to a “one-step” adsorption equilibrium model (site + monomer → hemimicelle). For all surfaces where adsorption occurred, the free energy of PEO-PPO-PEO surface association was more negative (in some cases several times so) than that for micellization
in plain water [169]. AFM scans of P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}) adsorption from water on hydrophilic silica at four times the cmc revealed adsorbed globular shapes with a 20-30 nm diameter and a 1 nm vertical dimension [171]. The adsorbed aggregates had a central core of PPO and a PEO corona, similar to the micelles formed in water at dilute concentrations.

PEO-PPO-PEO – laponite clay dispersions exhibit interesting phase behavior such as gelation, making them useful as rheology modifiers [181, 182]. Laponite particles are disk shaped with a large aspect ratio, comprising large faces with thin edges, making them markedly different from the spherical and cylindrical surfaces often encountered. SANS investigation of various PEO-PPO-PEO block copolymers adsorbing from water on laponite, including P84 (EO\textsubscript{19}PO\textsubscript{43}EO\textsubscript{19}), P85 (EO\textsubscript{26}PO\textsubscript{46}EO\textsubscript{26}), P94 (EO\textsubscript{21}PO\textsubscript{49}EO\textsubscript{21}), P103 (EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}), P104 (EO\textsubscript{27}PO\textsubscript{61}EO\textsubscript{27}), F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}), and F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}), found that the adsorbed amount was controlled by the total molecular weight and the PEO block molecular weight, similar to hydrophobic surfaces [183]. At 25 °C, F108 and F127 (0.87 and 0.90 mg/m\textsuperscript{2}, respectively) adsorbed in higher amounts than PEO-PPO-PEO with smaller PEO blocks (all other block copolymers attained between 0.44 and 0.56 mg/m\textsuperscript{2}). The layer thicknesses were also significantly higher for F108 and F127 than the other PEO-PPO-PEO block copolymers (by 2-4 times), indicating that the block copolymers adsorbed via the PPO block with their EO groups extended out into solution. PEO-PPO-PEO with lesser anchor fractions (fraction of the block copolymer anchored to the surface) achieved both larger adsorbed amounts and layer thicknesses. The reduction in anchor fraction left more adsorption sites open for further block copolymer chains to adsorb, which simultaneously caused greater steric repulsion within the PEO brush and thus greater extension into solution. Unlike PEO homopolymers adsorbing on laponite [138, 184], PEO-PPO-PEO
displays layer thicknesses which are very similar at both the faces and edges, which is contrast to PEO homopolymers [183].

2.4.1.3. Nanocarbons

Carbon nanotubes are an emerging technology with applications in chemical sensors, energy storage, catalysis, and drug delivery [185-187]. However, effective dispersion of hydrophobic single-walled carbon nanotubes (SWCNTs) is difficult, owing to short-range but strong van der Waals interactions [188]. The large molecular weight and strong affinity of PEO-PPO-PEO block copolymers to hydrophobic surfaces make them well suited to prevent aggregation of the nanotubes [188, 189]. A SANS investigation of F108 (EO_{132}PO_{50}EO_{132}) and F127 (EO_{100}PO_{68}EO_{100}) adsorption onto SWCNTs in water below the cmc demonstrated that PEO-PPO-PEO adsorb as single chains via the PPO block, with the PEO blocks forming a well hydrated outer layer [190]. Aqueous F127-SWCNT dispersions were further characterized as small SWCNT bundles having a highly hydrated (94%), 63 nm thick, diffuse adsorbed block copolymer layer below the cmt (1 wt% F127, 0.3 wt% SWCNT, by SANS) [191] (Figure 2.9). The surface coverage of F127 on SWNT dispersed in water (0.24 mg/mL) was probed by NMR at F127 concentrations ranging from 2.1 to 4.1 mg/mL [192]. The adsorbed amounts were nearly constant regardless of the F127 concentration, ranging from about 0.42 to 0.50 mg/mgs_{SWNT}, indicating strong interactions between PEO-PPO-PEO and the hydrophobic SWNT. Below the cmt, PEO-PPO-PEO adsorption at SWCNT occurred as single chains via the PPO block [193, 194]. Differential scanning calorimetry (DSC) and spin-probe electron paramagnetic resonance (EPR) measurements to probe adsorption of various PEO-PPO-PEO at SWCNTs in water showed that above the cmt, adsorbed PEO-PPO-PEO formed aggregates that resemble very
elongated micelles [194]. The formation of the aggregates occurred with reduced endothermic peaks in DSC measurements, indicating that already-adsorbed single chains acted as templates for the aggregates to form. It has been observed that SWCNTs can be colloidally stabilized with PEO-PPO-PEO block copolymers at concentrations well below the cmc or cmt, and that block copolymers with higher PPO/PEO ratios for a given PEO block size require lower loadings to achieve effective dispersion [193].

As described above, the adsorbed amount and ad-layer structure change above the cmc or cmt, lending an element of tunability to nanocarbon-based dispersions. The adsorbed layer structure of Pluronic F127 (EO\textsubscript{100}PO\textsubscript{68}EO\textsubscript{100}) on hydrophobic SWCNTs was reversibly changed by increasing or decreasing the system temperature across the cmt [195]. For example, layer thicknesses of 4.6 and 2.9 nm were measured as the temperature was raised from 20 to 60 °C. At the same time, the number of surface assemblies increased from 6 to 31 per SWCNT with the temperature increase, indicating that the F127 blobs more evenly coated the SWCNT surface. The temperature effect was argued to be a product of the increasing hydrophobicity of the PEO and PPO blocks with increasing temperature, and the hydrophobic SWCNT surface which hinders micelle formation. Hence, free energy must be minimized by coating the surface more effectively and shielding it from the water. The same study also revealed tunability of the adsorbed layer via addition of acid to the aqueous F127-SWCNT system [195]. The addition of 0.1 wt% 5-methylsalicylic acid (5-ms) decreased the layer thickness from 4.6 to 3.2 nm at 20 °C (and increased the number of assemblies from 6 to 23), thus accomplishing nearly the same effect as increasing the temperature to 60 °C. The 5-ms molecules are amphiphilic, and provide a thermodynamically friendly environment to both the F127 copolymers and SWCNTs, leading to
an increase of the F127 / SWCNT interfacial area accomplished by minimizing the size, and increasing the number, of adsorbed F127 assemblies [195].

PEO-PPO-PEO block copolymers have also been considered for the aqueous dispersion of graphene oxide (GO) sheets [196-198]. Similarly to hydrophobic CNTs, these block copolymers adsorb via the PPO block, which adsorbs in a collapsed thin state, while the PEO blocks form a well-hydrated brush. A “sweet spot” of the PPO/PEO ratio was found to exist which allows the concentration of stabilized GO sheets to be maximized [198]. The “sweet spot” is driven by competing factors: the block copolymer must have a large enough PPO block to interact strongly with the GO sheets, but a PEO block length long enough to overcome short range van der Waals attractive forces. PEO-PPO-PEO block copolymers F68 (EO_{76}PO_{29}EO_{76}), F77 (EO_{56}PO_{34}EO_{56}), and F87 (EO_{61}PO_{40}EO_{61}) were the most effective of nineteen different PEO-PPO-PEO block copolymers evaluated (F68, F77, and F78 had the largest PEO blocks) [198]. Dispersion of GO sheets in electrolytic environments via PEO-PPO-PEO has also been assessed recently. GO sheets which were oxidized to the point of becoming hydrophilic were stabilized by F127 in aqueous NaCl solutions with low PEO-PPO-PEO doses [199]. The low dose requirement was attributed to the diminished hydrophobic character of the GO sheets, meaning that the F127 did not have much area to anchor via the PPO block, and so lower, but sufficient, quantities of F127 adsorbed.

2.4.1.4. Role of Particle Curvature

While specific physical and chemical interactions are major factors in determining the adsorbed amount, surface coverage (and density), and adsorbed layer configuration of PEO-PPO-PEO
block copolymers, the geometry of the substrate also plays a role. Sedimentation field flow fractionation experiments, utilized to determine the hydrodynamic layer thickness and adsorbed amount of polymer, was used to study the adsorption of PEO-PPO-PEO block copolymers on polystyrene of various radii in water and above the cmc [200]. It was determined that highly hydrophilic PEO-PPO-PEO (F68 [EO\textsubscript{76}PO\textsubscript{29}EO\textsubscript{76}], F88 [EO\textsubscript{103}PO\textsubscript{39}EO\textsubscript{103}], and F108 [EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}]) adsorbed with increasing surface density (polymer/nm\textsuperscript{2}) as the particle diameter increased. F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}), for example, displayed an adsorption area change from 20 to 10 nm\textsuperscript{2}/molecule as the polystyrene particle diameter increased from 69 to 212 nm. As a result of the increased packing of F108 chains on the surface, steric repulsion built within the PEO brush, causing the chains to “stand up” and extend further into solution: the corresponding layer thicknesses for F108 were 6 and 14 nm at the 69 and 212 nm diameter particles, respectively [200].

By monitoring how the cmc varies under different conditions and comparing it to the cmc, it is possible to ascertain the influence of surface properties on the adsorption between PEO-PPO-PEO block copolymers (and other amphiphiles), surfaces, and solvents. The cmc of P105 (EO\textsubscript{37}PO\textsubscript{58}EO\textsubscript{17}) adsorbing from water on protonated silica nanoparticles of different size and concentration was recently studied by dye solubilization [166]. By comparing the ratio cmc/cmc, insight was obtained as to the influence of surface area and curvature on PEO-PPO-PEO adsorption. The cmc of P105 was found to decrease as the total amount of particle surface area increased, for silica nanoparticles of 10.6, 16.6, and 26 nm diameter (Figure 2.10, top panel) [166]. This occurred because there were more anchoring sites for the PEO blocks, and so a greater number of enthalpically favorable interactions between the silica and block copolymer
could occur. The csmc also changed based on the particle diameter (Figure 2.10, bottom panel). Rather than collapse into a single straight line, the trends for each particle size diverged, and ultimately the low diameter SM-type particles (10.6 nm versus larger 16.6 nm and 26 nm diameter) allowed for the lowest csmc. This curvature effect was attributed to lateral freedom afforded to the adsorbed polymers at highly curved interfaces [201] which makes the adsorption and arrangement of the polymers less difficult. An investigation of F68 (EO_{76}PO_{20}EO_{76}), F98 (EO_{118}PO_{45}EO_{118}), P104 (EO_{27}PO_{61}EO_{27}), P105 (EO_{37}PO_{56}EO_{37}), and F108 (EO_{132}PO_{50}EO_{132}) adsorbed layer thicknesses on latex of various diameter at fixed block copolymer concentration above the csmc of each found that the layer thickness increased with particle diameter (reduced curvature) [54]. An illustration of the effect of curvature on the PEO-PPO-PEO adsorbed layer structure below the csmc is given in Figure 2.11.

Summarizing section 4.1, we note that the adsorption properties of PEO-PPO-PEO block copolymers are dictated by the block copolymer composition and the hydrophobicity of the substrate. In general, flatter conformations of tightly bound PEO-PPO-PEO layers are observed on hydrophobic substrates below and above the cmc or cmt, with increases in both adsorbed amount and layer thickness above either of these values [168, 171]. PEO-PPO-PEO with longer PPO blocks (higher PPO/PEO ratios) result in higher adsorbed amounts on hydrophobic interfaces. Above the cmc or cmt, the adsorbed layer structure on hydrophobic surfaces has been observed to resemble aggregates. The block copolymers are anchored by the PPO blocks, while the PEO blocks extend into solution. On the other hand, PEO-PPO-PEO adsorbs via the PEO blocks on hydrophilic surfaces and with less sensitivity to the PPO/PEO ratio [174]. Below the cmc or cmt, single chains adsorb. However, above the cmc or cmt, aggregates are formed with
dimensions which resemble micelles in solution [166, 169, 202]. These micelle-like assemblies on the solid-liquid interface stand in contrast to the “blobs” observed for PEO-PPO-PEO block copolymers on hydrophobic interfaces. The geometry of the solid-liquid interface is also a determining factor, with particle radius [166] and shape [183, 198] playing an important role in determining the adsorbed layer structure. A summary of this information is provided in Table 2.1. In the following sections we review how additives and environment (temperature, added solvents, salts, and polymers) interrupt the delicate enthalpy-entropy balance to alter adsorption characteristics of PEO-PPO-PEO and other PEO-containing amphiphiles. This control of microscale assembly is useful for the design and development of new materials.

2.4.2. Effect of Additives on Entropic and Enthalpic Factors in Adsorption

Particle chemistry and curvature affect the organization of PEO-PPO-PEO block copolymers on the solid-liquid interface by constraining (i) the number of available polymer configurations (entropy) and also (ii) the number of available binding sites (enthalpy). However, further modification of PEO-PPO-PEO adsorption can be accomplished by the introduction of additives. These influence the substrate and block copolymer solution properties, which leads to modification of the adsorbed structure of block copolymers. The additives, which may behave as displacers [112], are able to modify both bulk [81] and solid-liquid interfacial self-assembly properties of PEO-PPO-PEO molecules. Besides serving as tools with which to modify rheological properties of suspensions, these can also give insight into the interactions between solvent, polymer, and adsorbing surface, thus divulging guiding principles for the formulation of composites. In this section we review the effects of various additives on the bulk solution and surface assembly properties of PEO-PPO-PEO block copolymers. We also present relevant
findings on the effects of additives in PEO homopolymer and PEO-containing surfactant systems.

2.4.2.1. Effect of Added Organic Solvents

The influence of added organic solvents including formamide, ethanol, and glucose, on the self-assembly and organization of PEO-PPO-PEO in water has been well studied [82, 164, 203, 204]. Solvents which are selective towards one block or the other (PEO or PPO) cause changes to the morphology of assembled PEO-PPO-PEO, resulting in a diverse array of ordered and disordered structures across solvent/block copolymer concentration and temperature ranges. The ability of solvents to tune the structure is related to basic thermodynamic interactions between the solvent and polymer which control solubility and thus the self-assembly properties of the block copolymers. The influence of added organics on PEO-PPO-PEO and PEO-containing polymer adsorption has not been studied to the same extent [115, 116, 151, 205-207]. Early studies using NMR relaxation showed that PEO homopolymers can be displaced from aqueous silica dispersions by the addition of polar organic solvents which have a high affinity for the surface and therefore compete for adsorption sites [112]. Useful information about polymer-solvent-surface interactions can be gained from these types of systematic displacer studies. Thin layer chromatography, for example, was used to evaluate the polymer-surface interaction energies for a variety of homopolymers (polystyrene, poly(butyl methacrylate), PTHF, PMMA, and PEO) along with organic additives (ethyl ether, THF, pyridine, to name a few) adsorbing on silica and alumina [114].
The impact of the polar organic solvents dimethylsulfoxide (DMSO), dimethyformamide (DMF), and glycerol on the solution micellization and adsorption behavior of Pluronic P105 (EO$_{37}$PO$_{56}$EO$_{37}$) were recently probed by dye-solubilization and capillary viscometry [208]. These solvents are useful for various applications, including as cosolvents in ionic liquid mixtures (DMSO) [209], reaction media for the functionalization of cellulosic fibers (DMF) [210], and rheology modifiers in lyotropic liquid crystalline-based gels for pharmaceutical applications [211]. Due to their small size and ability to form hydrogen bonds with other molecules, these solvents can compete with PEO-PPO-PEO molecules at hydrophilic, oxide-based surfaces. Figure 2.12 shows the influence of added DMF (top panel), DMSO (middle panel), and glycerol (bottom panel) on the cmc and csmc of Pluronic P105 in aqueous dispersions of protonated silica nanoparticles (10.6 nm diameter) [208]. The trends for DMSO were similar to that of glycerol. The increase in csmc (toward the cmc) with additive concentration indicated that PEO-PPO-PEO assembly on the particle surface became thermodynamically unfavorable at higher added organic solvent concentrations. Capillary viscometry measurements on the aqueous PEO-PPO-PEO – silica nanoparticle dispersions revealed a decrease in the adsorbed layer thickness with increasing concentrations of DMF, DMSO, and glycerol (Figure 2.13) [208]. The decrease in adsorbed layer thickness was interpreted as the displacement of PEO-PPO-PEO molecules from the surface by the organic solvent molecules and is supported by the apparent suppression of surface micellization as indicated by the increased csmc values at higher organic solvent concentrations. Hence, the maxima in csmc in Figure 2.12 signify the cdc and represent the maximum effectiveness of the additive in modulating the structure of the adsorbed PEO-PPO-PEO layer. The cdc values were found to be about 20, 10, and 5 wt%, for DMF, DMSO, and glycerol, respectively (0.1 wt%
protonated silica nanoparticles) [208]. The effectiveness of the added solvents correlated with their capability to form hydrogen bonds with the silica surface (glycerol can form three bonds per molecule, DMF and DMSO can form one) [212]. The polar organic solvent molecules preferentially adsorbed because of their small size, while the large PEO-PPO-PEO molecules faced considerable rearrangement during adsorption, resulting in an entropy penalty and thus more positive free energy of adsorption [208]. SANS studies of F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}, 0.01 and 1.0 wt\%) adsorbing on CB (100 nm diameter) in water and in binary mixtures of various organic solvents (24 °C) indicated modulation of the adsorbed layer size by the solvents [113]. In water only, the CB + F127 diameter changed from 118 to 146 nm (adsorbed monolayers to micelle-like assemblies) as the F127 solution concentration was increased from 0.01 to 1.0 wt\%. The change in CB + F127 diameter was altered in the presence of added organic solvents for the same F127 solution concentrations, however. In mixtures of water-ethanol and water-formamide the CB + F127 diameter changed from 108 to 128 nm and from 110 to 133 nm as the F127 solution concentration was increased from 0.01 to 1.0 wt\%, respectively. The impact on the size of surface assemblies mirrors that of ethanol and formamide effects on P105 micelles in solution [82].

Short-chain alcohols can also modify the PEO-PPO-PEO adsorbed layer by altering the solvent quality for a certain block. QCM-D measurements of P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}) adsorbing from water (25 °C) on polypropylene in binary water-ethanol and water – 1-pentanol mixtures (4 and 8 g/L tested in both cases) showed that ethanol decreased the adsorption below and above the cmc by improving the solvency of the PEO groups [213]. The longer 1-pentanol alcohol led to increased adsorbed amounts below the cmc because it reduced the solubility for P105. However,
decreased amounts (relative to water-only isotherms) were observed above the cmc. The reduction in adsorbed amount in the presence of 1-pentanol above the cmc was attributed to the very low Gibbs free energy of micellization: -31.5, -28.5, and -29.5 kJ/mol for P105 micellization in mixtures of water - 1-pentanol (8 g/L), water-ethanol (8 g/L), and pure water, respectively. In short, there must be an energetic advantage to adsorption on the surface in order for the micelles to dissociate and unimers to adsorb. The same conditions were evaluated at a hydrophilic cellulose surface with similar results, but with drastically reduced adsorbed amounts (nearly seven-times higher adsorption in the case of 4 and 8 g / L added 1-pentanol on cellulose) [213].

Besides being useful in creating surface layers of differing structure, added organics were also found to modify the bulk micellization properties of PEO-PPO-PEO block copolymers beyond the cdc by contributing to the hydrophilic (DMF) or hydrophobic (DMSO and glycerol) character of P105-containing silica dispersions. Similar effects to those observed in the silica-bearing dispersions in Figure 2.12 have been noted for PEO-PPO-PEO block copolymer in binary aqueous solutions with glucose, glycerol, and other solvents [214]. Glucose and glycerol both have been found to reduce the cmc of P105 and F127. Glucose addition to aqueous Pluronic P105 solution has also been reported to alter the micelle shape, from spherical to ellipsoid [204]. Solvents which are more hydrophobic than water (on the basis of their octanol-water partition coefficient), such as DMF, do not cause a reduction in available hydration, thereby disfavoring micellization in water. In the case of Pluronic P105, DMSO and glycerol were confirmed to behave as cosolvents above the cdc in aqueous silica-bearing dispersions [208].
Study of the solution and adsorption properties of a PEO-containing amphiphilic polymer comprised of a poly(dimethylsiloxane) chain and grafted PEO (900 units) and PPO (300 units) blocks (Mw = 11,500 Da) in binary mixtures of water and various polar organic solvents revealed similar solvent effects to those described above [215-217]. The PEO-containing amphiphile formed micelles on the surface of CB in water above the cmc. However, the addition of small amounts (10 vol%) of glycerol or ethanol reduced or increased the adsorbed amount of the amphiphile on CB, respectively. In the case of ethanol, a csmc was not achieved in the amphiphile range studied, which is opposite to the effect of glycerol, which showed a csmc similar to that of plain water. The adsorbed layer structure on CB in plain water and binary solvents resembled that of micelles, indicating a preference of the amphiphile chains to associate with themselves versus the solvent and CB surface. However, the size of these surface assemblies was modulated by the cosolvents. Above the cmc, adsorbed layer thicknesses (obtained by DLS) decreased from 31 (in plain water) to 22, 16, and 19 nm in 80% water – 20% ethanol, 80% water – 20% formamide, and 80% water – 20% glycerol, respectively. Interestingly, the plain water and water-ethanol solvents resulted in solution micelles and adsorbed micelles of the same size. In formamide and glycerol the adsorbed layer thickness were smaller, but still much higher than those found below the cmc at monolayer coverage. Thus, without special processing, the adsorbed layer thickness of PEO – containing amphiphiles on colloidal surfaces can be tuned to give desired structure / property relationships. Additionally, it appears that experimental observations of cosolvent effects in PEO-PPO-PEO block copolymer-containing systems are also applicable to other types of PEO-containing amphiphiles.
2.4.2.2. Effect of Added PEO Homopolymers and Surfactants

The influence of added surfactants and polymers on the solution micellization behavior of PEO-PPO-PEO block copolymers has been studied in detail. Just a few examples include studies of the micellization behavior and modified structures reported for the addition of linear nonionic [218-220] and ionic surfactants [221-226] and biosurfactants such a bile salts [227, 228]. Fewer studies are available, however, which cover competitive adsorption of PEO-PPO-PEO block copolymers in the presence of added amphiphiles. The increased number of binding sites per chain makes the competitive adsorption of polymers an interesting comparison to that of small added organic molecules.

Mixtures of PEO homopolymers and PEO-PPO-PEO block copolymers in particle-bearing dispersions form an interesting scenario because of their similar adsorption mechanisms on hydrophobic and hydrophilic surfaces. The addition of short PEO homopolymers (200 and 600 Da) and Pluronic P105 (EO$_{37}$PO$_{56}$EO$_{37}$) into aqueous dispersions of protonated silica nanoparticles (10.6 nm diameter) was recently investigated [229]. Fluorescence spectroscopy, used to detect the formation of hydrophobic domains similar to those of PEO-PPO-PEO micelles, showed that there was a small apparent increase in the csmc in silica-bearing dispersions as PEO homopolymer was added. In 0.10 wt% silica nanoparticles, the csmc rose from 0.02 wt% to 0.04 and 0.08 wt% for PEO 200 and PEO 600, respectively [229]. The increase in csmc was significantly less than that observed for P105-silica dispersions with added organic solvents [208]. Additionally, the decrease in adsorbed layer thickness was less pronounced for the addition of PEO homopolymers relative to added DMSO, DMF, and glycerol. Total reductions of 3 and 5 nm of the adsorbed layer were measured when PEO 200
and 600 were added, respectively, up to 5 wt% [166]. The final layer configuration was estimated to be that of mixed PEO-PPO-PEO aggregates-PEO homopolymer chains (Figure 2.14). The heterogeneous surface mixture may occur due to competing enthalpy-entropy considerations. The block copolymer, which will adsorb loosely and at lower surface density as micelle-like aggregates with the PEO blocks serving as the anchor, faces less configurational entropy penalties compared to the very short PEO homopolymers. On the other hand, the PEO homopolymer can adsorb in a flat configuration to the surface at sites left available at the surface, perhaps fitting between adsorbed micelles.

The influence of nonionic polymers and surfactants on PEO homopolymer adsorption has been studied previously; such findings could prove applicable to PEO-PPO-PEO block copolymer adsorption. For example, it was found that pre-adsorbed PEO 8650 Da was displaced from the silica particle surface at low surface coverages by PEO 4250, 8650, and 22,000 Da at concentrations of $4 \times 10^{-6}$, $2 \times 10^{-6}$, and $1 \times 10^{-6}$ M, respectively [137]. Nonionic surfactants have also been investigated for their ability to desorb PEO homopolymers. A low molecular weight surfactant, polyoxyethylene alkylphenol (Igepal 720), was utilized to desorb pre-adsorbed PEO 100 kDa and 600 kDa from the surface of colloidal polystyrene at room temperature [230]. The reduction in PEO homopolymer adsorbed amount and changes in the adsorbed layer thickness were heavily dependent on the PEO homopolymer molecular weight and the solution concentration of both PEO and surfactant (displacer). Specifically, PEO desorption was more difficult at low surface coverages, where the homopolymer was adsorbed in a train configuration. The timescales of the desorption experiments were on the order of several days, owing to the low molecular weight of the surfactant in comparison to that of the PEO homopolymers, which take a long time to detach and diffuse away from the particle surface [230]. Short, nonionic $C_nEO_j$
surfactants have been found to preferentially adsorb versus larger PEO homopolymers (between 4250 and 167,700 Da) on silica [231]. Surfactants with higher aggregation numbers on the silica surface were more capable of desorbing adsorbed PEO homopolymers. Interestingly, the surfactant performance was correlated to the critical surface aggregation concentration (csac, equivalent to the csmc). When the csac became equal to the cmc, the surfactant could not preferentially adsorb over the PEO homopolymers [231].

Modification of the adsorbed amount and layer structure of PEO-PPO-PEO block copolymers can also be accomplished through the introduction of sodium dodecyl sulfate (SDS) [232, 233]. SDS is an anionic surfactant whose adsorbed layer structure on the solid-liquid interface can be influenced by the addition of competitively adsorbing polymers and changes in system pH [234]. Adsorption experiments of Pluronic F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}) and SDS on silica wafers in aqueous solution of varying ionic strength showed that SDS can control the adsorbed amount and also shape the adsorbed polymer layer [232]. SDS and F108 chains formed aggregates in solution, with SDS providing electrostatic repulsion between chains within the aggregates, between the aggregates themselves, and between aggregates and the silica surface. Figure 2.15 captures the adsorption properties of the aqueous SDS-F108-silica system. In the top panel, a reduction in total polymer adsorbed amount upon addition of SDS is seen. This results from an increased number of electrostatic interactions between SDS-F108 aggregates and the silica surface. Second, the typically irreversible adsorption of F108 was found to be reversible and path-dependent at 0.10 and 150 mM NaCl when co-adsorbed with SDS. The adsorbed amount of pure aqueous F108 (represented by the bars on the ordinate axes) is different after introduction of SDS and then subsequent washing with aqueous F108 (to remove SDS) at both 0.10 and 150 mM NaCl (the symbol at 0.0 mM SDS concentration, Figure 2.15, bottom panel). The
reversibility derives from reduced F108 surface contacts (and thus a weaker state of adsorption), as SDS consumes some of these binding sites. The enhancement in total polymer adsorbed amount at low SDS concentration at 150 mM NaCl is thought to arise from decreased lateral repulsion between adsorbed aggregates, resulting in more free space for aggregates to adsorb (NaCl may strengthen the adsorption of the aggregates on the particle surface) [232]. Similar mixed aggregate adsorption behavior has been observed in force curves obtained utilizing AFM to study the forces between a silica nanoparticle and plate in mixtures of SDS and F108 [233]. The amount of SDS required to achieve a depletion force was reduced from 16 mM to less than 4 mM when 10,000 ppm F108 was included in the system.

The competitive adsorption on solid-liquid interfaces of PEO-PPO-PEO block copolymers and biologically-relevant molecules such as proteins has also been investigated. A radio labeling technique along with X-ray photoelectron spectroscopy (XPS) was used to track the co-adsorption of Pluronic F68 (EO76PO29EO76) and collagen (300 nm long, 1.5 nm diameter) on PET in aqueous solution [235]. In the absence of F68, collagen adsorption proceeded similarly to that of a polymer adsorbing on a hydrophobic surface, achieving relatively high plateau adsorbed amounts (0.6 – 0.7 μg/cm) and forming an absorbed structure comprising oblong granules about 6 layers thick. When adsorption was carried out in the presence of F68 (10 μg/mL), the adsorbed amount of collagen never exceeded 0.15 μg/cm in the concentration range studied (up to about 100 μg/mL). AFM results for the adsorbed layer were similar to those without F68, suggesting a soft surface with large assemblies [235]. The complex, antimicrobial peptide nisin (Mw 3500 Da) has been observed to adsorb on silanized silica surfaces coated with F108, which is dissimilar to other proteins [236, 237], including bovine serum albumin (BSA) [235]. The nisin
was likely trapped within the PEO brush that forms when PEO-PPO-PEO anchors on hydrophobic surfaces in aqueous environments.

2.4.2.3. Effect of Added Salts

Dissolved ions in aqueous solution alter the hydrogen bonding network of water to varying degrees according to the Hoffmeister series; the ability of ions to distort the water structure trends with their radius and polarizability in most cases [238]. In this context, added ions may be viewed as modifiers of the solvent quality, with implications for the micellization and adsorption of dissolved amphiphiles. Dissolved salts can also lead to specific molecule-ion interactions which must be considered [239]. The impact of dissolved ions on the cloud point, micellization thermodynamics, and micelle structure of aqueous solutions of PEO-PPO-PEO has been well studied [240-244]. The influence on the cmc or cmt generally depends on the extent to which dissolved ions change the water structure and thus the hydration state of the block copolymer. The added salts LiCl, KCl, NaCl, and NaBr, for example, were found to depress both the cmt and cloud point (CP) of L64 (EO13PO30EO13), while NaSCN and urea increased both quantities. The effects were correlated with the ion radius and heat of solvation [240]. SANS study of Pluronic P84 (EO15PO43EO19) showed that the aggregation number increased from 72 to 142 as the KCl concentration was increased from 0 to 2 M. The micelle cores increased in size as salt was added, while the hard-sphere radius remained nearly constant, indicating dehydration of the PEO corona [241].

The influence of added salts on PEO-PPO-PEO adsorption has also been relatively well studied. However, the impact of dissolved ions on the adsorption is difficult to generalize. A given substrate will behave differently in the presence of salts based on its chemistry (i.e., oxide,
silanol-bearing surfaces versus non-oxide surfaces). Similarly, water-soluble polymer moieties, especially in block copolymers, require varying levels of hydration to remain soluble. As discussed above, added salts can reduce or enhance this hydration based on how they interact with the water structure. Our group recently investigated the effects added NaCl, CaCl$_2$, and MgCl$_2$ on the micellization and surface assembly properties of Pluronic P105 (EO$_{37}$PO$_{56}$EO$_{37}$) in aqueous silica nanoparticle dispersions (10.6 nm diameter) at low pH (~ 3) [245]. All added salts decreased the cmc of PEO-PPO-PEO in water, with Ca$^{2+}$ and Mg$^{2+}$ causing a more drastic reduction in the cmc compared with NaCl for the same chloride anion content (in the absence of silica). The salts also altered the csmc, above which P105 adsorbs as micelle-like aggregates on the silica surface [166]. Fluorescence spectroscopy showed that the formation of hydrophobic domains in the dispersions was disfavored at low salt concentrations, with a maximum csmc (i.e., cdc) occurring for each salt which depended on the salt type and silica concentration. The salt effectiveness in maximizing the csmc, based on the salt concentration, was ordered CaCl$_2$ > MgCl$_2$ > NaCl. The increase in csmc was attributed to electrostatic repulsion between salt adsorbed on the PEO blocks of P105 (where salt may gather as a function of the number of EO units [246]) and ions which may have been adsorbed on the silica surface. A decrease in the csmc beyond the cdc, which occurred for each added salt, was likely caused by the formation of solution-phase micelles due to the reduced solvent quality. Adsorption beyond the cdc could also explain the decrease in csmc values, as the solvent quality could have been poor enough to overcome the suspected repulsion near the silica surface [245].

Early adsorption studies of Pluronic P75 (EO$_{23}$PO$_{35}$EO$_{23}$) in aqueous dispersions of hydrophobic polystyrene latex showed increased adsorbed amounts when KCl, CaCl$_2$, or Na$_2$SO$_4$ was added [247]. Added CaCl$_2$ caused a four-fold increase in the adsorbed amount compared with the zero
salt condition, and was more effective in promoting adsorption than the other two salts. This trend occurred despite the fact that KCl is more effective in reducing PEO solvency, hinting that a specific ion-surface-PEO block interaction may be responsible for the observed results. In a case opposite to a hydrophobic surface, ellipsometry studies of Pluronic F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) adsorbing on hydrophilic silica wafers at 22 °C and pH 6 revealed an apparent hindrance to adsorption and surface assembly upon addition of NaCl [248]. For F127, the adsorbed amount and hydrodynamic thicknesses were reduced from 2.6 to 0.4 mg/m\textsuperscript{2} and from 7.5 to 1.0 nm, respectively, in the presence of 0.10 M NaCl [248]. The decrease in adsorbed amount was attributed to dissociation of silanol groups as the ionic strength of the system was increased (the pH was about 6, where silanol dissociation proceeds to a low degree in the absence of added ions [142, 249]). Thus the surface and solvent type play a significant role when considering salt effects on adsorption.

PEO-PPO-PEO block copolymers have shown promise as stabilizing agents in particle dispersions at high ionic strengths due to their adsorbed conformations in the presence of salts. F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) was shown to successfully disperse CNTs in aqueous NaCl solutions up to 0.154 M NaCl by adsorbing and wrapping the CNTs with the PEO blocks in an extended conformation. This enabled steric repulsion to occur, preventing aggregation due to electrostatic and hydrophobic forces [250]. However, as the solvent quality for PEO-PPO-PEO decreases and the adsorbed layer becomes more collapsed, the effectiveness of the steric repulsive barrier can decrease. AFM study of F127 (0.01 wt\%) adsorbing on glass spheres in aqueous-Na\textsubscript{2}SO\textsubscript{4} solution showed that the repulsive interaction distance shrank from 30 to 15 nm as the salt concentration was increased from 0.4 to 0.5 M [251]. At the same time, the force required to compress the adsorbed layer decreased from 150 to 50 μN/m, indicating that the PEO blocks,
which were previously in a buoy state, had collapsed to thin adsorbed layers. Interestingly, a regime called “restabilization” was identified for the adsorption of L35 (EO$_{11}$PO$_{16}$EO$_{11}$), L64 (EO$_{13}$PO$_{30}$EO$_{13}$), and P75 (EO$_{23}$PO$_{35}$EO$_{23}$) on latex in the presence of added salts (not all cases, however) [252]. Restabilization refers to the increase in the dispersion stability ratio (determined by DLS) after the ratio had reached a minimum. The restabilization was thought to occur because of the growth of micelles or micelle-like aggregates in solution [252]

The influence of added salt on the adsorption of PEO homopolymers and nonionic surfactants has also been studied, with mixed findings. It was reported that the adsorbed amounts (measured by reflectometry) of PEO 43,520 Da adsorbing from water on a silica wafer decreased from about 0.31 to 0.13 mg/m$^2$ at pH 6 upon changing the NaCl concentration from 0 to 0.1 mmol/L [253]. Further, the pH corresponding to the point of zero surface excess of PEO homopolymer was shifted lower by increasing the NaCl concentration. On the other hand, the plateau adsorbed amounts for PEO 100 kDa on 40 nm diameter silica dispersed in water showed an increase in the adsorbed amount upon addition of different salts, including CaCl$_2$ and MgCl$_2$ (Figure 2.16) [254]. NMR solvent relaxation also showed an increased in the density of PEO segment trains on the silica surface upon addition of salt. The adsorbed amount of a low charge, PEO-rich polyelectrolyte, PEO$_{45}$MEMA:METAC-2 (where MEMA is monomethyl ether methacrylate and METAC is methacryloxyethyl trimethylammonium chloride), on silica wafers was also found to decrease as the ionic strength increased for a given pH. This was argued to be the result of ion competition on the silica surface (from the electrostatic interaction side) and reduced PEO-silanol affinity (from the hydrogen bond interaction side) [255].
2.4.3. PEO-PPO-PEO Adsorption on Air-Liquid and Liquid-Liquid Interfaces

The amphiphilic nature of PEO-PPO-PEO block copolymers allows them to organize on soft interfaces i.e., air-liquid and liquid-liquid interfaces. Study of the adsorption characteristics and layer structure on these interfaces is relevant to applications in foaming, oil dispersion, and emulsification for e.g., drug delivery, to name a few. Here we present a brief review of PEO-PPO-PEO adsorption on these soft interfaces as a comparison to the solid-liquid interface adsorption discussed previously.

The adsorption of PEO-PPO-PEO on the air-water interface is driven by the reduced solvency of the PPO block in water. Surface tension measurements show that increasing the concentration of PEO-PPO-PEO in the bulk solution leads to a decrease in surface tension until the cmc is attained [78], similar to that of lower molecular weight nonionic C₆EO₃ surfactants [256]. Two breaks in the surface tension versus PEO-PPO-PEO concentration have been observed, the second (higher concentration) of which corresponds to the cmc. The first, low concentration break is attributed to an intermediate step involving restructuring of the adsorbed layer [78]. Overall, the adsorbed structure of PEO-PPO-PEO molecules evolves with concentration in four distinct stages. In the first stage, PEO-PPO-PEO lies flat on the surface with the PPO and PEO blocks lying in plane with each other. Here, the surface area per adsorbed molecule is the highest. As the concentration increases, the block copolymer chains continue to adsorb but must pack more tightly, and the chains adopt an inverted “U” configuration similar to that of PEO homopolymer discussed earlier. The third stage involves further packing of the inverted “U” – shaped chains. This has been experimentally observed by sum frequency generation (SFG) vibrational spectroscopy, which showed that the PPO blocks became more highly ordered as the
block copolymer concentration increased [257, 258]. The final adsorption stage, where the cmc is attained, is represented by a tightly adsorbed layer and micelle formation in the bulk. Surface pressure measurements have shown that the final adsorbed layer resembles a well hydrated PEO brush [259]. Neutron reflectivity studies of Pluronic F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) at a concentration above the cmc (0.5 wt\%) on the water-hexane interface (a system very similar to the air-water interface with respect to the solvent-block interactions) showed that the PEO blocks stretched outward into the aqueous solution (about 9 nm), while the PPO blocks sank slightly into the hexane phase [260].

The adsorbed area per molecule for PEO-PPO-PEO was found to be a function of the number of EO units (area per molecule $\sim N_{\text{EO}}^{1/2}$) [78]. Temperature was also found to affect the adsorbed area, due to dehydration of the PEO blocks upon temperature increase. For the homologous series of Pluronics P103 (EO\textsubscript{17}PO\textsubscript{60}EO\textsubscript{17}), P104 (EO\textsubscript{27}PO\textsubscript{61}EO\textsubscript{27}), P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}), and F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}) the adsorbed area per molecule decreased from 62 to 52 \(\text{A}^2\), 77 to 67 \(\text{A}^2\), 99 to 83 \(\text{A}^2\), and 152 to 135 \(\text{A}^2\), as the temperature was increased from 25 to 35 °C, respectively [78]. The temperature impact is similar to that of added salts. The cation Li\textsuperscript{+}, which impacts PEO-PPO-PEO bulk solution behavior to a higher extent than its ionic radius would predict [240], was found to increase the surface pressure of F68 adsorbed on the air-water interface at lower block copolymer concentrations (Li\textsuperscript{+} concentrations of 0.1 and 1.0 M). The increased surface pressure began in the first adsorption configuration stage, where the block copolymers lay flat at the interface (Figure 2.17). This was likely due to coulombic effects within the PEO layers, leading to repulsion and compaction of the adsorbed layer [261]. Surface tension measurements for aqueous Pluronic F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) solutions revealed a sharper decrease between the characteristic first and second breaks when just 0.1 M NaCl was added,
potentially indicating a change to the adsorbed structure [248]. Interestingly, ellipsometry data did not reveal a change in the adsorbed amount or layer thickness upon addition of NaCl (about 3 mg/m² and 9 nm for the plateau adsorbed amount and thickness, respectively). These effects were attributed to a salting-out effect of the salt on the hydrophilic PEO units [248].

By comparison, the liquid-liquid interface is more challenging to study. However, studies of linear PEO-PPO-PEO [262-265] and modified (diblock [266] and branched [267]) PEO-containing block copolymers have yielded useful information on the adsorbed layer configuration and methods of modulation, which are relevant to applications such as cosmetics and drug delivery vehicles with increased blood circulation times. Disjoining pressure, defined as the force per area between two phases, has been used to study the interaction forces between oil droplets coated with PEO-PPO-PEO block copolymers [32, 33, 263]. For Pluronic-type block copolymers adsorbing on the oil-water interface, the disjoining pressure was shown to be predominantly a function of steric repulsion between PEO tails [263]. Dilatational rheology, ellipsometry, and surface pressure measurements of F68 (EO76PO29EO76), L64 (EO13PO30EO13) and P9400 (EO21PO50EO21) adsorbing on the n-hexane-water interface revealed four distinct regions of adsorption [268]. Each phase represented a change in block copolymer conformation, ranging from flat to mushroom-like as the block copolymer concentration (and disjoining pressure) increased. Adsorption occurred on the interface via the PPO block, with the PEO blocks acting as buoys. The PPO blocks of PEO-PPO-PEO block copolymers with higher PPO/PEO ratios were found to penetrate the oil phase to a larger extent [268]. The degree of penetration into the (oily) polydimethylsiloxane (PDMS)-water interface for a series of PEO-PPO-PEO block copolymers was shown to significantly impact both the adsorbed amount and layer thickness [269]. In comparison to cross-linked PDMS (more solid-like than liquid-like), the
adsorbed area per block copolymer was decreased, owing to penetration of the PPO blocks into the liquid-like oil phase. This behavior also resulted in higher layer thicknesses, as the insertion of PPO into the oil phase led to increased repulsion between the PEO blocks, which in turn led to greater extension of PEO into the aqueous phase [269]. Neutron reflectivity measurements of Pluronic F127 (EO\(_{100}\)PO\(_{65}\)EO\(_{100}\)) adsorbing on the hexane-water interface at a concentration higher than the cmc also showed penetration into the oil phase, and an extremely extended conformation of the PEO chains (~4.5 \(R_g\)) [260]. In contrast, SANS studies of PEO-PPO-PEO adsorption at the perfluorodecalin-water interface did not show penetration of the block copolymer into the oil phase [265]. Poloxamer 188 (PEO\(_{76}\)PPO\(_{30}\)PEO\(_{76}\)) and Poloxamer 407 (PEO\(_{98}\)PPO\(_{69}\)PEO\(_{98}\)) attained maximum adsorbed layer thicknesses of about 5 and 16 nm, respectively. This was in both cases larger than the \(R_g\) of each block copolymer in solution. Despite the stretched layer, the SANS data showed that the center of mass of the adsorbed layer was only about 2.3 and 3.5 nm from the interface for Poloxamer 188 and 407, respectively, indicating a loop-tail diffuse layer that was still well-bound to the interface [265].

The adsorbed layer structure on the liquid-liquid interface may be altered by the oil type, emulsion temperature, and the presence of additives. SANS measurements on oil-in-water emulsions comprising either 1,3,5-trimethylbenzene (TMB) or 1,2-dichlorobenzene (DCB) (an aromatic or aliphatic oil, respectively) and stabilized by Pluronic P123 (EO\(_{20}\)PO\(_{70}\)EO\(_{20}\)) showed that the swollen micelle diameter depended on the oil type [270]. Micelle radii were found to increase from 7 to 10 nm or from 6.5 to 8.2 nm as the oil-to-polymer mass ratios increased from 0.10 to 0.53 (TMB) or 0.22 to 0.55 (DCB), respectively (similar structural change for both oils, in this case). However, the aggregation number for DCB-containing micelles was smaller compared with TMB-containing micelles (177 versus 211 block copolymer molecules per DCB-
or TMB-containing micelle at similar oil-to-polymer mass ratios, ~ 0.2) owing to more favorable interactions between DCB and water. SANS studies of Poloxamer 188 (EO\textsubscript{76}PO\textsubscript{30}EO\textsubscript{76}) and Poloxamer 407 (EO\textsubscript{98}PO\textsubscript{69}EO\textsubscript{98}) adsorption on fluorocarbon and hydrocarbon oil-in-water droplets revealed subtle differences in the block copolymer configuration, likely caused by solubility differences between the anchor blocks and the oil type. While the adsorbed amount and layer thickness trends were the same with respect to the two PEO-PPO-PEO block copolymers at both oils, 407 adsorbed in smaller amounts and in a more contracted form on the hydrocarbon oil compared with the fluorocarbon oil. On the other hand, 188 was slightly more expanded in its thickness on the hydrocarbon oil-water droplet.

The addition of ethanol to the TMB- and DCB-containing emulsions discussed above caused surprising differences in the number of P123 micelles formed. On one hand, added ethanol reduced the relative volume fraction of micelles in non-oil containing systems (pure water and Pluronic) due to improved solubility of the block copolymer [270]. On the other hand, the relative volume fraction of micelles in oil-containing systems was increased. This was caused by a decrease in the surface tension of the oil-water interface by the ethanol, allowing stable swollen micelles to form at lower block copolymer concentrations (Figure 2.18) [270]. The addition of various electrolytes and increased temperature (below the cloud point) on PEO-PPO-PEO adsorption on the liquid-liquid interface has also been reported [271, 272]. The addition of NaCl to oil-in-water perfluorodecalin emulsions with Poloxamer 188 (PEO\textsubscript{76}PO\textsubscript{30}PEO\textsubscript{76}) did not reveal any impact to the adsorbed amount (ranging from 1.4 to 2.0 mg/m\textsuperscript{2} over the NaCl range of 0 to 1.5 M) according to SANS [272]. On the other hand, the center of mass of the adsorbed layer increased from about 2 to 2.9 nm abruptly at 0.6 M added NaCl, before again decreasing to about 2 nm at 1 M NaCl. The change in block copolymer configuration was attributed to the
release of PEO loops from the interface as the NaCl concentration reached the critical amount (0.6 M), owing to weakened anchoring of the block copolymer in the presence of the electrolyte. The case is somewhat surprising, considering that layers typically collapse as the solvent quality decreases. A similar, but weaker, effect on the location of the center of the adsorbed mass away from the interface was noted as the emulsion temperature was increased from 25 up to 54 °C, with a maximum occurring at 45 °C. This was not attributed to PEO dehydration, but rather release of the PEO loops from the interface in a manner similar to that of added NaCl. Finally, emulsion properties, such as droplet size and stability, can be modulated by judicious choice of PEO-PPO-PEO HLB or emulsion pathway, even for emulsions of the same final composition [273]

2.4.4. Adsorption Properties of Other PEO-Containing Block Copolymers

We have focused primarily on PEO-PPO-PEO block copolymers in the previous section. However many other PEO-containing block copolymers exist which are relevant to industrial formulations and biomedical applications. Examples include diblock copolymers of PEO and PPO, and triblock copolymers with added side-groups or different hydrophobic components. In this section we briefly describe the equilibrium adsorption properties of some recently-studied block copolymers to enable comparison with the widely used Pluronics.

2.4.4.1. Modified PEO-Containing Triblock Copolymers

Triblock copolymers of the PEO-PTHF-PEO type, where THF is tetrahydrofuran, contain a slightly more hydrophobic central block than PEO-PPO-PEO. The adsorption of PEO-PTHF-PEO block copolymer adsorption proceeds similarly to that of PEO-PPO-PEO, displaying
Langmuir-type adsorption profiles [165, 274]. Ellipsometry measurements of various PEO-PTHF-PEO architectures show a slight dependence of the PEO and PTHF block sizes and total molecular weight, on the plateau adsorbed amounts on hydrophobically-modified (with dimethyloctylchlorosilane) silica slides in water [274]. The triblock copolymers studied ranged from 3200 Da (EO\textsubscript{25}THF\textsubscript{14}EO\textsubscript{25}) up to 11900 Da (EO\textsubscript{112}THF\textsubscript{28}EO\textsubscript{112}), which both displayed adsorbed amounts of 2.4 mg/m\textsuperscript{2} [274]. At low surface coverages (about < 1 mg/m\textsuperscript{2}) the adsorbed layer thickness was low for all block copolymers tested, around 3 nm or lower, owing to a train configuration for the PEO and PTHF blocks on the surface. At intermediate surface coverages, around 1 – 1.5 mg/m\textsuperscript{2}, desorption of the PEO blocks resulted in a rapid increase in the layer thickness. As the surface coverage increased further, the adsorbed layer thickness reached a plateau. The height of the plateau correlated positively with the length of the PEO blocks and was attributed to repulsion between the PEO blocks in solution (e.g., 6 and 3 nm for EO\textsubscript{112}THF\textsubscript{28}EO\textsubscript{112} and EO\textsubscript{25}THF\textsubscript{14}EO\textsubscript{25}, respectively) [274].

PEO-PTHF-PEO adsorption on hydrophilic silica resulted in markedly different behavior than on the hydrophobically-modified silica [202]. Specifically, the adsorbed amounts were reduced while the layer thicknesses were increased, owing to a difference in specific polymer block-surface interactions. In the case of EO\textsubscript{86}THF\textsubscript{14}EO\textsubscript{86}, for example, the adsorbed amounts were 2.4 and 0.8 mg/m\textsuperscript{2} on hydrophobically-modified and hydrophilic silica, respectively. At the same time, the adsorbed layer thicknesses observed on the hydrophilic silica surface were several times higher than those observed on hydrophobic silica, indicating self-assembly of the block copolymer into micelle-like aggregates (Figure 2.19). The csmc, where self-assembly and rapid layer thickness increases began, was over one order of magnitude below the cmc of the triblock
copolymers in water. The adsorbed surface assemblies result from a stronger attraction between the PTHF blocks relative to their attraction to the hydrophilic silica surface (similarly to PPO blocks in PEO-PPO-PEO). AFM and time-resolved fluorescence spectroscopy studies on PEO-PTHF-PEO adsorbing from water on hydrophilic silica showed the presence of micelle-like aggregates which were generally smaller than micelles formed in the bulk [275]. Additionally, it was found that smaller PEO-PTHF-PEO block copolymers resulted in more evenly distributed surface aggregates. The PEO-PPO-PEO block copolymer F127 (EO100PO65EO100) was also evaluated on the silica surface and displayed similar adsorbed structures, however the cmc was higher (around 0.7 – 0.9 cmc) than for PEO-PTHF-PEO block copolymers. The reduced cmc of PEO-PTHF-PEO compared with PEO-PPO-PEO was attributed to the more hydrophobic nature of the PTHF block relative to the PPO block of PEO-PPO-PEO block copolymers. PEO-PPO-PEO block copolymers with added terminal functionality have also been of recent interest [276-278]. The adsorption of F127 (EO100PO65EO100) with attached poly(N-isopropylacrylamide) (PNIPAm110) end-groups on hydrophobic gold was investigated using QCM-D, ellipsometry, and AFM [277]. In such a case, there are multiple solvent-block relationships which can drive the micellization and adsorption behavior of the block copolymer. The hydrophobic PPO and PNIPAm110 blocks both acted as anchors to the hydrophobic gold, and interestingly the adsorption mode and configuration were found to be influenced by the LCST of the PPO and PINPAm110 groups (LCSTs of 31 and 34 °C, respectively). The average wet adsorbed layer thicknesses after rinsing (obtained by QCM-D) were 5.0, 15.8, 389, and 9.3 nm at temperatures of 20, 31, 34, and 40 °C, respectively. The dried (and thus non-solvated) layer thicknesses (obtained by ellipsometry) were 6.2, 9.6, 260.7, and 8.5 nm at 20, 31, 34, and
40 °C, respectively. The increase in layer thickness at 31 °C was attributed to reaching the LCST of PPO, which became condensed on the solid-liquid interface. The surprisingly large increase in the layer thickness at 34 °C (greater than the hydrodynamic radius of the block copolymer micelle, ~ 53 nm at 40°C) was ascribed to the adsorption of multi-layers of associated aggregates. AFM height images and plots confirmed the existence of a tall adsorbed layer (Figure 2.20) [277]. As the temperature was increased, the adsorbed block copolymer layers became better defined. The adsorption of F108 (EO\textsubscript{132}PO\textsubscript{50}EO\textsubscript{132}) with cationic end-groups poly(2-dimethylaminoethyl methacrylate) (DMAEMA\textsubscript{24}) from water on silica, polypropylene, and cellulose was recently probed by QCM-D and SPR [276]. The adsorption mechanism was found largely to depend on the surface type, with solvent quality and electrostatic effects (contributed from the end-groups) dominating adsorption behavior on cellulose and silica, and hydrophobic interactions with the PPO blocks dominating on polypropylene [276].

So-called “reverse” Pluronics have also been studied on the solid-liquid interface via neutron reflectivity, AFM, and SEM [279]. These reverse copolymers have the block sequence PPO-PEO-PPO. For two commercially available PPO-PEO-PPO block copolymers 17R4 (60% PPO) and 17R2 (80% PPO) adsorbing from water, the adsorbed layer structure composition on a Ti-coated surface was modulated by the PEO block size [279]. In both cases, the block copolymers were adsorbed via the PPO blocks. In the case of 17R2 (PO\textsubscript{15}EO\textsubscript{10}PO\textsubscript{15}), the adsorbed layer thickness was split into a PPO layer of about 1.8 nm thick a PEO shell about 1.0 nm thick. However, for 17R4 block copolymers (PO\textsubscript{15}EO\textsubscript{26}PO\textsubscript{15}) the surface PPO layer was only about 0.5 nm while the PEO shell was about 2.1 nm [279]. The thin nature of the PPO layer in 17R4 was considered to occur either from reduced adsorption of the PO segments (because of the larger
and more water-soluble EO groups) or due to a flatter adsorbed conformation of the 17R4 on the Ti-water interface. The larger PEO layer thickness was found in 17R4 by virtue of its longer PEO block [279]

2.4.4.2. PEO-Containing Diblock Copolymers

PEO-PPO diblock copolymers behave similarly to PEO-PPO-PEO triblock copolymers adsorbing on hydrophobic and hydrophilic surfaces in water. AFM images of EO$_{316}$PO$_{94}$ adsorbed on hydrophobic silica and hydrophilic mica revealed micelle-like aggregates above the bulk cmc of the diblock copolymer (23 °C) [280]. At low concentrations, well below the cmc, adsorption on both surfaces began with the formation of a monolayer which became more brush-like with increasing concentration. The PEO-PPO molecules adsorbed on hydrophobized silica via the PPO blocks, while adsorption occurred more weakly on mica via the PEO blocks. Above the cmc, 33 nm diameter surface assemblies were observed on the silica surface, which is close to the hydrodynamic diameter of the micelles in water (42 nm at 25 °C). The structure of these assemblies was that of an adsorbed PPO core with a PEO brush. On the other hand, a soft layer of loosely packed spherical micelle-like aggregates was formed on the mica surface, the diameter of which depended strongly on the AFM frequency (Figure 2.21) [280]. Such structures have been previously predicted by computer simulation [281]. These micelle-like aggregates were attached via the PEO blocks and comprised of a PPO core and PEO corona. The surface micelles could easily be displaced from the mica surface, indicating the weaker interaction of PEO-mica in comparison to PPO-silica [280]. The adsorption of diblock copolymers of PEO and polyisoprene (PEO-PI) on mica has also been studied by AFM [282]. Unlike in ref [280], thin films of polymer and mica were dried prior to inspection. Mica contains multiple layers of bound
water, which allows for rearrangement of the adsorbed polymer layer with time (as the bound water slowly leaves the mica layers). The PEO-PI block copolymer, which was applied at a solution concentration above the cmc, was first observed to adsorb in a configuration resembling single chains (in terms of dimension). As the water left the mica surface some of these chains assembled into micelle-like globules as the attraction between the PI blocks grew [282].

The adsorption properties of many other types of diblock copolymers comprising PEO and a different hydrophobic monomer are relevant to industrial and especially biomedical applications [283-292]. The adsorption of various PEO-poly(ethyl glycidyl ether) (PEO-PEGE) diblock copolymers on the silica-water and silica-ethylammonium nitrate (EAN, an ionic liquid) interfaces was recently characterized [290]. The PEGE block is more oxygenated and bulky than PPO, which will modify its adsorption properties relative to those of PEO-PPO diblock copolymers. The layer structure on the silica-water interface, determined by AFM, was found a function of the PEO block length. Adsorbed layers (about 7 nm), elongated aggregates (about 30 nm diameter), and neatly-packed spherical micelles (about 32 nm diameter) were observed at 0.1 wt% bulk solution concentration for adsorbed EO\textsubscript{54}EGE\textsubscript{109}, EO\textsubscript{115}EGE\textsubscript{109}, and EO\textsubscript{178}EGE\textsubscript{109}, respectively [290]. The diameter of the EO\textsubscript{178}EGE\textsubscript{109} micelles was similar to that of EO\textsubscript{316}PO\textsubscript{94} micelles on silica. Substitution of water for EAN further exacerbated the role of the PEO blocks. EO\textsubscript{54}EGE\textsubscript{109} did not adsorb, while EO\textsubscript{115}EGE\textsubscript{109}, and EO\textsubscript{178}EGE\textsubscript{109} formed bilayers and slightly coalesced micelles, respectively. The nearest-neighbor micelles in water and EAN were 32 and 29 nm, respectively, which is attributable to a reduced extension of the PEO blocks (EAN is a poorer solvent than water for PEO) [290]. The adsorption of PEO – poly(L-lysine) (PEO-PLL) on silica nanoparticles (22 nm diameter) in water showed that the size of the PLL block (which
adsorbs on silica preferentially compared to PEO) controlled the adsorption density and resulting layer structure [288]. At the maximum adsorbed amount, the adsorption density was highest for diblock copolymers with the smallest PLL block sizes. As a result of mutual repulsion within the outer PEO layer, the configuration changed from brush to somewhere in between a brush and mushroom-like layer, as the PLL block length increased. The diblock copolymer with the shortest PLL block length was the most effective at inhibiting BSA (protein) adsorption [288].
2.5. Select Applications for PEO-Containing Amphiphiles

Polymer adsorption on solid-liquid and also soft interfaces can drastically impact system properties which benefit an array of emerging applications and techniques [293]. The subsequent sections on coatings, emulsification, and drug delivery, serve to illustrate how amphiphilic polymer adsorption can influence material performance and open up new avenues in already well-established areas of application.

2.5.1. Coatings

PEO-containing block copolymers have been reported to improve the dispersion and rheological properties of paints, which improves color development [294, 295]. PEO-PPO-PEO block copolymers are able to adsorb on hydrophobic pigment surfaces via the PPO block and use their PEO end blocks as barriers against particle aggregation. Block copolymers with longer PEO end groups are more effective in this regard [294]. Half-times of sedimentation for a variety of PEO-PPO-PEO with different molecular weights and PPO/PEO ratios showed that F108 (PEO$_{132}$PPO$_{50}$EO$_{132}$) was the most effective at preventing sedimentation of hydrophobic carbon black (11 nm diameter) and β-copper phthalocyanine (β-CuPc, 0.1 μm) particles [296]. The sedimentation times (720 hours in both cases) were several times longer than the second most effective block copolymer, PO$_8$EO$_{22}$PO$_8$, which achieved 288 and 240 hours for β-CuPc and carbon black, respectively [296].

Due to their self-assembly properties on surfaces, PEO-PPO-PEO block copolymers have been investigated for their ability to “template” surfaces such that a secondary adsorbed polymer layer can be adsorbed in a specific pattern [297, 298]. This process first involves the growth of a
“primary” adsorbed block copolymer layer on the interface, before subsequent growth of a secondary layer via reintroduction of the “templated” surface to a polymer solution. The goal of this exercise is to elicit a secondary surface of specific structure. While interesting layers (such as concentration-dependent formation of lamellae) have been observed to grow after solvent evaporation of deposited PEO-PPO-PEO on surfaces with pre-adsorbed block copolymers, this form of templating is not believed to be caused by the nature of the pre-adsorbed layer [297, 298]. It is however a useful way to achieve larger ad-layers with potentially useful or functional structures.

PEO-PPO-PEO block copolymers show promise in forming primary layer thin films [299]. In high concentrations, PEO-PPO-PEO block copolymers are capable of forming highly-ordered 3D networks. The networks allow for effective dispersion of mesoporous clays, which translates to greater accessibility to the pores [300] and can e.g., boost chemical sensor performance. The influence of block copolymer concentration on the development of adsorbed ordered phases gives a facile method for creating nanopatterned surfaces. The structure of adsorbed lamellar layers of an asymmetric triblock copolymer (EO_{208}PO_{69}EO_{2}) which were formed via spin-casting of the block copolymer from toluene onto hydrophilic silica substrates showed high sensitivity to the initial block copolymer concentration (Figure 2.22) [301]. At the lowest concentration evaluated, the block copolymer formed a layer with the PEO blocks anchored to the surface and the PPO blocks forming a shield from the toluene solvent. As the toluene evaporated, free floating block copolymers continued to adsorb at the layer, with the PPO blocks of unadsorbed molecules mingling with the PPO blocks of the already-tethered block copolymers, thus forming
a lamellar layer. Further increase in concentration led to higher surface coverage and eventually a disappearance of the multiple bilayers into a single film [301]

Owing to their low toxicity, PEO-PPO-PEO block copolymers have found use as coatings in biomedical applications [302-306]. The adsorption of the block polymers has been shown to reduce the adhesion of colloids, salts, and bacteria to model surfaces via steric repulsion from the PEO blocks [307, 308]. PEO-PPO-PEO block copolymers [309-312] and PEO-based C;EO; surfactants [109] are also useful for minimizing the adsorption of proteins on particles. PEO-PPO-PEO block copolymers of high molecular weight and high PEO/PPO ratio were the most effective at inhibiting the adsorption of fibrinogen and BSA on hydrophobic surfaces. [306]. The surface hydrophobicity was also observed to be a key factor in the effectiveness of Pluronic F108 (EO_{132}PO_{50}EO_{132})-coated stainless steel (SS) to inhibit adsorption of the bacteria *pseudomonas*, as observed in adsorption studies on SS and hydrophobized SS [310]. The root cause for the difference in performance is the adsorbed layer structure, which depended on the surface hydrophobicity. On a hydrophilic surface in an aqueous environment, attachment of the block copolymer occurs via the PEO blocks, with the PPO blocks adopting a condensed profile. On hydrophobic surfaces, however, adsorption occurs with the PPO blocks, while the PEO blocks extend outward into water to form a brush. Pluronic F68 (EO_{76}PO_{30}EO_{76}) adsorbed on hydrophobically-coated titanium and stainless steel successfully mitigated adsorption of bovine serum albumin, fibrinogen, and cytochrome C [309]. Pluronics also are being examined for their ability to protect membrane pores for improved filtration, by improving the membrane hydrophilicity (and thus repelling hydrophobic fouling agents) and more effectively dispersing and fixing engineered nanoparticles around membrane pores [313, 314].
2.5.2. Emulsions

PEO-PPO-PEO block copolymers and PEO-based amphiphiles are effective emulsifiers for a variety of (water) immiscible oily products, such as silicones [315]. They fulfill this function by adsorbing on the liquid-liquid interface, thereby providing steric stabilization for micro- and macro-emulsions [69, 155, 269, 316-318]. The length of the PEO blocks of PEO-PPO-PEO block copolymers was found to correlate positively with the plateau adsorbed layer thickness on the PDMS-water interface, in a manner similar to adsorption on hydrophobic solid-liquid interfaces (Figure 2.23) [262]. However, the plateau adsorbed layer thickness appeared to be slightly higher on the PDMS-liquid interface than the hydrophobic latex-water interface: 14 versus 8 nm at EO = 100. The stronger correlation on the PDMS-water interface versus the hydrophobic latex and hydrophilic silica-water interfaces (Figure 2.23) was attributed to the adsorption mechanisms for each surface (which dictated the adsorption configuration and layer thickness). On silica, hydrogen bond formation led to a more flat conformation, while loops and tails were present to a higher degree on the two hydrophobic surfaces. On the PDMS surface, the block copolymers penetrated into the oil droplet, which led to reduced adsorbed areas per block copolymer and thus greater steric repulsion between the PEO blocks, which protruded further out into aqueous solution, in comparison to “hard” latex particles [262]. Pluronics F127 (EO₁₀₀PO₆₅EO₁₀₀) and F68 (EO₇₆PO₂₀EO₇₆) have recently been investigated for their ability to competitively adsorb with bile salts on the oil-water interface, where their large PEO blocks act as a steric barrier and the PPO blocks cover the interface well [319]. Pluronics F127 and F68 also were studied for their ability to decrease surface tension between olive oil and water, towards the goal of controlling the digestion rate of lipids for “designer” foods [320].
The adsorption of PEO-PPO-PEO block copolymers onto nanoparticles can enhance microemulsion stability and also give them an element of tunability [40, 321, 322]. Aqueous emulsions with vinyl acetate (VAc), silica nanoparticles, and one of three different PEO-PPO-PEO block copolymers showed that the VAc droplet size depended strongly on the block copolymer HLB and concentration, and system temperature [321]. Additionally, emulsion phases were produced at block copolymer concentrations below the cmc when nanoparticles were present. It was demonstrated that if the HLB of the stabilizing colloidal particles was reversed by modification with added organic solvent, then the emulsion could be reversed (i.e., from oil-in-water to water-in-oil) [323]. Pluronic F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) adsorption on ZnO nanoparticles also showed the synergistic effect in reducing the surface tension between oil (n-decane) and water [324]. These combined particle-block copolymer emulsions may play a significant role in the clean-up of oceanic oil spills, where they can form Oil-Mineral-Aggregates (OMA) in coastal areas [325]. There is potential synergism between OMAs and added chemical dispersants, but a better understanding of the complex interactions at play must be obtained [245, 326, 327]. PEO-PPO-PEO block copolymers also show promise for use as fixatives for the reparation of salty, loose-sand environments (e.g., over-farmed land). In such a case, the adsorbed amount of block copolymer and the emulsion stability are influenced by salts. Pluronic L35 (EO\textsubscript{11}PO\textsubscript{16}EO\textsubscript{11}) showed enhanced microemulsion stability in systems with sec-butyl alcohol, n-heptane, and brine, relative to SDS (Figure 2.24) [328]. This was determined by the width of the salinity range in which a middle-phase microemulsion was observed (60 and >70 g/L for SDS and L35, respectively).
2.5.3. Drug Delivery

There is intense scrutiny of PEO-PPO-PEO block copolymers for use in pharmaceutical and biomedical applications currently, owing to their low toxicity, adsorption properties, and tunable nature [24, 329-333]. Various PEO-PPO-PEO block copolymers have been investigated as drug delivery vehicles because of their amphiphilic character and relatively small hydrodynamic radii, which allow for easy adsorption and passage through membranes [334-337]. Though the drug storage capacity of amphiphilic micelles depends on factors such as drug type, amphiphile, and drug mixture ratio, the solubilized amount appears to track with the amphiphile HLB [334]. Thus PEO-PPO-PEO, because of its variable PEO/PPO ratio, will offer flexibility in selection of the appropriate block copolymer for a given drug. The use of Pluronic F127 (EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100}) as a gel-like printing ink for vascular networks has been recently investigated [338, 339]. This block copolymer was selected because of its low cell toxicity, its thermo-reversible gelation characteristics, and ability to organize into continuous structures on the target substrate. Pluronic F127 also stabilizes carbon nanotubes (an emerging technology in targeted drug delivery) in saline solutions by adsorbing with its hydrophobic PPO blocks and providing steric repulsion with its PEO blocks [250]. PEO homopolymers of 1500 and 35,000 Da were found not suitable for stabilizing the carbon nanotubes, owing to their less extended conformation [250].

PEO-PPO-PEO adsorption on nanoparticles for targeted drug delivery is attractive because of the opportunities presented by engineered nanoparticles [340]. The sensitivity of PEO-PPO-PEO conformation to temperature, and also its HLB, have been identified as useful levers in controlling drug release. Pluronic P123 (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}), conjugated with a 2,000 Da polyethyleneimine chain, acted as a “gate” which could house and then release drugs upon
decreasing the system temperature from 35 to 20 °C (over the cmt transition). The drug release corresponded to a change in the adsorbed layer structure (on Fe₃O₄ nanoparticles) from self-assembled structure to extended brush upon cooling at the target delivery site, thus allowing the drug to release (Figure 2.25) [341]. The HLB of the PEO-PPO-PEO block copolymers L61 (EO₂PO₃₁EO₂) and L64 (EO₁₃PO₃₀EO₁₃) was correlated to the cumulative release amounts of methylene blue (used as a drug analog) from Fe₃O₄ nanoparticle - 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) lipid bilayers [303]. L61, with its lower HLB value and longer PPO block, caused greater interference in the lipid bilayer, allowing the methylene blue to escape more easily. Specifically, a four-fold lower cumulative release was observed for L64, which is the more hydrophilic of the two Pluronics considered in this study [303]. A summary of the roles which PEO-PPO-PEO block copolymers play in coatings, emulsions, and drug delivery applications is given in Table 2.2.
2.6. Conclusions

In this review we have discussed several key facets of PEO-containing amphiphile adsorption on the solid-liquid interface. As a baseline, fundamentals of polymer adsorption borne from theory and modelling were discussed. The adsorption of PEO homopolymers on various interfaces was then reviewed to serve as a control for the discussion of PEO-containing amphiphiles, which comprise diverse chemical groups and thus represent more complex adsorption properties. PEO is a ubiquitous polymer which, when part of their chemical molecular structure, enables surfactants and block copolymers to adsorb on many types of surfaces with tunable adsorbed layer structures. The solvophilic-solvophobic dual nature of PEO-containing amphiphiles allows for fine tuning of the adsorbed layer structure by rather simple methods. The layer structure resulting from such manipulation directly impacts the micro- and macro-phase system properties. Thus, such systems are tunable, especially to external stimuli, allowing for the design of “smart” systems. PEO-containing amphiphiles, especially PEO-PPO-PEO-type [342-344], tend to be low in toxicity, making them suitable for use in biotechnological applications. The major topics covered in this review are: (i) thermodynamics of adsorption for general homopolymers and block copolymers; (ii) the adsorption mechanism and properties of PEO homopolymers; (iii) the adsorption mechanism and isotherm of PEO-containing amphiphiles; (iv) surface characteristics (chemistry, geometry) and additives which modulate the adsorption properties of PEO-PPO-PEO block copolymers; (v) the adsorption of modified PEO-containing amphiphiles (those with different hydrophobic groups or unique architectures); and (vi) applications which benefit from the adsorption properties of PEO-PPO-PEO block copolymers.
PEO homopolymers are much less amphiphilic than the PEO-containing amphiphiles reviewed here. However, the differences in interfacial behavior which result from the reduced amphiphilic character make for a useful contrast to the amphiphiles and especially PEO-PPO-PEO block copolymers. The common mechanism of adsorption between PEO homopolymers and PEO-containing amphiphiles also makes the study of PEO homopolymers sensible, as does the wide variety of applications which rely on PEO homopolymers for their function. The adsorption kinetics of PEO homopolymers are relatively fast, on the order of minutes even for high molecular weight (several hundred thousand Da) chains, and are characterized as mass-transport limited. The adsorbed amount and structure of PEO homopolymers on the solid-liquid interface are highly dependent upon the surface chemistry and the polymer molecular weight. PEO homopolymers will tend to adopt flatter conformations when the attachment mechanism is hydrogen bond formation between PEO ether oxygens and a hydrophilic substrate. Adsorption on hydrophobic surfaces such as latex occurs through hydrophobic interactions and generally results in larger hydrodynamic thicknesses and adsorbed amounts, as the polymer adopts conformations with higher adsorbed loop fractions than train fractions. For PEO ~ 150 kDa adsorbing from water, the adsorbed amounts and hydrodynamic layer thicknesses were 1.5 and 0.7 mg/m$^2$ and 120 and 102 nm on hydrophobic latex and hydrophilic silica, respectively [126]. Unlike strong amphiphiles, PEO homopolymers adsorb in simple train-loop-tail configurations on the solid-liquid interface.

Nonionic PEO-containing amphiphiles express diverse solution and adsorption properties. In aqueous solution, polymer chains will self-assemble into micellar structures in order to reduce unfavorable segment-solvent interactions. The morphology of the ordered structures can be tuned
by the addition of organic solvents, which further alter the intermolecular interactions between the assembling chains and solution. At low concentrations, PEO-PPO-PEO block copolymers adsorb in a train-loop-tail configuration on the solid-liquid interface. In a fashion similar to PEO homopolymers, the adsorbed amount depends strongly on the surface chemistry. For example, Pluronic P75 (EO\textsubscript{23}PO\textsubscript{35}EO\textsubscript{23}) plateau adsorbed amounts on hydrophobic polystyrene and hydrophilic silica particles in water were found to be 7 [168] and 0.2 [175] mg/m\textsuperscript{2}, respectively. The formation of loops on hydrophobic surfaces is responsible for the large disparity in adsorbed amounts. On both hydrophilic and hydrophobic surfaces, PEO blocks extend outward into the aqueous solution and contribute significantly to the adsorbed layer thickness. The PEO blocks act as the attachment point on hydrophilic surfaces; the PPO segments are the attachment point on hydrophobic surfaces.

Above the csmc, PEO-PPO-PEO chains will preferentially self-assemble into aggregates on the particle surface at a concentration known as the csmc. This behavior, which is markedly different than that observed for PEO homopolymers, presents itself as a jump in the adsorption isotherm below or near the cmc or cmt of the amphiphile in plain solvent. The self-assembly is also associated with a change in the hydrodynamic layer thickness. A diversity of systems in which PEO-PPO-PEO adsorption occurs, measured by various different methods (e.g., DLS, AFM, SANS) have revealed that the block copolymer surface aggregates closely resemble the structure and size of PEO-PPO-PEO micelles formed in plain solvent. Factors which alter the interactions between polymer segment-surface-solvent can be utilized to modulate adsorption properties, including the concentration at which self-assembly of PEO-PPO-PEO occurs on a surface (the csmc). Increasing the amount of area available for adsorption results in a decrease in the csmc
(observed, e.g., for the Pluronic P105-aqueous protonated silica system csmc, which decreases from 0.20 to 0.02 wt% as the nanoparticle concentration increases from 0.01 to 0.10 wt%) [166]. Similarly, increasing particle curvature reduces the csmc, as adsorbing chains have greater lateral configurational entropy [166]. The presence of additives, including organic solvents, PEO homopolymers, and mono- and divalent salts, impact the organization of PEO-PPO-PEO molecules on surfaces by simultaneously changing the surface and bulk solution properties.

Adsorption of PEO-containing amphiphiles also occurs on soft interfaces, including the air-liquid and liquid-liquid interfaces. The primary benefit of the preferential location of these molecules on liquid-liquid interfaces is to reduce the surface tension, thereby stabilizing immiscible phases. PEO homopolymers tend to adsorb as 2-D monolayers on the air-liquid interface, building surface pressure until a plateau is reached, corresponding to about 0.35 mg/m$^2$ [148]. Beyond this, entropy losses due to unfavorable chain constriction result in collapse of the layer. PEO-PPO-PEO block copolymers also strongly adsorb on the air-water interface, but their adopted configuration is comparably more complex. At low concentrations, PEO-PPO-PEO adsorbs in an extended configuration, which gives way to an inverted “U” shape at higher concentrations, as the PPO block attempts to reduce contact with aqueous solvent [78]. PEO-PPO-PEO block copolymers also adsorb on the oil-water interface. Poloxamers 188 (EO$_{106}$PO$_{68}$EO$_{100}$) and 407 (EO$_{76}$PO$_{29}$EO$_{76}$) adsorbing on the perfluorodecaline-water interface were found by SANS to adsorb with both the PEO and PPO blocks attached to the interface. The adsorbed layer thickness of Poloxamers 407 and 108 were found to be about 16 and 5 nm, respectively, indicating again the importance of long PEO tails to the layer thickness [265]. The adsorption properties of PEO homopolymers and PEO-PPO-PEO block copolymers are illustrated in Figure 2.26.
PEO-containing amphiphiles offer a high degree of flexibility because of their amphipathic nature. Differences in block affinity allow them to be compatible with numerous solvents and also surface types. Their highly tunable mesoscale ad-layer structures allow for usage in the stabilization of coatings, emulsification of oils, and for precise controlled release of hydrophobic medications. Addressing demands in new and existing applications requires improved knowledge of specific polymer segment-particle-solvent interactions, such that guidelines for formulating novel materials may be suggested. Further understanding of the adsorption properties of PEO-PPO-PEO block copolymers will allow for expansion in fields including oil spill dispersion [245], drug delivery [22, 67], and synthesis of functionalized nanoparticles [21].

Acknowledgments

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Figure 2.1. Adsorption isotherms of PEO homopolymers adsorbing from water onto macroporous silica gel at 25 °C. PEO molecular weight: (+) 20,000, (Δ) 100,000, (○) 600,000, and (⊕) 4,000,000. The adsorbed amount (y-axis, mg/m²) rises steeply with the polymer bulk concentration (x-axis, g/kg). Longer homopolymers achieve greater adsorbed amounts [131]. Reprinted with permission from ref [131]. Copyright 1993 American Chemical Society.
Figure 2.2. Desorption of pre-adsorbed PEO homopolymers (tagged with a fluorescent marker) in self-exchange studies on silica glass using TIRF. The legend, at right, indicates the molecular weight (Da) of the PEO homopolymers. The value Tau-50 indicates the time when half of the tagged PEO homopolymer has been removed from the surface by competing untagged PEO [123]. Reprinted with permission from ref [123]. Copyright 2001 American Chemical Society.
Figure 2.3. Adsorption isotherms of PEO homopolymer of various molecular weights adsorbing onto silica nanoparticles (10 nm diameter, silica particle concentration 0.1g/10mL) from water at room temperature [130]. Reprinted from ref [130], Copyright 2008, with permission from Elsevier.
Figure 2.4. The surface excess of (Δ) $\text{C}_{16}\text{EO}_8$ and (◆) $\text{C}_{14}\text{EO}_6$ on an oxidized silicon wafer at pH 6 and 24 °C obtained by optical reflectometry. Top panel: surface excess in units of mg/m$^2$. Bottom panel: surface excess in units of μmol/m$^2$. The logarithmic x-axis represents the surfactant concentration as a fraction of its cmc in plain water [158]. Reprinted with permission from ref [158]. Copyright 2010 American Chemical Society.
Figure 2.5. Adsorption isotherms of three PEO-PPO-PEO triblock copolymers. P65 (EO$_{19}$PO$_{29}$EO$_{19}$) (○), F68 (EO$_{76}$PO$_{29}$EO$_{76}$) (●), P105 (EO$_{37}$PO$_{56}$EO$_{37}$) (▼), and three nonionic PEO-containing surfactants UCON 50-HB-400 (R-PO$_{10}$EO$_{13}$) (■), UCON 50-HB-660 (R-PO$_{13}$EO$_{17}$) (■), and UCON 50-HB-5100 (R-PO$_{33}$EO$_{44}$) (▲), where R represents a butyl group, on polypropylene in water as determined by QCM-D. Adsorbed amounts before rinsing (a) and after rinsing (b) are shown. The rinse step serves to remove loosely bound amphiphiles from the surface. The bulk amphiphile concentrations on the x-axis are normalized to the cmc of each amphiphile. Temperature 25 °C, flowrate 0.1 mL/min [169]. Reprinted from ref [169], Copyright 2015, with permission from Elsevier.
Figure 2.6. The change in relative viscosity with increasing nanoparticle volume fraction as measured by capillary viscometry in aqueous dispersions of protonated silica (10.6 nm) containing Pluronic P105 (EO$_{37}$PO$_{56}$EO$_{37}$) at 20 °C. The change in relative viscosity becomes significantly more rapid (and positive) as the PEO-PPO-PEO concentration rises above the cmc [166].
Figure 2.7. The adsorbed layer thickness, estimated from QCM-D, of Pluronic F127 (EO_{100}PO_{65}EO_{100}) adsorbing from aqueous solution on surfaces of varying hydrophobic character. Large values of the water contact angle indicate hydrophobic surfaces [180]. Reprinted with permission from ref [180]. Copyright 2009 American Chemical Society.
**Figure 2.8.** Schematic of the adsorbed conformation of PEO-PPO-PEO block copolymers below the csmc at (a) hydrophilic and (b) hydrophobic surfaces, and (c) above the csmc at hydrophobic surfaces.
Figure 2.9. Schematic of a model that fits SANS data well for the adsorption of Pluronic F127 (EO$_{100}$PO$_{65}$EO$_{100}$) on SWCNTs in water at a temperature below the cmc of F127 in water. $R_{\text{core}}$ is the radius of the SWCNT bundle, $R_g$ is the radius of gyration of adsorbed polymers, and $N_{\text{agg}}$ is the aggregation number (the number of F127 molecules in a micelle). Pluronic F127 adsorbs with PPO blocks on the SWCNT interface, while the PEO blocks are well solvated and extend into the solution [190]. Reprinted with permission from ref [190]. Copyright 2011 American Chemical Society.
Figure 2.10. The ratio $c_{smc}/c_{cmc_0}$ of Pluronic P105 (EO$_{37}$PO$_{56}$EO$_{37}$) is plotted against nanoparticle wt% (top panel), calculated number of nanoparticles per liter of water (middle panel), and nanoparticle surface area per liter of water (bottom panel) for (●) 10.6 nm (SM), (▲) 16.6 nm (HS), and (■) 26.0 nm (TM) diameter protonated silica nanoparticles at 22°C [166]. Reprinted from ref [166], Copyright 2013, with permission from Elsevier.
Figure 2.11. Schematic of the influence of decreasing particle curvature (increasing radius) on the adsorbed layer conformation of PEO-PPO-PEO block copolymers in aqueous solution. As the particle radius decreases (illustrated at left), the block copolymers can reach laterally to adsorption sites, resulting in a lower adsorbed thickness. Increasing the particle radius leads to a more extended polymer conformation (illustrated at right) [54].
Figure 2.12. The cmc of Pluronic P105 (EO₃₇PO₅₆EO₃₇) in the presence of (●) 0.01 wt% and (▲) 0.1 wt% protonated silica nanoparticles (10.6 nm diameter), and the cmc of Pluronic P105 (■), are plotted against the organic solvent concentration in various water-organic solvent mixtures at 22 °C [208]. Reprinted from ref [208], Copyright 2013, with permission from Elsevier.
Figure 2.13. The adsorbed layer thickness of Pluronic P105 (EO\textsubscript{37}PO\textsubscript{56}EO\textsubscript{37}) adsorbing from water onto protonated silica nanoparticles (10.6 nm diameter) at 20 °C is influenced by the amount and type of added organic solvent: glycerol, DMF (dimethylformamide), and DMSO (dimethylsulfoxide). At zero or low added organic solvent concentrations, Pluronic P105 molecules self-assemble on the silica surface. As more solvent is added, Pluronic P105 is displaced from the particle surface and forms micelles in the bulk solution [208].
**Figure 2.14.** Schematic of the adsorbed layer configuration resulting upon addition of short PEO homopolymers (200 and 600 Da) and Pluronic P105 (EO\(_{37}\)PO\(_{56}\)EO\(_{37}\)) block copolymer to aqueous dispersions of protonated silica nanoparticles (10.6 nm diameter) at 20 °C. The added PEO homopolymer results in a slightly depressed layer thickness and heterogeneous surface comprising adsorbed PEO-PPO-PEO micelle-like aggregates and PEO homopolymers compared to dispersions with no additives [229].
Figure 2.15. (a). The surface excess amount (SDS and Pluronic F108 [EO$_{132}$PO$_{50}$EO$_{132}$] co-adsorbing) on silica wafers in water decreases as the SDS concentration increases. This occurs due to increasing electrostatic interactions. The amount of SDS required for total desorption is modulated by the ionic strength. (b). The adsorbed amount of SDS / F108 aggregates is enhanced at low SDS concentration and high ionic strength. Shaded bars on each ordinate indicate the adsorbed amount at all ionic strengths of pure Pluronic F108 adsorbing from water. (○) 0.10 mM, (▽) 10 mM, and (■) 150 mM NaCl. [232]. Reprinted with permission from ref [232]. Copyright 2001 American Chemical Society.
Figure 2.16. The adsorbed amount of PEO homopolymer 100 kg/mol on colloidal silica (40 nm diameter) in water (no temperature stated) at 1 mM concentration of added salts: (x) No salt, (Δ) NaCl, (□) CaCl₂, (◊) MgCl₂, and (○) LaCl₃ [254]. Reprinted with permission from ref [254]. Copyright 2006 American Chemical Society.
Figure 2.17. The surface pressure, measured by the Wilhelmy plate method, of Pluronic F68 (EO$_{76}$PO$_{29}$EO$_{76}$) in water with added Li$^+$ cation. The effect of added salt is to increase the adsorbed amount by modulation of the surface structure via coulombic interactions [261]. Reprinted from ref [261], Copyright 2013, with permission from Elsevier.
Figure 2.18. The relative volume fraction of Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) micelles (defined as the volume of fraction of micelles in the presence of ethanol to the volume fraction of micelles in the absence of ethanol) in aqueous solution with added oil and ethanol determined by SANS at 35°C. (x) pure polymer, (■) 0.5 DCB/polymer ratio, (○) 0.5 TMB/Polymer ratio. In the absence of oil, the effect of ethanol is to decrease the micelle volume by rendering the solvent more hydrophilic. When oil is present, the ethanol decreases the surface tension between water and oil, allowing micelles to form at slightly lower block copolymer concentrations [270]. Reprinted with permission from [270]. Copyright 2005 American Chemical Society.
Figure 2.19. The adsorbed layer thicknesses of PEO-PTHF-PEO block copolymers adsorbing onto hydrophobic (“h-silica”) and hydrophilic (“silica”) silica wafers from water at 25 °C measured by ellipsometry [165]. Pn – m denotes the number of segments in EO_{n/2}THF_mE_O_{n/2}. Reprinted with permission from ref [165]. Copyright 1998 American Chemical Society.
Figure 2.20. AFM height images of PNIPAm\textsubscript{110}-F127-PNIPAm\textsubscript{110} adsorbed on hydrophobic gold at temperatures of (a) 20 °C, (b) 31 °C, (c) 34 °C, and (d) 40°C. The height profile displayed (at right of each AFM image) corresponds to the region indicated by the solid line on the AFM image. Below the LCST of both PPO and PNIPAm, the adsorbed layer structure is smooth and flat. As the LCST increases above that of PPO (31 °C) and finally to that of PNIPAm (34 °C), as pictured in (c) and (d), globular assemblies are observed coating the gold surface. The ordering becomes more well-defined at higher temperature [277]. Reprinted from ref [277], Copyright 2012, with permission from Elsevier.
Figure 2.21. AFM images of $\text{EO}_{316}\text{PO}_{94}$ adsorbed on silica and mica from solutions of varying block copolymer concentration at 23 °C [280]. Aggregates of about 33 nm diameter were observed on silica. Micelle-like spherical aggregates grew on the hydrophilic mica interface. The diameter of the spherical aggregates was highly dependent on the AFM tip frequency. Reprinted with permission from ref [280]. Copyright 2004 American Chemical Society.
Figure 2.22. Schematics of the adsorbed layer configuration of the asymmetric triblock copolymer \( \text{EO}_{208}\text{PO}_{69}\text{EO}_{2} \) spin-coated onto hydrophilic silica from toluene solution. The different panels correspond to initial block copolymer concentrations of (a) 1 g/L, (b) 2 or 3 or 3.4 g/L, (c) 3.6 or 4 g/L, and (d) 4.5 g/L. The films were allowed to anneal and dry at 45 °C prior to inspection with AFM [301]. Reprinted with permission from ref [301]. Copyright 2014 American Chemical Society.
Figure 2.23. The plateau adsorbed layer thickness of various PEO-PPO-PEO block copolymers on (○) silica, (□) latex, and (△) a PDMS droplet, plotted versus the number of EO units per PEO block. The layer thicknesses were determined by electrokinetic measurements at 25 °C. Reprinted with permission from ref [262]. Copyright 2001 American Chemical Society.
Figure 2.24. Microemulsions of (a) SDS / sec-butyl alcohol / n – heptane / brine and (b) Pluronic L35 (EO$_{11}$PO$_{16}$EO$_{11}$) / sec-butyl alcohol / n – heptane / brine at 318 K. Both amphiphiles achieve optimum solubility of oil and brine in application ranges relevant to ecological restoration of salt- and oil-laden areas [328]. Reproduced from ref [328] with permission from the Royal Society of Chemistry.
Figure 2.25. The adsorption of Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) conjugated with a 2,000 Da poly(ethyleneimine) chain onto magnetite nanoparticles can act as a drug carrier with a temperature-modulated “gate.” Modulation of the system temperature causes the Pluronic adsorbed layer conformation to change, allowing for timely release of hydrophobic drugs [341]. Reprinted with permission from ref [341]. Copyright 2007 American Chemical Society.
Figure 2.26. Schematic summarizing the adsorption of PEO homopolymers and PEO-PPO-PEO block copolymers on various surfaces
<table>
<thead>
<tr>
<th>Surface Type</th>
<th>PEO Homopolymers</th>
<th>PEO-Containing Amphiphiles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrophobic Solid-Liquid Interface</strong></td>
<td>· Adsorption via CH₂-CH₂ backbone to surface</td>
<td>· Adsorption via hydrophobic moieties (e.g., alkyl chain, block)</td>
</tr>
<tr>
<td></td>
<td>· High affinity, Langmuir adsorption isotherms which generally scale with Mw</td>
<td>· High affinity Langmuir isotherms observed below cmc</td>
</tr>
<tr>
<td></td>
<td>· Loops and tails are prevalent</td>
<td>· Single chain adsorption below cmc, with formed PEO brush extending into solution</td>
</tr>
<tr>
<td></td>
<td>· Adsorbed amounts are increased due to growth of loops and tails</td>
<td>· Increased adsorbed amounts at lower amphiphile HLB values</td>
</tr>
<tr>
<td></td>
<td>· Hydrodynamic layer thicknesses are enhanced due to loops and tails</td>
<td>· Step change increase in adsorbed amount and hydrodynamic layer thickness near the cmc which generally scales with Mw</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Above cmc or cmt self-assembled aggregates form at the interface</td>
</tr>
<tr>
<td><strong>Hydrophilic Solid-Liquid Interface</strong></td>
<td>· Adsorption via hydrogen bonding of ether oxygens to surface</td>
<td>· Adsorption via hydrogen bonding of PEO ether oxygens with surface</td>
</tr>
<tr>
<td></td>
<td>· Langmuir adsorption isotherms which generally scale with Mw</td>
<td>· Langmuir adsorption isotherms observed below cmc</td>
</tr>
<tr>
<td></td>
<td>· Trains more prevalent than large loops and tails</td>
<td>· Single chain adsorption below cmc, low layer thicknesses due to flat conformation; both PEO and hydrophobic moiety segments near the surface</td>
</tr>
<tr>
<td></td>
<td>· Decreased adsorbed amounts owing to flat conformations</td>
<td>· Step change increase in adsorbed amount and layer thickness above cmc which generally scales with Mw</td>
</tr>
<tr>
<td></td>
<td>· Hydrodynamic layer thicknesses reduced due to flat conformations</td>
<td>· Above cmc, micelle-like aggregates form on the surface</td>
</tr>
<tr>
<td><strong>Air-Liquid Interface</strong></td>
<td>· Adsorption via CH₂-CH₂ backbone</td>
<td><strong>PEO-PPO-PEO Only</strong></td>
</tr>
<tr>
<td></td>
<td>· Flat adsorption profile at interface at low concentrations</td>
<td>· Adsorption occurs via hydrophobic moiety (e.g., PPO block for PEO-PPO-PEO block copolymers)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Decrease in surface tension with adsorbed</td>
</tr>
</tbody>
</table>
· An inverted “U” shape forms at higher adsorbed concentrations as surface pressure increases due to steric repulsion
· Near 0.35 mg/m² entropy is minimized and monolayers collapse leading to maximized extension of homopolymer into aqueous phase
· Amount to a constant value which marks the cmc (two breaks observed in surface tension vs. concentration plot)
· Block copolymers lay flat at interface at low concentrations
· Structural rearrangement of layer into ordered, inverted “U” – shapes as concentration increases (PEO blocks extending into solution) prior to the cmc
· Adsorbed area per molecule scales ~ $N_{EO}^{1/2}$

<table>
<thead>
<tr>
<th>Liquid-Liquid Interface</th>
<th>PEO-PPO-PEO Only</th>
</tr>
</thead>
<tbody>
<tr>
<td>· Adsorption at oil-water interface via CH₂-CH₂ backbone</td>
<td>· Adsorption at oil-water interface via PPO blocks, with PEO forming an extended brush</td>
</tr>
<tr>
<td>· Reduced adsorbed layer thickness in comparison to amphiphiles</td>
<td>· Oil type determines penetration depot of PPO into oil phase, which determines adsorbed layer configuration (deeper penetration results in more extended PEO brush)</td>
</tr>
</tbody>
</table>

**Table 2.1.** General properties of adsorption on solid-liquid, air-liquid, and liquid-liquid interfaces for PEO homopolymers and PEO-containing amphiphiles, including PEO-PPO-PEO block copolymers.
<table>
<thead>
<tr>
<th>Application</th>
<th>Block Copolymer Function</th>
<th>Adsorption Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Coatings</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paints</td>
<td>· Enhanced stability of aqueous pigment dispersions for improved color and shelf-life via steric repulsion</td>
<td>· Low bulk concentrations (e.g., 0.5 w/v% [296])</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Adsorption to hydrophobic pigments via PPO block, with PEO blocks extending out into solution to form a well-hydrated brush</td>
</tr>
<tr>
<td>Nanopatterned surfaces</td>
<td>· Microphase separation of polymer blocks into different domains at an interface (ordered structures with varying range) for e.g., localizing nanoparticles</td>
<td>· Adsorbed block copolymer layer structures can be modulated by the bulk solution concentration</td>
</tr>
<tr>
<td>e.g., thin films, 3D ordered dispersions)</td>
<td></td>
<td>· Single bilayers (thin films) form at low concentrations (e.g., &lt; 1.0 g/L [301])</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Intermediate concentrations (e.g., 2 – 3.4 g/L) lead to thick, lamellar thin film structures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· High concentrations (e.g. 4.5 g/L) lead to single, entangled, densified, bilayer</td>
</tr>
<tr>
<td>Anti-fouling</td>
<td>· Form steric barrier around particle to mitigate against adsorption of undesirable cosolutes (e.g., proteins, salts)</td>
<td>· Protein or bacteria adsorption is reduced as the PEO-PPO-PEO concentration approaches the cmc</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· PEO-PEO-PEO of high Mw and high PEO/PPO ratios inhibit adsorption of proteins and bacteria most effectively due to large PEO blocks which form a steric barrier</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Hydrophobic surfaces allow construction of a well-hydrated PEO brush (adsorption of block copolymer via PPO blocks)</td>
</tr>
<tr>
<td><strong>Emulsions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solubilization and dispersion of oily products in water</td>
<td>· Solubilize oil droplets and provide steric stabilization against coalescence, creaming, etc.</td>
<td>· Plateau adsorbed layer thicknesses increase with increasing PEO/PPO ratio</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Adsorption via PPO block, which can penetrate into the oil droplet; deeper penetration depths achieve higher layer thicknesses due to steric repulsion</td>
</tr>
<tr>
<td><strong>Drug Delivery</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drug delivery vehicles</td>
<td>· House drugs for transport through lipid layers</td>
<td>· Ramping of temperature above the cmc causes conformational change of adsorbed</td>
</tr>
<tr>
<td>· Release drugs via structural transitions at different temperatures</td>
<td>layer from extended (“open”) to micelle-like (“closed”)</td>
<td></td>
</tr>
<tr>
<td>· Higher PPO/PEO ratios disrupt lipid-bilayer configuration to higher degree allowing for passing of PEO-PPO-PEO drug delivery vehicles</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.2.** Function conferred by PEO-PPO-PEO block copolymers to applications in coatings, emulsions, and drug delivery.
Chapter 3

Competitive Adsorption Between PEO-Containing Block Copolymers and Homopolymers at Silica

Chapter 3 Abstract

The ability to manipulate polymer adsorption is useful for applications involving colloidal stabilization, e.g., paints, cosmetics, lubricants, and mineral and waste-water treatment. We have an on-going interest on the use of organic molecules for modulating the aqueous solution and adsorption properties of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) block copolymers. In the present study, the influence of low molecular weight PEO homopolymer on the adsorption of a representative PEO-PPO-PEO block copolymer (Pluronic P105: EO_{37}-PO_{56}-EO_{37}) on the surface of protonated silica nanoparticles dispersed in water is investigated. Pluronic P105 forms hydrophobic domains on the surface of protonated silica at a critical surface micelle concentration, c_{smc}, of 0.02 wt% in the presence 0.1 wt% silica nanoparticles in water, well below the cmc of Pluronic P105 in water (0.6 wt%). Dye solubilization experiments reveal an increase in the PEO-PPO-PEO block copolymer critical surface micelle concentration with increasing amounts of added PEO homopolymer. The resulting critical displacer concentration, c_{dc}, for PEO homopolymer of molecular weights 200 and 600 Da was measured to be 0.1 wt% and 0.07 wt%, respectively, in the presence of 0.1 wt% silica nanoparticles. Capillary viscometry measurements indicate a decrease in the adsorbed layer thickness at the protonated silica surface with increasing PEO homopolymer concentration. The data presented herein are consistent with a physical model which considers “patches” of PEO-PPO-PEO block copolymer and PEO homopolymer adsorbed on the silica surface.
3.1. Introduction to Chapter 3

Polymer-particle interactions play an important role in the design of products and processes. Relevant examples include paints [1], dairy products [2], drug delivery carriers [3, 4], wastewater treatment [5], mineral processing [6, 7], and nanoparticle synthesis [8, 9]. Many of the dispersed particles in these examples are lyophobic and thus predisposed to coalescence and aggregation [10]. However, the introduction of polymers can serve to prevent detrimental aggregation via steric or electrostatic repulsion [11-14].

Poly(ethylene oxide) (PEO) is a nonionic water-soluble polymer that is commercially available in a broad range of molecular weights [15]. PEO is an important constituent of many nonionic surfactants and block copolymers. Amphiphilic block copolymers containing PEO are well-known for their ability to self-assemble into a variety of morphologies under selective solvent conditions [11]. The concentration at which these block copolymers and other surfactants begin to self-organize in solution is known as the critical micelle concentration (cmc) [14]. In systems where particles are present, these functional polymers will start organizing on the particle surface at a concentration known as the critical surface micelle concentration (csmc) [16-18]. PEO-PPO-PEO block copolymers, commercially available as Pluronics or Poloxamers, are a well-studied family of water soluble polymers that exhibit surface active properties [19]. Pluronics derive their amphiphilic behavior from the central hydrophobic poly(propylene oxide) (PPO) block. In an aqueous environment, Pluronics form micelles which have a PPO core and a hydrated PEO corona; the opposite occurs in an oil-dominated environment [20, 21]. The micellization behavior of these molecules has been well characterized [21, 22].
PEO homopolymers and PEO-containing amphiphiles will adsorb on surfaces under favorable thermodynamic conditions [18, 23] with kinetics playing a role [24]. Several factors, including solvent temperature and quality, polymer molecular weight, ratio of hydrophilic block size to hydrophobic block size, and substrate size, are known to influence the nature of adsorption [25-30].

The introduction of displacers into particle dispersions is a method for modulating the free energies associated with adsorption. Displacers are additives which cause desorption of (and replace) molecules from surfaces [31, 32]. The concentration at which a competitive molecule has completely displaced another from a surface is known as the critical displacer concentration (cdc) [31]. Molecular additives introduce an additional degree of freedom into a system, increasing the number of interfacial interactions (e.g., solvent-displacer, particle-displacer, and polymer-displacer) that contribute towards the value of the cdc. Various polymers [31, 33, 34] and organic molecules [1, 35-37] have been shown to be effective displacers of long-chain molecules from surfaces.

Generally, longer molecules lead to high adsorbed amounts and make for strong displacers. Char et al. demonstrated this in studying the competitive adsorption behavior of PEO homopolymers of varying length on colloidal silica [38]. Studies have also used displacers which are shorter or lower molecular weight than the adsorbate, and which rely upon differences in affinity to a particular surface, to cause displacement. Kling and Ploehn showed that a nonionic surfactant, Igepal 720 (~720 Da), displaces pre-adsorbed PEO homopolymer (100 kDa to 600 kDa) from polystyrene particles [33]. The time-scale of such desorption was shown to be a function of PEO concentration and molecular weight. Specifically, when PEO homopolymer was introduced at
low concentration, which led to a more flattened surface conformation, the polymer was more
difficult to desorb. Higher molecular weight PEO molecules were difficult to desorb, due to the
larger number of contacts as well as chain entanglement [33]. These two themes were echoed in
the work by Chen et al. [35]. Van der Beek et al. used small organic molecules with a strong
surface selectivity in order to displace PEO homopolymer from silica in water [32]. Finally,
Postmus et al. have studied the use of various PEO-containing nonionic surfactants as displacers
of PEO homopolymer [39]. It was found that, as the surfactants and PEO have a similar affinity
for the hydrophilic silica wafers employed, a critical molar mass became the determining factor
in which surfactant could displace PEO of various molecular weights; this agreed with earlier
findings [31, 40].

Our group has recently reported on the effects of nanoparticle concentration, surface area, and
solution temperature upon the self-assembly of a representative PEO-PPO-PEO block copolymer
on the surface of silica nanoparticles dispersed in water [18]. We observed that the csmc is lower
than the cmc, reflecting dehydration of the anchoring micellar PEO blocks due to the hydrogen
bonding interaction with silica. We have also shown how the small organic molecules
dimethylformamide (DMF), dimethylesulfoxide (DMSO), and glycerol impact organization of
PEO-PPO-PEO chains on the silica surface and in bulk solution, acting as displacer agents [37].
At present, little work has been reported on systems where the displacer and adsorbate are of
similar selectivity to a particular surface, and, further to the point, of identifying displacers which
can both displace from a surface and impact the micellization behavior of amphiphilic molecules.

The model system utilized for the current study is an aqueous dispersion of protonated silica
nanoparticles stabilized by Pluronic P105 PEO-PPO-PEO block copolymer. PEO homopolymers
of varying number of EO units and concentration are introduced as competitive molecules. PEO is a commonly used additive which can serve as either a stabilizer or flocculent in several varying applications [41-43]. PEO homopolymer also shares an affinity [44] and adsorption mechanism with PEO-PPO-PEO block copolymer for oxide surfaces. Silica provides an attractive surface for both PEO-PPO-PEO and PEO homopolymer to adsorb on and thus allows for an opportunity to observe the displacer effect. Adsorption is driven for both PEO homopolymer [45] and PEO-PPO-PEO block copolymer [18, 22, 29] chains by hydrogen bond interactions between the ether oxygen of PEO and the silanol groups that dot the silica surface.

In what follows, results on the cmc, csmc, and adsorbed layer thickness, as obtained by fluorescence spectroscopy and capillary viscometry, respectively, are described. The observed phenomena are then interpreted in the context of a possible mechanism.
3.2. Materials and Methods

Pluronic P105 poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer, obtained from BASF and used as received, was used for this study. Pluronic P105 has a nominal molecular weight of 6500 Da, which corresponds to a central block consisting of about 56 PO units and 2 outer blocks of 37 EO units each. Poly(ethylene oxide) homopolymers of nominal molecular weight 200 and 600 Da (5 and 14 EO units, respectively) were obtained from Polysciences (Warrington, PA) and used as received. The root-mean-square end-to-end distance is about 2.3 nm and 2.6 nm, respectively, for PEO 200 and PEO 600 in water over the temperature range 0 - 100°C [46].

Ludox® SM-30 silica nanoparticles were obtained from Grace Davidson (Columbia, MD) as a gift. The silica particles as received were dispersed in water at pH~10 and are negatively charged (zeta potential -70mV [47]) and electrostatically stabilized. SAXS characterization of the nanoparticles indicates an average diameter of 10.6 nm and a relatively low polydispersity (0.16) [18]. All solutions examined here were made to pH ~ 3 to ensure that the silica nanoparticle surface silanol groups were protonated and available for hydrogen bond interactions with PEO.
3.3. Characterization

3.3.1. Sample Preparation

Aqueous PEO homopolymer solutions were first prepared, in concentrations ranging from 0 up to 1 wt% for fluorescence measurements and up to 5 wt% for viscosity measurements. Next, silica nanoparticles were mixed into the solutions, followed by addition of small amounts of hydrochloric acid to adjust the pH to approximately 3. Samples for viscosity experiments were completed by direct addition of Pluronic P105 to the appropriate PEO-silica stocks to achieve a total final Pluronic P105 concentration of 2 wt%. The concentration of PEO-PPO-PEO block copolymer was set at this level to ensure a micellar solution [22]. The samples were then allowed to equilibrate ~24 hours under rolling at room temperature prior to measurement. To prepare samples for fluorescence, a 1 wt% solution of Pluronic P105 was made by mixing the appropriate PEO-silica stock directly with P105. This additional stock was allowed to equilibrate for several hours and then used to dilute the PEO-silica stock to achieve total final Pluronic concentrations in the range of 0.001 – 5 wt%. These samples were allowed to equilibrate ~24 hours under rolling at room temperature. As has been shown before [34, 39], the sequence of polymer addition throughout sample preparation did not affect the final results.

3.3.2. Fluorescence Spectroscopy

Pyrene (Fluka, Switzerland) was used to measure the micropolarity of the prepared dispersions [48]. A Hitachi 2500 fluorescence spectrophotometer was used to record the emission intensities of the solubilized pyrene in the 340 – 460 nm range at 22°C. Pyrene, which is highly soluble in hydrophobic domains, emits five vibronic peaks. The ratio of the intensities of the first and third
peaks indicates the polarity of the local environment. Specifically, a decrease in the value of I₁/I₃ indicates decreasing polarity, and thus a growing presence of hydrophobic domains formed by the PEO-PPO-PEO block copolymer [48]. Values of I₁/I₃ plotted versus a logarithmic scale of Pluronic P105 concentration have been used to determine the cmc or csmc of each system (see Figure 3.1) [18, 37]. These plots resemble sigmoidal curves, the second inflection point of which is indicative of the formation of hydrophobic domains, and thus the cmc or csmc. In order to estimate the cmc and csmc values, two lines were drawn for each sigmoidal: one line through the apparent “down slope” and one through the apparent lower plateau region. For the system at hand, the intersection of these two lines is used to identify the cmc and csmc values. Interestingly, for a majority of systems with and without nanoparticles, the smallest addition of PEO homopolymer causes a slight reduction in I₁/I₃ values (approximately 0.01 – 0.1 units) as compared to values obtained for Pluronic P105 in aqueous solution (with or without nanoparticles). In most cases, the I₁/I₃ values for nanoparticle-containing Pluronic P105-PEO solutions and non-nanoparticle containing solutions become nearly identical at the maximum PEO homopolymer concentration tested (1 wt%).

### 3.3.3. Capillary viscometry

The adsorbed layer thickness on the nanoparticle surface is obtained by measuring the kinematic viscosities of PEO-containing silica-Pluronic dispersions. The layer thickness is accessible through calculation of the slope of relative viscosity versus the silica volume fraction [18, 37]. Sample viscosities were measured using Cannon-Fenske Routine – type viscometers and used to derive layer thickness as well as critical displacer concentrations, as discussed previously [18, 37].
3.4. Results and Discussion

3.4.1. Hydrophobic Domain Formation

In order to identify trends in cmc and csmc, plots of cmc or csmc versus PEO homopolymer concentration (Figure 3.2) were constructed from data obtained from Figure 3.1. Three notable features emerge from Figure 3.2. The first is that in the absence of nanoparticles, increasing the PEO 200 and 600 concentrations slightly impacts the micellization of the PEO-PPO-PEO block copolymer. The second feature is the decrease in csmc with increase in nanoparticle concentration. This occurs regardless of added PEO homopolymer molecular weight and concentration. A final characteristic is an increase in csmc values with increasing PEO homopolymer concentration up to a plateau, which is observable for both PEO 200 and PEO 600 and all nanoparticle concentrations examined.

A comparison of the effect of the PEO homopolymer on the csmc and cmc is useful in interpreting the displacer phenomenon. In Figure 3.2 it is apparent that neither the PEO homopolymer concentration nor its molecular weight, impact the measured cmc; plotting cmc versus PEO concentration results in a nearly flat line across the tested range. This lack of interaction in solution between PEO homopolymer and Pluronic P105 has been attributed to the fact that PEO homopolymers are readily soluble in water, and so are not solubilized by the hydrophobic micelle core (and only sparingly in the PEO-rich micelle corona) [49]. In aqueous dispersions of protonated silica nanoparticles, the PEO homopolymer concentration and molecular weight cause a change in the csmc. When no PEO homopolymer is present, the csmc is markedly lower than the cmc. The difference between cmc and csmc is a direct consequence of hydrogen bonding between PEO of the block copolymer and silanol groups on the protonated...
silica surface. Specifically, the hydrogen bond formation drives water away from the anchor PEO blocks, thereby decreasing their size and reducing stearic repulsion, which in turn lowers the free energy [18]. However, a sharp increase in the csmc occurs upon addition of PEO 200 or PEO 600 homopolymers. The csmc values climb toward cmc-like values until a plateau is reached. The beginning of the plateau region is identifiable as the critical displacer concentration (cdc) and, for the purpose of this study, represents the point at which the PEO homopolymer no longer impacts the PEO-PPO-PEO surface concentration.

The cdc values of the system being studied here may be estimated from the plateau regions shown in Figure 3.2. In the presence of 0.01 wt% protonated silica nanoparticles, the cdcs for PEO 200 and PEO 600 are ~ 0.07 and 0.05 wt%, respectively. As the nanoparticle concentration increases to 0.1 wt%, the cdc values increase to ~ 0.1 and ~ 0.07 wt% for PEO 200 and PEO 600, respectively. Overall, the trend observed is that the $cdc_{\text{PEO 600}} < cdc_{\text{PEO 200}}$. This implies that PEO 600 appears more effective in modulating the PEO-PPO-PEO block copolymer adsorption behavior than is PEO 200. Despite the 10-fold increase in nanoparticle surface availability, the cdc values increase only slightly (by approximately 4%). This could be indicative of co-adsorption of the PEO-PPO-PEO block copolymer and the PEO homopolymer, a scenario to be described later.

### 3.4.2. Polymer Organization on the Silica Surface

Adsorbed layer thickness data, obtained by capillary viscometry for systems where the concentration of Pluronic P105 in solution was well above the cmc and csmc, are plotted versus added PEO homopolymer concentration in Figure 3.3. In aqueous silica dispersions containing Pluronic P105, we have measured the adsorbed layer thickness to be about 15.7 nm [18].
According to Figure 3.3, the layer thickness on the silica nanoparticles decreases upon addition of just 0.002 wt% PEO, and then levels off to a value of about 12 nm for PEO 200 and 10 nm for PEO 600. The final layer thickness in both cases seems rather high given the apparent complete displacement of PEO-PPO-PEO block copolymer by PEO homopolymer that is indicated by fluorescence spectroscopy. Recall that in the absence of silica particles, the addition of PEO homopolymer has a slight effect on the cmc of the PEO-PPO-PEO block copolymer. However in the presence of silica, the csmc values are significantly impacted by the addition of PEO homopolymer. Below the plateau (cdc) observed in Figure 3.2, the csmc values increase sharply, intimating that the Pluronic P105 is being hindered from forming surface assemblies on the particle-liquid interface as more PEO homopolymer is added. Thus we would have expected a significant decrease in adsorbed layer thickness. However, this is not what we have observed in the case of low molecular weight PEO homopolymer (Figure 3.3). To explain the reason behind the discrepancy, we discuss three different scenaria: (i) complete displacement of PEO-PPO-PEO block copolymer from the silica surface by PEO homopolymer, (ii) transition from whole micelles [18] to hemimicelles by PEO-PPO-PEO block copolymer, and (iii) partial desorption of the block copolymer occurring at the solid-liquid interface, where some silanol sites are covered by PEO homopolymer and others are covered by PEO-PPO-PEO block copolymer assemblies.

First we analyze scenario 1 where we take PEO homopolymer to be completely displacing the Pluronic P105 from the silica surface. Bearing in mind that self-assembly for PEO-PPO-PEO block copolymers on silica occurs at lower concentrations than in the bulk solution due to hydrogen bonding and subsequent contraction of the PEO blocks due to dehydration, the increase in csmc values may be connected to an unavailability of hydrogen bonding (i.e., silanol) sites, which have been covered by the PEO homopolymer. Two sub-cases are possible, namely a
monolayer coverage or an extended (‘crew-cut’) coverage of PEO homopolymer on the surface. Though our observed adsorbed layer thickness is high, previous work has shown that the layer thickness is dependent upon adsorbed amount, with higher adsorbed amounts leading to more densely packed and extended chains [50]. It is possible to estimate the adsorbed amount of PEO by way of mass balance using cdc values. This calculation is based on the assumption that all PEO homopolymer in the system is adsorbed on the silica surface at the cdc – an assumption that will overestimate the adsorbed amount, as a large amount of PEO will likely remain in the bulk solution away from the particle surface. Completing this calculation reveals that 2.8 and 1.9 mg/m$^2$ of PEO 200 and PEO 600 were adsorbed when 0.1 wt% silica nanoparticles were present, respectively. Taking 0.16 nm$^2$ as the surface area covered by an EO unit [51] and taking the nominal surface area of 360 m$^2$/g of SM-30 nanoparticle, we find that just 0.46 mg/m$^2$ of PEO homopolymer are required to form monolayer coverage on SM-30 (assuming flat conformation). Since we have assumed that EO unit surface area is constant relative to molecular weight, only one theoretical monolayer coverage value is obtained. In reality, there would be a difference between the actual required adsorbed amounts, due to molecular weight influence on adsorption configuration, but this difference is likely miniscule between PEO 200 and PEO 600. The second possibility is that the homopolymer adopts an extended conformation. Rotational Isomeric State (RIS) models [46] have shown that a fully extended PEO 600 chain in water should stand to about 7 nm length. If the calculated adsorbed amount is indeed so high, the PEO homopolymer chains may be adopting the extended conformation. However, this case is less plausible for two reasons: one is the (likely) over-estimation of the adsorbed PEO amount, and the second is that the extended length of PEO 600 (the longest possibly reached) is still lower than the thickness value obtained by capillary viscometry.
The second scenario is the transition from whole to hemimicelles by the PEO-PPO-PEO block copolymer, considered here as a potential disturbance caused by added PEO homopolymer to the self-assembly of the Pluronic P105 block copolymer on the surface of protonated silica. The number of hemimicelles organized on the surface can be computed as the total projected surface area of a nanoparticle divided by the area per hemimicelle. Taking the SM-30 nanoparticle diameter of 10.6 nm and assuming a hemimicelle radius of 10 nm (so chosen from the adsorbed layer thickness data for PEO 600 homopolymer in Figure 3.3), we can fit an average of one hemimicelle on the particle surface, which represents approximately 5.9 mg/m$^2$ of Pluronic P105 on the nanoparticle surface. We have previously shown that 2 wt% Pluronic P105 forms an adsorbed layer thickness of 15.7 nm at a surface coverage of 8 mg/m$^2$ on SM-30 particles, [18] thus such a scenario seems plausible. However, a hemimicelle-type surface assembly would imply a large fraction of the PPO blocks being in direct contact with the hydrophilic silica surface. Such contact has been shown to be repulsive, according to a van Oss analysis of the surface free energy [18]. On the other hand, PEO-silica contact is favorable (also by the van Oss approach). Finally, it is conceptually difficult to imagine one hemimicelle per particle. Thus, the formation of hemimicelles is considered unlikely.

The third scenario is that complete desorption of the PEO-PPO-PEO block copolymer is not occurring, and the observed thickness is an average over adsorbed PEO-PPO-PEO assemblies and PEO homopolymer. Displacement occurs because of specific free energy changes between block copolymer, displacer homopolymer, and solvent, as well as special affinities for the adsorbing surface. However in our system, Pluronic P105 and the PEO homopolymers [52] share nearly the same affinity for the surface. As explained above, we have previously [37] used the van Oss analysis [53] to quantify the affinity of PEO, PPO, and water for the silica surface. The
analysis suggests that PEO experiences an attraction to silica whereas PPO does not (-1.1 mJ/m$^2$ versus 5.5 mJ/m$^2$ for PEO and PPO, respectively, for total combined free energy of apolar and polar interfacial interactions). Being that both the block copolymer and homopolymer share an affinity with silica, adsorption will be dictated by molecular weight [38, 53]. Here there are a few trade-offs to consider. The drivers for the PEO-PPO-PEO block copolymer adsorption include longer, anchoring, PEO blocks, as well as reduced solubility in water as compared to the short PEO homopolymer. From an entropic standpoint, the block copolymer fairs much better upon adsorption than the homopolymer, owing to the larger number of bonds around which it may rotate. However, the short PEO homopolymers may have greater “sticking” power, due to the fact that each EO unit is expected to adsorb to the silanol groups in the dilute regime [54]. This balancing act could lead to a heterogeneous particle surface: smaller block copolymer assemblies and patches where only PEO homopolymer is adsorbed. A schematic of the patch model is given in Figure 3.4.

The literature does not offer much guidance regarding co-adsorption between non-interacting macromolecules which share an affinity to a given surface. Postmus et al. carried out sequential as well as simultaneous adsorption experiments for various molecular weight PEO homopolymers and PEO-containing nonionic surfactants on hydrophilic silica wafers [39]. By tracking the surface excess after rinsing the silica with a pure component or a mixture, and then by rinsing with solvent, they could determine the effects of molecular weight and cmc on adsorption. Two simultaneous addition experiments showed that neither the surfactant nor the polymer could be completely desorbed after solvent rinsing. However it was unclear what the surface structure was (i.e., surfactant adsorbed to polymer, patches, etc.). Interestingly, they did observe that rinsing the “hybrid layer” silica with one of the pure components would lead to that
component dominating the surface [39]. Ghodbane et al. studied the competitive adsorption of various PEO homopolymers and two different PEO-containing nonionic surfactants and found that a critical molar mass exists which dictates whether PEO homopolymer or surfactant would adsorb [40]. They describe a mode of adsorption which involves coexistence of surfactant aggregates and homopolymer on the surface. However after some time, the more weakly attracted species would desorb from the surface, as a function of molecular weight [40].

Finally, while cdc values are very similar, PEO 600 appears to outperform PEO 200 when cdc is the metric. An assignable cause for the advantage that PEO 600 carries could be the following. PEO 200 and PEO 600 are very similar in size and both are expected to adopt a flat surface conformation and to pay similar entropic energy penalties. The greatest difference in their spontaneous adsorption would then be the number of particle-segment contacts that occur, which is greater for PEO 600. This is in agreement with the fact that adsorption scales up with the degree of polymerization [53, 54].

3.4.3. Comparison with Other Displacers

The data presented here suggest a partial displacement of Pluronic P105 PEO-PPO-PEO block copolymer by PEO homopolymer. In this light we can draw comparison to other displacers, glycerol, dimethylformamide, and dimethylsulfoxide, which our group has previously studied [37]. Using the mass-balance method and assumption of complete desorption of Pluronic P105 from silica that we used above, we find the following for 0.1 wt% nanoparticle concentration: PEO 600 can displace 4.11 mg Pluronic P105 per mg of PEO 600, while PEO 200, glycerol, DMSO, and DMF displace 2.88, 0.058, 0.029, and 0.014 mg Pluronic P105 per mg displacer, respectively. The displacers are compared on a mole fraction basis in Figure 3.5a. PEO 200 and
PEO 600 data are plotted against EO mole fraction, which is an equivalent way of plotting layer thickness versus attachment points for the homopolymer to the silica. From this plot it is evident that glycerol and DMSO are most effective and very similar in their ability to disrupt PEO-PPO-PEO organization on the particle surface. Finally, for very similar mole fractions, all three organic solvent molecules cause greater decreases in the layer thickness than the PEO homopolymer, intimating that they experience a greater affinity to the silica surface. Indeed, the free energy of adsorption for these organic solvent molecules at silica was found to be greater than that for PEO at silica [37]. On a weight percent basis, the story is slightly different, as shown in Figure 3.5b. In this case, glycerol appears to lower the adsorbed layer thickness at lower concentrations compared to all other additives.

By the fluorescence data / mass-balance comparison, it would appear that the two PEO homopolymers are much stronger displacers than the small organic solvents. While the term “displacer” may not be most appropriate in the case of PEO homopolymers, since complete removal of the PEO-PPO-PEO block copolymer is not occurring, low molecular weight PEO homopolymers still act as modifiers for adsorption and organization of PEO-PPO-PEO block copolymer at the silica surface.
3.5. Conclusions

The adsorption of polymers on particles is of practical importance to numerous industrial and natural applications, including mineral processing, paper-making, and various foodstuffs. Developing an understanding of how to manipulate polymer adsorption is thus an important undertaking. We have evaluated the use of PEO homopolymers as potential displacer agents which could control interfacial and bulk solution properties of PEO-PPO-PEO block copolymers.

The influence of PEO homopolymer upon Pluronic P105 PEO-PPO-PEO block copolymer organization on the protonated silica-water interface is to increase the csmc, up to a plateau, which is identified as the critical displacer concentration. Based on the cdc values and plateaus, PEO 600 and PEO 200 appear to influence the interfacial free energy of adsorption for PEO-PPO-PEO block copolymer to an equivalent degree. It is important to note that addition of PEO homopolymer in any of the concentrations tested here has a negligible effect on the micellization of PEO-PPO-PEO block copolymers in water.

Despite the elimination of hydrophobic domain formation upon addition of PEO homopolymer, the observed decrease in the adsorbed layer thickness is not commensurate with complete displacement of the PEO-PPO-PEO block copolymer from the surface. A scenario of a heterogeneous silica surface, covered by patches of PEO homopolymers and PEO-PPO-PEO block copolymers, is consistent with the experimental observations discussed here. While this is in contrast to many studies which have discussed competitive adsorption between the same homopolymers of different molecular weight [38, 55-57] and between PEO homopolymers and PEO-containing surfactants [33, 34], reports exist which have identified a heterogeneous surface mixture [39] as a mechanism of adsorption and desorption.
Acknowledgments

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Figure 3.1. Pyrene fluorescence emission intensity $I_1/I_3$ 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.
Figure 3.2. 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.
Figure 3.3. 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%).
Figure 3.4. Schematic of the heterogeneous “patch” model. PEO homopolymer, PEO-PPO-PEO chains, and PEO-PPO-PEO assemblies can be found on the silica surface. Some chains of PEO homopolymer and the PEO-PPO-PEO block copolymer remain in solution, away from the surface. PEO-PPO-PEO micelles also exist in solution.
Figure 3.5. Adsorbed layer thickness versus (a) mole fraction and (b) weight percent of additive (displacer) for aqueous dispersions of 10.6 nm protonated silica nanoparticles, Pluronic P105, and additive, at pH ~ 3. The decrease in adsorbed layer thickness is indicative of displacement suppression of PEO-PPO-PEO block copolymer surface assemblies by the following additives: glycerol (▲), dimethylformamide (●), dimethylsulfoxide (■), PEO 200 (◄), and PEO 600 (►).
Chapter 4

Mono- and Divalent Salts as Modifiers of PEO-PPO-PEO Block Copolymer Interactions with Silica Nanoparticles in Aqueous Dispersions

Chapter 4 Abstract

Colloidal stabilization of nanoparticle dispersions is central to applications including coatings, mineral extraction, and dispersion of oil spills in oceanic environments, which often involves oil-mineral-aggregates (OMAs). We have an ongoing interest in the modulation of amphiphile micellization and adsorption behavior in aqueous colloidal dispersions in the presence of various additives. Here we evaluate the effect of added salts CaCl2, MgCl2, and NaCl on the micellization and adsorption behavior of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic P105 (EO37PO56EO37). In 0.10 wt% silica nanoparticle (10.6 nm average diameter) dispersion, adsorbed block copolymer layer formation begins at a critical surface micelle concentration (csmc) of 0.02 wt%, well below the critical micellization concentration (cmc) of Pluronic P105 in water. Dye solubilization experiments demonstrate an increase in the csmc upon addition of each salt. Each added salt reaches a level of maximum effectiveness in its ability to disfavor Pluronic P105 adsorption on the silica surface. These peak levels occur at concentrations of 0.005, 0.03, and 0.05 M for CaCl2, MgCl2, and NaCl, respectively, in the presence of 0.10 wt% silica nanoparticles. We explain these results in the context of an electrostatic displacer mechanism and discuss possible connections to OMA-dispersant formation.
### 4.1. Introduction to Chapter 4

Polymers which comprise one or more chemically-different groups have a tendency to adsorb on various interfaces, including solid/liquid and liquid/liquid [1, 2]. The observed surface activity is a matter of the polymer solubility and specific interactions between the polymer and interface. Block copolymers, which comprise chemically-different polymer blocks in the same chain, are of wide-spread interest to industrial and academic research [3, 4]. Block copolymers often exhibit amphiphilic behavior as the solvent affinity of each block is typically different. This allows them to adsorb in complex configurations on solid/liquid interfaces, as well as to decrease the surface tension along oil/water interfaces in a manner analogous to low molecular-weight surfactants [2, 5]. Block copolymers are useful in multi-interface, multi-component systems, including coal flotation separation [6], ink dispersions [7, 8], and cosmetics formulations [9]. Building knowledge around interfacial behavior is thus important for the development of nanostructured materials and products which are tunable by environmental properties (i.e., temperature, pH).

The behavior of block copolymers with dispersed particles in the presence of various additives is also relevant to oil spill dispersion. The various chemical treatments applied to oceanic oil spills contain surfactants and polymers which hasten the breakup of oil slicks into droplets by reducing the surface tension between oil and water [10]. At the same time, the formation of oil-mineral aggregates (OMAs), composed of dispersed oil droplets and clay or silica particles [11, 12], occurs spontaneously through an aggregation method attributable to electrostatic interactions between the particles and polar compounds in oil [10]. The OMAs can be considered as a form of Pickering emulsion, where finely divided oil droplets are stabilized by particles. If sediment is
available, and the turbulence (mixing) of salt-water, oil, and particles is sufficient, OMA formation can be an effective means to clean oil-coated shorelines [13]. Ultimately the oil fate depends on a variety of factors, including the local weather, oil type and viscosity, particle type and size, ocean temperature, salinity, and the presence of dispersants. The nonionic and ionic dispersants utilized in oil spill cleanup, in addition to interacting with the oil / water interfaces, can also conjugate with available mineral-oil complexes, leading to the formation of dispersant-laden OMAs, also known as dirty marine snow. While dispersants aid OMA formation by breaking the oil into smaller droplets [10], their association with OMAs can also lead to the sedimentation of undesirable chemicals onto the seabed, and thus the ecosystem. Changes in density (through variation of aggregate size) can also lead to the formation of oil-laden OMAs which do not settle, but rather sink to a given depth beneath the ocean surface and then move about with currents.

Amphiphile adsorption on solid/liquid and liquid/liquid interfaces represents a critical process in dispersant-OMA aggregate formation. Thus understanding how environmental variables can influence adsorption in such systems is useful. Ultimately the nature of adsorption can be devolved into a discussion on the free energy of adsorption, or enthalpy and entropy, and how these are influenced by changing environmental conditions. A fundamental concept in the regulation and characterization of adsorption is the use of displacers. This concept may be interpreted in terms of segmental adsorption energies ($\chi_s$) and critical adsorption energies ($\chi_{sc}$) [14]. Macromolecules can adhere to a surface provided the segment/surface contact free energy is more favorable than the surface/solvent contact free energy. By adding a second molecule to the system which competes for surface sites with the macromolecule, the adsorption of the macromolecule can be modulated. A critical point exists, known as the critical displacer
concentration (cdc), where all of the adsorbed macromolecules have been replaced by the more energetically favorable displacers [14-16]. Detailed information pertaining to interaction energies and specific molecular affinities are highlighted through such an exercise. A variety of displacers may be used, such as polymers and surfactants [14, 16-18] as well as organic molecules [19, 20].

Non-ionic, poly(ethylene oxide) (PEO) - containing block copolymers are widely used and studied because of their interfacial activity and commercial availability [3, 21]. Their amphiphilic nature allows them to adsorb with different conformations on various interfaces, including air/liquid, liquid/liquid, and solid/liquid. Recently, our group has considered the adsorption properties of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO$_x$-PO$_y$-EO$_x$) triblock copolymers, commercially available as Pluronics® or Poloxamers. We have found that PEO-PPO-PEO adsorbs on silica nanoparticles in dilute aqueous solution under acidic conditions, via hydrogen bond formation between the ether oxygen of poly(ethylene oxide) and silanol (Si-OH) groups on silica nanoparticles [22]. Above a certain critical surface micelle concentration (csmc) the PEO-PPO-PEO chains will self-assemble on the particle surface to form a layer similar in thickness and microenvironment to micelles that form in solution in the absence of dispersed particles [23]. The csmc is considerably lower than the critical micelle concentration (cmc) of the PEO-PPO-PEO block copolymer in aqueous solution and can be modulated by pH, temperature, and particle size and concentration [22]. We have also found that the addition of small, polar organic molecules, including glycerol, dimethyl sulfoxide (DMSO), and dimethyl formamide (DMF), disfavor the adsorption of PEO-PPO-PEO block copolymers onto silica nanoparticles [24]. The smaller molecules enjoy a lower free energy of adsorption than the larger polymers, resulting in nearly complete impediment to adsorption of the block copolymers as reflected in an identifiable cdc for each displacer. The cdc is dependent on particle
concentration, or equivalently, the available adsorption area. PEO homopolymer chains will also compete with PEO-PPO-PEO block copolymers for adsorption sites on the silica surface. However, due to the small difference in the adsorption free energy between short PEO (200 and 600 Da) and the longer PEO-PPO-PEO block copolymer (6500 Da), a heterogeneous surface layer of both the homopolymer and block copolymer forms on the silica nanoparticles [25].

The study reported herein demonstrates how mono- and divalent salts influence the adsorption of PEO-PPO-PEO block copolymers onto silica particles dispersed in water. We have selected this system as an initial approximation to the environment of chemical dispersants in the ocean, where dissolved salts and clay and silica particulates are abundant. We first present the role of dissolved salts on the micellization behavior of PEO-PPO-PEO block copolymers, and then describe the influence of salt on the adsorption behavior of PEO-PPO-PEO. We compare three mechanisms by which the added salts may be influencing the adsorption behavior. Finally, a discussion of cloud point and precipitation data reveal phenomena occurring in our model system which highlight its potential for further study of OMA-dispersant interactions.
4.2. Materials and Methods

4.2.1. Materials

Ludox® SM-30 silica nanoparticles were obtained from Grace Davidson (Columbia, MD) as a gift. The silica particles as received are dispersed in water at pH~10 and are negatively charged (zeta potential -70 mV [26]). The nanoparticles were previously characterized using small-angle X-ray scattering, which indicated a 10.6 nm average diameter and a polydispersity of 0.16 [22]. Pluronic P105 poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer, obtained from BASF (Vandalia, IL) and used as received, was utilized as a model dispersant for this study. Pluronic P105 has a nominal molecular weight of 6500 Da, and consists of a central block of 56 PO units and two end-blocks of 37 EO units each. We chose three chloride salts for study: sodium chloride (EMD, Gibbstown, NJ), calcium chloride dihydrate (Fisher Scientific, Fair Lawn, NJ), and magnesium chloride hexahydrate (J.T. Baker, Center Valley, PA). Each salt was used as received. All solutions were prepared using MilliQ-treated deionized water (18 mΩ).

4.2.2. Sample Preparation

Aqueous salt-nanoparticle dispersions were prepared by first mixing the silica nanoparticles into deionized water at pH of approximately 3, so adjusted by the addition of hydrochloric acid. This was followed by introduction and mixing of the salt into the dispersion until fully dissolved. The salt-particle dispersions were prepared in salt concentrations ranging from 0.001 – 0.5 M and nanoparticle concentrations of 0.01 and 0.10 wt%. The salt concentration range covered here passed up to and beyond the calcium, magnesium, sodium, and chloride ion concentrations in
artificial seawater [27]. The salt-particle stock solutions were then used to create a 1 wt% solution with Pluronic P105, which was allowed to equilibrate under rolling for several hours. Finally, the 1 wt% Pluronic P105 stock solution was diluted with the appropriate salt – nanoparticle stock to achieve solutions with concentrations ranging from 0.001 – 5 wt% Pluronic P105. These samples were left under rolling for several hours at room temperature prior to testing by fluorescence.

The introduction of nanoparticles into the salt-polymer aqueous solution results in an increase in the number of competing interactions and also a reduction in the system colloidal stability. For polymer-salt-particle stocks with high salt and/or silica nanoparticle concentrations, precipitation onto the glass walls of the vials and eventual phase separation was observed. We endeavored to produce polymer-bearing stocks as low as 0.25 wt% Pluronic P105, but some level of precipitation persisted. While this introduces some uncertainty in our reported salt and nanoparticle concentrations, it should not affect the results and conclusion drawn in this work. In order to minimize the impact of possible dispersion instability on our reported results, polymer-bearing stocks were utilized as soon as possible, samples were measured within 24 hours of being produced, and each sample was rotated end-over-end multiple times prior to filling the sample cuvette.

4.2.3. Cloud Point

The cloud point (CP), recorded here as a function of Pluronic P105 concentration rather than temperature, was noted for each silica – salt dispersion combination at six P105 concentrations ranging from 0 - 5 wt%. The cloud point was defined (visually) as the onset of turbidity. Any precipitation observed on the walls of the glass vials in which the polymer-salt-particle samples
were stored was also recorded. The nanoparticle-salt dispersions (no added PEO-PPO-PEO) were resistant to coagulation, likely due to the strong hydration layer surrounding the protonated silica particles.

4.2.4. Fluorescence Spectroscopy

Pyrene (Fluka, Switzerland) was used to probe the micropolarity of the prepared dispersions [28]. A Hitachi 2500 fluorescence spectrophotometer was used to record the emission intensities of the solubilized pyrene in the 340 – 460 nm range at 22°C. Pyrene, which is highly soluble in hydrophobic domains, emits five vibronic peaks, the ratio of the intensities of the first to third peaks of which indicates the polarity of the local environment. Low values of $I_1/I_3$ indicate decreased polarity, interpreted as hydrophobic domain formation by the PEO-PPO-PEO triblock copolymer [28]. Values of $I_1/I_3$ plotted versus the logarithm of Pluronic P105 concentration have been used to determine the cmc and csmc of each system (see Figure 4.1) [22, 24]. The resulting plots are sigmoidal, and the second inflection point of the curve is indicative of the formation of hydrophobic domains, and thus the cmc or csmc [25]. In order to extract the cmc and csmc values, two lines were drawn for each sigmoidal plot: one line through the apparent “down slope” and one (horizontally) through the apparent lower plateau region. We have taken the intersection of these two lines as the cmc and csmc values. It should be noted that the cmc and csmc transition occurs over a range of amphiphile concentrations, which are centered about our reported values [21].
4.3. Results and Discussion

4.3.1. Impact of Salts on Hydrophobic Domain Formation in Water

Plots of pyrene I/I₃ ratio versus the logarithm of Pluronic P105 concentration are displayed in Figure 4.1. Across the top row of Figure 4.1 (in the absence of nanoparticles), the influence of salt type and concentration can be observed on the PEO-PPO-PEO self-assembly in aqueous solution. The effect of each salt is to cause a slight increase in the cmc followed by a significant decrease as the salt concentration is increased. To make these changes more apparent, we have extracted cmc and csmc data from Figure 4.1 and plotted them in Figures 4.2 and 4.3, which show the trend in cmc and csmc versus the chloride anion and salt molar concentrations, respectively. The decrease in cmc begins at lower salt concentrations for CaCl₂ and MgCl₂ (~0.03 M) than for NaCl (~0.08 M). At the highest salt concentration tested, 0.50 M, cmc values of 0.02, 0.04, and 0.10 wt% P105 were found for CaCl₂, MgCl₂, and NaCl – bearing solutions, respectively. Taken together, these data indicate that the divalent salts are modifying the micellization process of PEO-PPO-PEO more drastically than the monovalent salt.

The spontaneous micellization of PEO-PPO-PEO block copolymers in water has been attributed to a negative entropy contribution to the micellization free energy [29]. This outweighs a positive enthalpic contribution, a penalty which is associated with packing of the PPO chains into the micelle core and rearrangement of PEO groups into the micelle corona. Typically, factors including larger PPO segments, higher molecular weights, and increased temperatures, on their own or in combination, lower the cmc of PEO-PPO-PEO [29]. The addition of certain salts to aqueous solutions of PEO-PEO-PPO has been shown to decrease the critical micellization temperature (cmt), cmc, and CP. The exact mechanism by which solvated ions modify PEO-
PPO-PEO micellization is not completely resolved, but it seems to follow from the Hofmeister series. Ions, depending on their ionic radius and valence, will act as “structure-makers” or “structure-breakers” with respect to the water structure [30]. Strong hydrogen bonds formed between water molecules are responsible for water structure, and this network can be either enhanced or disrupted depending on the presence of ions. The Hofmeister series, which orders cations and ions in terms of their ability to “salt-out” or “salt-in” proteins in water, is an analogous concept to structure-breakers and –makers. The impact of a structure-making ion is to strengthen the water structure and thereby reduce the hydration of the dissolved solute. Structure-breakers enhance the hydration of the solute.

The dehydration mechanism of salt-induced reduction in critical micellization temperatures is still unclear, but has been argued to be a product of thermodynamic interactions between ions, water, and polymer. In the case of Pluronic L64 (EO13PO30EO13), the enthalpy of micellization was observed to increase with addition of NaCl, while the cmt decreased [31]. This indicates that the entropy of micellization must increase, perhaps driven by the release of ions bound near the polymer during the unimer-to-micelle transition [31]. On the other hand, water can be removed from hydrated PEO blocks due to the depletion of salt ions between the PEO block and the salt-concentrated bulk solvent. The depletion occurs because of a difference in polarity between the salt ion and bound water, and the low polarizability of the PEO block, resulting in repulsion between the two. As PEO blocks approach each other, water molecules constrained in the PEO hydration layer are expelled to the salt-concentrated bulk solution, where they enjoy higher entropy [32]. The removal of water from the PEO blocks leads to an increased attractive interaction between the PEO blocks, thus promoting micellization [33].
The influence of structure-breaking and –making ions has been discussed in several studies which evaluate cmc, cmt, and CP data for a variety of aqueous PEO-PPO-PEO block copolymer – salt combinations. In two independent publications which measure the influence of salts on Pluronic L64, the order of effectiveness of ions in terms of their ability to reduce the cmt and CP ranked as follows: Cl\(^-\) > Br\(^-\) [31, 34] and Na\(^+\) > K\(^+\) > Li\(^+\) [31]. In the case of Pluronic F127 (EO\(_{100}\)PO\(_{65}\)EO\(_{100}\)), Na\(^+\), Cl\(^-\), SO\(_4\)^{2-}, and PO\(_4\)^{3-} were all effective at reducing the cmt and CP, an effect attributed to their structure-making properties and thus ability to dehydrate the PPO and PEO segments of F127 [35]. The addition of KCl to semi-dilute (5 and 10 wt%) aqueous solutions of Pluronic P84 (EO\(_{19}\)PO\(_{39}\)EO\(_{19}\)) shows a marked increase in both aggregation number and spherical micelle (hydrophobic) core size, owing to dehydration of the EO-based micelle corona [36]. In all of the aforementioned cases, anions of smaller ionic radii are found more effective in their ability to suppress the cmt and CP of aqueous PEO-PPO-PEO block copolymer solutions. However, ordering cation effectiveness is not as straightforward, as the ion radius rule does not always work [31]. That being said, the authors of ref. 31 do point out that Li\(^+\) is a very strongly hydrated cation, and thus may have a larger effective radius in water than can be deduced from the periodic table, explaining its diminished effect in comparison to larger cations.

To make clearer the influence of the cations and anions in our system, we plot the cmc versus chloride concentration for each added salt in Figure 4.2. Presenting the cmc data normalized to chloride concentration accounts for the fact that, on a salt molar basis, MgCl\(_2\) and CaCl\(_2\) bear twice as many chloride anions per mole of salt. Figure 4.2 reveals a gentler decrease in slope for NaCl in comparison to the other two salts, which indicates that the cation radius may still be playing an important role and that the observed difference is not simply due to a difference in the number of anions present at the same salt concentration. A comparison between Ca\(^{2+}\) and Mg\(^{2+}\)
yields little difference in the required amount of cation to decrease the cmc. This can be attributed to the similarity in size (and likely hydration shell size) between the two cations.

4.3.2. Influence of Salts on Hydrophobic Domain Formation on the Silica Surface

A notable feature of Figure 4.1 is a shift of the second inflection point in the sigmoidal $I_1/I_3$ curves to lower PEO-PPO-PEO concentrations upon introduction of silica nanoparticles. Put another way, the formation of micelle-like surface aggregates with hydrophobic domains occurs at lower concentrations of PEO-PPO-PEO block copolymers than for the formation of micelles in plain water. The decrease in PEO-PPO-PEO block copolymers required for the formation of hydrophobic domains on the particle surface has been attributed to the enthalpically favorable hydrogen bond formation between the ether oxygen of the Pluronic P105 chain PEO groups and silica silanol groups [22]. As the surface area available for adsorption increases, the free energy of micellization decreases, driven by the increasing number of bonds formed [22].

Another feature of nanoparticle-bearing dispersions in Figure 4.1 is the change in the location of the second inflection point of each sigmoidal curve upon addition of salt. This indicates that the added salts are modulating the adsorption and surface self-assembly process of PEO-PPO-PEO block copolymers. In order to understand the impact of salt on the adsorption of Pluronic P105 onto the protonated silica, it is useful to track the progression of csmc values as the amount of salt in the dispersion is increased (see Figure 4.3).

For dispersions containing 0.01 wt% silica nanoparticles, the general trend for each added salt is to cause a sharp and significant increase in the csmc until a well-defined maximum is reached. After this maximum, there is a long, sloping decrease in the csmc. In the cases of CaCl$_2$ and
MgCl₂, this decrease continues below the csmc value measured at 0 M of added salt, indicating that the dissolved ions have become the dominant factor in controlling the formation of hydrophobic domains. The maximum values of csmc and corresponding added salt concentrations can be used as a means to compare the effectiveness of each salt at modulating the hydrophobic domain formation of PEO-PPO-PEO on the silica surface. For 0.01 wt% dispersions, the maximum csmc values are: 1.0 wt% at 0.03 M, 0.9% at 0.05 M, and 0.6% at 0.08 M for CaCl₂, MgCl₂, and NaCl, respectively. In the case of 0.10 wt% silica nanoparticle dispersions, a significant increase in the csmc is again observed upon addition of salt, followed by a less steep decay in values. This time all three salt types display a csmc at 0.5 M of added salt that is similar to the csmc obtained for the same dispersion without added salt. The max csmc and corresponding salt concentrations for each salt at 0.1 wt% silica nanoparticles are: 0.5 wt% at 0.005 M, 0.15 wt% at 0.03 M, and 0.25 wt% at 0.05 M, for CaCl₂, MgCl₂, and NaCl, respectively. The significant difference for the peak csmc values between 0.01 wt% and 0.10 wt% silica nanoparticle dispersions is further evidence for the reduction in free energy of surface micelle-like domain formation caused by the increased amount of particle surface area available for adsorption.

The presence of a maximum in the csmc versus salt concentration plots for all of the salt-particle dispersion pairings indicates that the self-association of PEO-PPO-PEO chains is initially being discouraged. Put another way, the free energy of hydrophobic domain formation is increasing. From this perspective, we can consider the salt concentration which corresponds to the peak csmc value for a given system to be the critical displacer concentration (cdc). For the purpose of this manuscript, we adapt the definition of the cdc to indicate the point at which the growth of hydrophobic domains at the particle surface has ceased. The cdc values for each salt-type are
recorded in Table 4.1. If we use the cdc values to compare the efficiency of each salt at altering the surface assembly and micellization of PEO-PPO-PEO, then we can rank them as $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl}$. This is consistent across both nanoparticle concentrations considered here (and is also in agreement with results for PEO-PPO-PEO aqueous solutions in the absence of nanoparticles). It should be noted that interpretation of the data for the 0.10 wt% SM nanoparticle – NaCl system was difficult, due to colloidal instability of the system.

We consider three different mechanisms as possible causes for the increase in csmc upon addition of salt. One is the binding of cations to the silica surface, which would interfere with the ability of the Pluronic P105 PEO blocks to form hydrogen bonds with the silica surface (i.e., a displacer competition mechanism) [37, 38]. The surface charge of colloidal silica has been shown to be close to zero below $\text{pH} \approx 4$ even in the presence of dissolved salts [39]. A neutral charge of the silica surface at low pH when salts are present indicates the possibility that some positively charged and also negatively charged sites exist on the silica surface [40], and that ion-exchange between the dissolved cations and anions and the hydrogen atoms of the silanol groups can take place [41]. Additionally, the binding to silica of several types of cations has been demonstrated to be energetically favorable, and so this could be taking place in our system [41].

It is interesting to note that the free energy of the metal-silica bond formation follows the order $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ [41]$, with $\text{Ca}^{2+}$ representing the most favorable free energy. This may explain why, on a cdc basis, $\text{Ca}^{2+}$ is more disruptive than the other cations tested.

A second mechanism could be a direct impact of the salt anions and cations on the micellization thermodynamics of the PEO-PPO-PEO block copolymer. As mentioned earlier, the presence of small amounts of NaCl increases the enthalpy penalty associated with self-assembly of PEO-
PPO-PEO block copolymers [31], which serves to increase the micellization free energy and delay the micellization onset. In the limit of zero nanoparticle concentration, the release of polymer-bound ions to the bulk upon self-assembly of block copolymer chains would effectively reduce the entropy penalty that occurs when the PPO blocks are constrained to the micelle core. However, a competing medium for the ions in our system are the protonated surface of the silica nanoparticles. If some of the ions are adsorbed on the silica surface, the expected increase in entropy would be diminished, compared to if the ions were able to move about freely in the bulk aqueous environment. This would result in an increase in the cmc values as salt is added.

A third potential explanation for the increase in cmc upon salt addition is the binding of cations to the PEO blocks of the PEO-PPO-PEO chains via specific affinity to the ether oxygen [42], which may interfere with the formation of hydrogen bonds and can also result in electrostatic repulsion between polymer chains and the silica surface, even if a small amount of cations and counter ions have adsorbed on the silica surface. This PEO-ion affinity has been observed for NaCl [43] and calcium- and magnesium thiocyanates [44]. The salt binding power of PEO and PEO-based alkyl derivatives increases with the number of EO units [44] and so can be expected to be quite large for the case of the much higher molecular weight Pluronic P105. An illustration of the cation binding effect is given in Figure 4.4. Cations replace hydrogen atoms on the silica silanol sites, and repel PEO-PPO-PEO chains, which can be expected to have a nontrivial number of cations adsorbed along the PEO segments. This causes a situation where the PEO-PPO-PEO chains and the silica particles experience some electrostatic repulsion, and in sum a displacer-type mechanism is at work. Beyond the cdc, the influence of structure-making ions on the solvent quality for PEO-PPO-PEO becomes dominant, and contributes to a reduced free energy of surface assembly and also micellization in the bulk solvent.
As noted earlier, in 0.01 wt% silica nanoparticle systems the csmc values for CaCl$_2$ and MgCl$_2$ are lower at 0.5 M salt concentration than at 0 M salt concentration, while the csmc is more similar at both salt concentrations in the case of NaCl. This trend at the 0.01 wt% particle condition is likely explained by a cosolvent effect. Specifically, as the salt concentration increases beyond the cdc, the solvent quality that the PEO-PPO-PEO block copolymer experiences due to free ions reaches such a poor state that adsorption becomes increasingly favorable. This effect has been observed before for aqueous PEO-colloidal silica systems containing various salts, including NaCl, CaCl$_2$, and MgCl$_2$, where not only the polymer adsorbed amount increases but the apparent polymer affinity to the surface does too, as evidenced by a linear increase in slope of the adsorption isotherm with solution ionic strength [45]. At 0.10 wt% particle loading, the csmc values for CaCl$_2$ and MgCl$_2$ experience less of an upward shift and recover the “starting” csmc at the maximum salt concentration considered (0.5 M). The apparent weaker effect of the salt at the high nanoparticle concentration could be due to greater cation/anion uptake by the particles, as a result of the increased particle surface area. This may lead to a slightly improved solvent quality and thus less favorable adsorption energy (i.e., a higher csmc). As a final comment, the more disruptive behavior of the divalent cations compared to the monovalent cation regarding the surface hydrophobic domain formation, in addition to more favorable silica-cation bond formation, could be explained by the larger charge density and size of the divalent cations (in a fashion similar to that observed for the influence of anions on PEO-PPO-PEO micellization [31]).

Comparison of cdc values from dye solubilization experiments allows us to assess the ability of different displacers to modulate the formation of surface hydrophobic domains by PEO-PPO-PEO on silica nanoparticles. In the context of other additives that we have evaluated using the
dye solubilization technique, the three salts of interest here rank in-between the homopolymers PEO 200 (EO\textsubscript{5}) and PEO 600 (EO\textsubscript{14}) \cite{25} and the three polar solvents glycerol, DMF, and DMSO \cite{24}. PEO 600 is the most influential with respect to molar concentration and this manuscript’s working definition of the cdc (concentration where csmc is at a maximum). The required molar concentration of each additive to attain cdc at the 0.01 and 0.10 wt\% nanoparticle loadings are given in Table 4.2. The results make sense conceptually. In the case of PEO homopolymers, we observed that a small amount of the homopolymer is required to partially disrupt PEO-PPO-PEO surface aggregate formation, due to a competition between the EO groups of the homopolymers and the PEO-PPO-PEO block copolymers for silanol sites. The net result is a heterogeneous surface coverage on the silica particles \cite{25}. Unlike a dissolved ion or even a small polar molecule (glycerol, DMF, DMSO), which all share an affinity for the silica surface, the homopolymers can consume many more available adsorption sites per added molecule. An interesting point to note is that, for added PEO homopolymer and small polar molecules, the required amount to achieve cdc increases as the nanoparticle loading increases. This stems from the fact that, if more surface sites are available, then more additive will be consumed by the surface. For all three tested salts the cdc either decreased or remained the same upon increasing from 0.01 to 0.10 wt\% dispersed particles: CaCl\textsubscript{2} required 50\% less, NaCl required 38\% less, and MgCl\textsubscript{2} required the same amount of salt, to achieve cdc despite the particle amount increase. This effect could be related to more rapid aggregation of the nanoparticles due to charge screening, and supports our belief that mechanism three is the better explanation of the displacer mechanism, i.e., some cations adsorb at the silica surface (and also at the PEO blocks of Pluronic P105), disfavoring PEO-PPO-PEO adsorption, but simultaneously hastening phase separation of the dispersion.
4.3.3. Interpretation of Cloud Point and Precipitation

We observed samples visually for cloud point across the PEO-PPO-PEO concentration range at a fixed temperature. In the case of 0.10 wt% silica nanoparticles, salt-particle-polymer dispersions rapidly became turbid (but not opaque) even at low Pluronic P105 concentrations (> 0.005 wt% P105), with MgCl₂ and NaCl forming the cloudiest samples. In 0.01 wt% silica dispersions across the entire examined salt concentration range (0 – 0.5 M): CaCl₂ samples were clear across the entire examined Pluronic P105 concentration range; MgCl₂ and NaCl samples showed the onset of turbidity at Pluronic P105 concentrations greater than ~ 3.0 wt% Pluronic P105. The appearance of a (likely) salt-polymer-particle precipitate on the glass walls of the sample tubes was observed for all 0.10 wt% silica dispersions, in addition to complete phase separation within 1-2 days. In 0.01 wt% silica dispersions, added CaCl₂ caused little-to-zero precipitate growth, followed by MgCl₂ and then NaCl. In all cases at 0.01 wt% silica nanoparticles, the precipitate growth was minor.

Two causes are likely for the colloidal instability inherent to this system. First is the reduction in aqueous solubility of the PEO-PPO-PEO block copolymer upon addition of salt. As the water structure is enhanced, the hydration of the PEO segments is reduced, resulting in a significant decrease of the critical solution temperature. Secondly, the silica nanoparticles, which in the absence of salt and polymer are stabilized by a strong hydration layer at low pH, are electrostatically screened at higher salt concentrations (when cations may exchange with the hydrogen atoms of the silanol groups). The PEO-PPO-PEO block copolymer, which is driven to the surface of the silica nanoparticles at high salt concentrations, could hasten particle aggregation and sedimentation via polymer bridging. The formation of OMAs, though not well
understood, is presently attributed to the aggregation of oil and clay/silica particulates mediated by ions [10]. The precipitation of salt-polymer-silica that we have observed at salt concentrations similar to those in the ocean may be evidence of an electrostatic mechanism which results in the binding of chemical dispersants to OMAs, resulting in potentially toxic “dirty marine snow.” OMAs vary in buoyancy and can travel in ocean currents, and can thus aid in the proliferation of synthetic dispersants [11, 12]. This mechanism could be expected to occur especially in more turbulent, coastal areas, where clay and silica are more abundant and well-mixed.
4.4. Conclusions

The adsorption of polymers or amphiphiles onto particles for colloidal stabilization of dispersions is of practical importance to numerous industrial and natural settings, ranging from cosmetics formulation to oil spill remediation. The latter includes cases where synthetic dispersants are applied to salt-water oil spills, leading to the formation of OMA-dispersant dirty marine snow which can result in the deposition of undesirable chemicals onto coral and sea beds, or in the formation of trapped underwater oil plumes, as has been the case in the Gulf of Mexico Deep Water Horizon Spill [46].

We have evaluated the influence of mono- and divalent salts in terms of their ability to modulate the micellization and adsorption behavior of a representative PEO-PPO-PEO block copolymer in aqueous dispersions with and without silica nanoparticles of 10.6 nm average diameter. Our system allows for the added salts to compete with PEO-PPO-PEO, and serves as a first approximation to the use of dispersants in seawater conditions. We used two different nanoparticle concentrations in order to test the effect of changing available adsorption surface area.

When salts were added to aqueous solutions of PEO-PPO-PEO, we found that both CaCl$_2$ and MgCl$_2$ decrease the bulk cmc to a similar extent, and both to greater extent than NaCl. The decrease in cmc becomes significant at higher salt concentrations. In the case of CaCl$_2$ and MgCl$_2$, there is approximately a two-order of magnitude decrease in the cmc, and nearly a full order of magnitude decrease for NaCl, at 0.5 M of added salt. These changes in micellization behavior can be attributed to an enhancement of the water structure due to the added salt, which results in dehydration of the PEO-PPO-PEO block copolymers, promoting micellization.
When nanoparticles are present, PEO-PPO-PEO block copolymers will adsorb and form micelle-like hydrophobic domains at a concentration well below the cmc in plain water, known as the csmc. The addition of salt to the system results in an increase in the csmc up to a maximum, followed by a decrease. The added salts act as mild displacers of PEO-PPO-PEO from the silica nanoparticle surface, as inferred from their disruption to hydrophobic domain formation according to our fluorescence spectroscopy data. In terms of cdc, CaCl$_2$ is more effective than MgCl$_2$, while both are more effective than NaCl, at modulating the hydrophobic domain formation of PEO-PPO-PEO. We believe that an electrostatic mechanism is at play, whereby cations adsorbing along the PEO segments of the PEO-PPO-PEO block copolymer and the protonated silica surface result in repulsion between the two. More negative free energies of bond formation to silica, and larger cation size, may explain the lower cdc values observed for divalent salts in comparison to NaCl.

Cloud point and precipitation data at room temperature indicate that our system may capture the electrostatic interactions involved in OMA-dispersant aggregate formation. Information obtained about the behavior of PEO-PPO-PEO block copolymers in this system can be useful for the design of better performing synthetic dispersants for oil spill remediation.

**Acknowledgments**

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References for Chapter 4


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[21] Alexandridis P., Hatton T. A. Poly(Ethylene Oxide)-Poly(Propylene Oxide)-Poly(Ethylene Oxide) Block Copolymer Surfactants in Aqueous Solutions and at Interfaces: Thermodynamics, Structure,


<table>
<thead>
<tr>
<th>Salt</th>
<th>0.01 wt% NP</th>
<th>0.10 wt% NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl(_2)</td>
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<td>0.005</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.08</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Table 4.1.** Values of the critical displacer concentration (cdc, M) interpolated from Figure 4.3.
<table>
<thead>
<tr>
<th>Additive</th>
<th>0.01 wt% NP</th>
<th>0.10 wt% NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>0.03</td>
<td>0.005</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>PEO 200</td>
<td>0.004</td>
<td>0.005</td>
</tr>
<tr>
<td>PEO 600</td>
<td>0.0008</td>
<td>0.0012</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.22</td>
<td>0.54</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.64</td>
<td>1.28</td>
</tr>
<tr>
<td>DMF</td>
<td>1.37</td>
<td>2.74</td>
</tr>
</tbody>
</table>

**Table 4.2.** A comparison of additive amount (M) required to achieve the cdc in nanoparticle – PEO-PPO-PEO block copolymer aqueous dispersions.
Figure 4.1. Pyrene fluorescence emission intensity $I_1/I_3$ ratio plotted against the Pluronic P105 block copolymer concentration in water for various salt concentrations: (●) 0 M, (▲) 0.01 M, (▼) 0.05 M, (►) 0.1 M, and (◆) 0.5 M. Left column: CaCl$_2$; middle column: MgCl$_2$; right column: NaCl. Top and bottom panels represent 0 and 0.1 wt% of dispersed silica nanoparticles. Temperature: 22°C. pH ~3.
Figure 4.2. Values of cmc of Pluronic P105 in water (no nanoparticles present) in the presence of (●) CaCl₂, (■) MgCl₂, and (▲) NaCl. Temperature: 22°C, pH ~ 3. The dotted lines are drawn to guide the eye.
Figure 4.3. Values of cmc and csmc of Pluronic P105 in the presence of (●) 0 wt%, (■) 0.01 wt%, and (▲) 0.1 wt% 10.6 nm protonated silica nanoparticles are plotted against the (top) CaCl$_2$, (middle) MgCl$_2$, and (bottom) NaCl molar salt concentration in the aqueous dispersion. Temperature: 22°C, pH ~ 3. The dotted lines are drawn to guide the eye.
Figure 4.4. Illustration of the cation binding effect at PEO at the cdc. Some cations exchange with hydrogen atoms at the silica surface, though not a sufficient amount to create a net positive surface charge. Cations also bind with the EO groups of the PEO-PPO-PEO block copolymer. This can lead to a repulsion between the polymer chains and the silica surface, disfavoring surface hydrophobic domain formation. Beyond the cdc, the salts act as a cosolvent, creating such a poor solvent quality that the polymer forms micelles in the bulk solvent.
Chapter 5

Self-Assembly of Polyethylene Glycol Ether Surfactants in Aqueous Solutions: Effect of Linker between Alkyl and Ethoxylate

Chapter 5 Abstract

The aqueous self-assembly behavior of two commercially available homologous series of poly(ethylene oxide)-containing surfactants based on a C_{10}-Guerbet hydrophobe is reported. The two families of surfactants, alkyl ethoxylates and alkyl alkoxylates, are available from BASF under the trade name Lutensol® XP- and XL-series, respectively. The latter incorporate propylene oxide (PO) units in the surfactant chain. Dye-solubilization was used to determine the critical micellization concentration of each surfactant at 22 and 50 °C. The PO-containing alkyl alkoxylates displayed lower cmc values which were also more sensitive to temperature. The Gibbs free energy, enthalpy, and entropy of micellization were computed from the cmc data and used to identify the contribution of each surfactant moiety (alkyl chain, PO unit, poly(ethylene oxide) (PEO) block) in controlling the cmc. The micellization properties are compared with compositionally similar surfactants with linear alkyl chains, yielding information about the effects of the Guerbet alkyl chain on micellization. Isothermal titration calorimetry was also used to characterize the cmc and enthalpy of micellization and generally compares well with dye solubilization results. Cloud point data reveal non-monotonic relationships for the Lutensol® surfactants with respect to composition, unlike linear alkyl chain surfactants. Finally, dilute solution viscosity measurements performed on some Lutensol® surfactants show change in slope near the cmc, indicating a structural change which tends to be more pronounced for surfactants with longer PEO blocks. The data presented herein enhance understanding of surfactant structure-property relationships required for industrial formulation.
5.1. Introduction to Chapter 5

The phase behavior of nonionic amphiphiles makes them useful for many applications, including lubrication, detergency, coatings, drug delivery, and oil-spill dispersion [1-3]. An important class of nonionic amphiphiles are those containing poly(ethylene oxide) (PEO). Surfactants with linear alkyl chains and PEO head groups, referred to commonly as C<sub>i</sub>EO<sub>j</sub>, have been well studied [4-6] and are important to the function of many industrial processes and products. These typically low molecular weight molecules self-assemble into micelles in dilute aqueous solution at the critical micellization concentration (cmc). The cmc is a fundamental physicochemical property that is useful for effective application of a surfactant system. The cmc depends largely on the chemical structure of the surfactant [7] and also on system variables such as temperature and solvent type [8]. As such, there is motivation to determine how these parameters impact the phase behavior of surfactants in general.

The influence of surfactant structure on the micellization behavior of C<sub>i</sub>EO<sub>j</sub> surfactants is well understood [9, 10]. A challenge when comparing physicochemical data for petroleum-based surfactants is polydispersity. So-called technical grade (commercially available) surfactants contain a range of components within a given sample. Therefore, some variation in physicochemical properties such as cmc, molar volume, and density, may be expected from batch to batch. Studies are also available with purified (homogeneous) surfactants. Linear C<sub>i</sub>EO<sub>j</sub> surfactants are characterized by low cmc values which decrease with increasing temperature [11] or alkyl chain length [12]. The cmc generally increases as the PEO block length increases. The interaction of the alkyl chain and PEO block with the solvent ultimately determines the cmc. The apolar, hydrophobic alkyl chain promotes micellization through the entropically favorable
process of restoring the hydrogen bond network of water [13]. PEO, on the other hand, prefers to be solvated by water and forms hydrogen bonds which act against micellization.

Molecules which possess a character between that of the hydrophobic alkyl chain and the hydrophilic PEO block modulate the self-assembly behavior of surfactants when included in the aqueous solution (as a co-solvent) or incorporated into the surfactant chemical structure. Propylene oxide (PO) is less hydrophobic in comparison to alkyl chains [14]. Despite this, a short poly(propylene oxide) block was found to oppose micellization (on a free energy basis) when incorporated into linear C\textsubscript{10}PO\textsubscript{n}EO\textsubscript{j} surfactants [15, 16]. The contribution of the PO units towards micellization changed depending on the PEO block length. Additionally, the presence of the PPO block led to increased temperature sensitivity relative to similarly structured C\textsubscript{10}EO\textsubscript{j} surfactants [16]. Molecules such as PO also influence the emulsification performance of other surfactants by acting as molecular “linkers” [17-19]. Adsorption along an oil-water interface by molecules which penetrate to different depths of the oil droplet results in an additional “extension” of the surfactant into the droplet. This motivates the study of molecular additives which could also be incorporated into a surfactant chain.

We report here on how the molecular characteristics of a homologous series of single-branch C\textsubscript{10}EO\textsubscript{j} and C\textsubscript{10}PO\textsubscript{n}EO\textsubscript{j} surfactants relate to their aqueous solution self-assembly properties. The surfactant alkyl chain is derived from a C\textsubscript{10} Guerbet chain [20] which has a branch on the β carbon relative to the PEO block. The surfactants are commercially produced by BASF under the trade name Lutensol®. Critical micellization concentration and associated thermodynamic data (Gibbs free energy, enthalpy, and entropy of micellization) are reported and compared with compositionally similar linear alkyl chain surfactants in order to ascertain the effect of the
branch. We comment on the role played by the alkyl chain, PEO head group, and added PO units, in the self-assembly behavior of the surfactants. Cloud point and dilute solution viscometry measurements are employed in order to gain further insight into the solution behavior and structure.
5.2. Experimental

5.2.1. Surfactants

Eleven commercial surfactants from the Lutensol XP® and XL® types were supplied as a gift from BASF. Both surfactant series are alkyl polyethylene glycol ethers synthesized from a C_{10}-Guerbet alcohol. The Guerbet hydrophobe differs from linear alkyl chains in that it contains an alkyl branch on the β-carbon (in reference to the head group), leading to distinct interfacial properties [20]. According to BASF [21, 22], the XP® and XL® series are based on poly(ethylene oxide) and alkylene oxide, respectively. PO units are incorporated into the XL®-series chain, but their number is not provided by the manufacturer. The available lot numbers and average physical characteristics of each surfactant are given in Table 1. The suffix number given in the commercial name is indicative of the average degree of ethoxylation (e.g., XP-30 comprises on average 3 EO units). Four laboratory compounds were also provided by BASF under the name ES-8928 (A, B, C, and D). The molecular weights of the ES surfactants are not provided by the manufacturer, but the structure is similar to that of the XL® surfactants.

The average molecular weights published by BASF are based on the hydroxyl number, which is defined as the milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of surfactant. The published molecular weight then describes the g/mol of the “functional” portion of the surfactant. This makes the interpretation of the molecular weight, important here for describing the surfactant composition and the calculation of thermodynamic properties, somewhat ambiguous. We have considered three methods of estimating the total surfactant average molecular weight and structure:
1) Assume that the published molecular weight (based on the hydroxyl number) is representative of the total average molecular weight of the surfactant: \( \text{MW(OH No.)} = \text{MW}_{\text{total}} \)

2) Assume that the total molecular weight can be calculated based on the atomic weights of the average chemical structure:

- XP-Series: \( \text{MW}_{\text{total}} = \text{MW(Geurbet Chain)} + \text{MW(EO}_n) + \text{MW(OH}_{\text{end cap}}) \)
- XL-Series: \( \text{MW}_{\text{total}} = \text{MW(Geurbet Chain)} + \text{MW(EO}_n) + \text{MW(PO}_n) + \text{MW(OH}_{\text{end cap}}) \)
- ES-Series: \( \text{MW}_{\text{total}} = \text{MW(C}_{10}\text{H}_{21}) + \text{MW(EO}_n) + \text{MW(OH}_{\text{end cap}}) \)

3) Assume that \( \text{MW}_{\text{total}} = \text{MW(OH No.)} + \text{MW(Guerbet Chain)} \)

Where

- \( \text{MW(Guerbet Chain)} = \text{MW(C}_{10}\text{H}_{21}) = 141 \text{ g/mol} \)
- \( \text{MW(EO}_n) = N_{\text{EO}} * 44 \text{ g/mol} \)
- \( \text{MW(PO}_n) \) is found as the difference between the published molecular weights (MW(OH No.)) of XP and XL series surfactants of the same average degree of ethoxylation, e.g.:
  - \( \text{MW(OH No., XL-70)} – \text{MW(OH No., XP-70)} = \text{MW(PO}_n) \)

- The equations for methods 1 and 3 assume that the molecular weight of the head group comprising EO (and PO in the XL® series) is adequately described by the published MW(OH No.).
Methods 1 and 2 led to very similar molecular weights for each surfactant in the XP series. This was not anticipated since the hydroxyl number-based molecular weight should only be sensitive to the ethylene oxide head group and any unreacted alcohol remaining in the sample. Method 2 requires estimation of the number of PO units in the XL series, which can be accomplished in two ways. The first approach is to find the difference between the hydroxyl number-based molecular weight and the Method 2 calculated weight without PO, and divide by 58 g/mol (molar mass of one PO unit) to find the number of PO units. The second approach is to find the difference between the published hydroxyl number-based molecular weight of XL and XP series surfactants of the same average degree of ethoxylation and divide by 58 g/mol to find the number of PO units. Both methods arrive at very similar estimates of \( N_{PO} \). The third method for calculating the total surfactant molecular weight leads to molecular weights which are higher than the other methods.

Despite small differences in the total molecular weight, the Gibbs free energies, enthalpies, and entropies of micellization calculated using each strategy were very similar. This being the case, we selected Method 1 for the XP- and XL-series, which seemed to sufficiently provide a total molecular weight representative of the overall structure (alkyl chain and head group). This is the same molecular weight provided by the manufacturer and is listed in Table 1. For the ES-series, we used Method 2 to calculate the molecular weights, since they are not published. We have assumed that there are no PO units in the calculation of ES-series surfactant molecular weights. We would still like to know \( N_{PO} \) for the XL-series surfactants. Since hydroxyl number-based molecular weights are published by BASF, we estimated \( N_{PO} \) for XL-50, XL-70, XL-90, XL-100, and XL-140 by dividing by 58 g/mol the difference in published hydroxyl number-based
molecular weights between XL and XP-series surfactants having the same average \( N\text{EO} \). This method led to erroneous \( N\text{PO} \) values for XL-80.

5.2.2. Sample Preparation

All samples were prepared gravimetrically. Samples for fluorescence spectroscopy were prepared by first mixing the Lutensol surfactant with deionized water (18 m\( \Omega \) resistance) to produce a stock solution. The stock solution was subsequently diluted with deionized water to produce samples with concentrations spanning the cmc. The concentrations were selected from pre-experiments in an effort to more precisely capture the cmc. Concentrations greater than 1 wt\% were produced by direct mixing of surfactant with deionized water. Kinematic viscosity and cloud point samples were produced in a similar manner. All samples were allowed to equilibrate for several hours under rolling at room temperature prior to testing.

5.2.3. Fluorescence Spectroscopy

Pyrene (Fluka, Switzerland) dissolved in ACS/USP grade ethanol was employed as a spectroscopic dye to measure the micropolarity of the prepared solutions [14]. Pyrene is readily soluble in hydrophobic environments (i.e., the micelle core in aqueous environment) and emits five peaks of the electronic vibrational fine structure following excitement (\( \lambda = 335 \text{ nm} \)). The ratio of the first to the third intensity peaks (\( I_1/I_3 \)) in each sample indicates the polarity of the local environment that pyrene is experiencing; the ratio decreases with decreasing polarity. A syringe was used to inject 2 \( \mu \text{L} \) of dye solution into a 3 g aqueous surfactant sample, resulting in overall pyrene and ethanol concentrations of about 0.7 \( \mu \text{M} \) and 0.07 vol\%, respectively (too low to affect the cmc). A Hitachi 2500 fluorescence spectrophotometer was used to measure the
emission intensity of pyrene in the 340 – 460 nm range at 22 °C and 50 °C. Plots of $I_1/I_3$ versus the logarithm of the surfactant concentration typically result in a sigmoidal shape. The second inflection point (between the apparent down-slope and lower plateau) is taken as the cmc. The inflection point was determined by drawing a line through the apparent down-slope and lower plateau. The intersection of the lines passing through the down-slope and lower plateau is the second inflection point and cmc [16].

### 5.2.4. Isothermal Titration Calorimetry (ITC)

A Microcal ITC200 calorimeter (Malvern, Worcestershire, UK) was used to perform ITC experiments [23, 24]. The sample cell was filled with deionized water and maintained at 20 °C. Aliquots (1.5 μL) of aqueous micellar surfactant solution were titrated into the sample cell at a fixed time interval while the syringe spun at 750 RPM. The concentrations of the titrant micellar solutions were several times above the cmc. As surfactant is titrated into the cell, heat due to mixing and demicellization (micelles dissociate into unimers in the dilute environment) is released. The instrument records the power required to cool the sample cell back to 20 °C, which, when integrated with respect to time, yields the change in heat per injection. A volume-specific quantity, the heat per injection can be normalized by the molar concentration of surfactant after each titration to produce a curve of change in enthalpy versus surfactant concentration.
5.2.5. Cloud Point

Cloud point experiments were conducted with 5 gram samples of aqueous surfactant solution placed in a sealed 20 mL test tube. The sealed test tube was fixed at approximately the center of a 50 mL beaker filled with distilled water. The heating rate of the beaker was controlled with a hot plate and the temperature monitored with a calibrated thermometer. Samples were tested at a surfactant concentration of 1 %w/w. In order to aid in observing cloud point, a solid background was placed behind the sample to serve as a contrast. The cloud point was defined as the temperature where the solid background became obscured to the eye.

5.2.6. Viscosity

Viscosity measurements of aqueous surfactant solutions were made at 24 °C using a Size 25 Cannon-Fenske Routine viscometer [25, 26]. Briefly, the time required for a surfactant solution to pass between two marked lines on the viscometer was recorded. The relative viscosity was calculated by dividing the recorded efflux time of the surfactant solution by that of pure water. At least two measurements per sample were collected and averaged together. The standard deviation in relative viscosity measurements was 0.0006. Surfactant concentrations were tested below and above the cmc (as determined by pyrene fluorescence spectroscopy).
5.3. Results and Discussion

5.3.1. Critical Micellization Concentration

The pyrene I₁/I₃ ratio data calculated from fluorescence spectra are plotted versus the logarithm of surfactant concentration in Figure 5.1. The I₁/I₃ data demonstrate an increase in the surfactant concentration corresponding to the second inflection point (i.e., the cmc) as the length of the PEO block increases. The location of the second inflection point is shifted lower for each surfactant at 50 °C compared with 22 °C. Additionally a downward shift in the I₁/I₃ values across the surfactant concentration range is noted at 50 °C, indicating that pyrene experiences a more hydrophobic microenvironment than at room temperature. This shift is likely a combined effect of conformational changes in both the solvent and the surfactant monomers and micelles at the elevated temperature [14].

The cmc of each surfactant at 22 and 50 °C was extracted from Figure 5.1 as described in the Experimental section and plotted versus the average number of EO units (N_{EO}) in Figure 5.2. The cmc increases approximately exponentially as the degree of ethoxylation increases. Some scatter in the data is attributable to polydispersity and possibly the presence of impurities in the commercially produced surfactants. At 50 °C, the cmc of each surfactant is lower than at room temperature, but the same trend of increasing cmc with N_{EO} remains. A clear offset between the XP- and XL-series cmc values exists at both temperatures, presumably driven by the presence of the PO units in the XL-series surfactants. The ratio of the cmc at 50 °C to that at 22 °C decreases as N_{EO} increases, indicating a temperature sensitivity that depends on the length of PEO block (Figure 5.2). There is also an apparent inflection point at N_{EO} = 8 for the XL-series in Figure 5.2, which may be an outlier.
In the following sections we rationalize the micellization of these surfactants in terms of their micellization thermodynamics. In particular, we focus on aspects of the surfactant composition, namely the PEO block length, number of PO units, and branching of the alkyl chain.

### 5.3.2. Thermodynamics of Micellization and Surfactant Composition

The micellization process of surfactants can be modeled by the Law of Mass Action, which assumes a thermodynamic equilibrium between unimers and micelles [13]. Assuming a reasonably large aggregation number (average number of surfactant molecules per micelle), the expression for the standard Gibbs free energy of micellization for nonionic surfactants can be written as:

\[
\Delta G^\circ_{\text{mic}} = RT \ln(X_{\text{cmc}})
\]  

(1)

where \( R \) is the ideal gas law constant, \( T \) is the absolute temperature, and \( X_{\text{cmc}} \) is the cmc in units of mole fraction. The molecular weights listed in Table 1 were used to calculate \( X_{\text{cmc}} \). The self-assembly of nonionic surfactants in aqueous solution is driven by the hydrophobic effect [1] and is a spontaneous process. Thus, \( \Delta G^\circ_{\text{mic}} \) is a negative value.

The standard enthalpy of micellization can be calculated by combination of Equation 1 with the Gibbs-Helmholtz equation to arrive at

\[
\Delta H^\circ_{\text{mic}} = -RT^2 \left( \frac{\partial \ln X_{\text{cmc}}}{\partial T} \right)
\]  

(2)

This expression for \( \Delta H^\circ_{\text{mic}} \) assumes a constant value of the enthalpy in the temperature range studied. \( \Delta H^\circ_{\text{mic}} \) arises from the restructuring of water molecules (bending, breaking of hydrogen
bonds) in order to accommodate the hydrophobic portions of the surfactant in aqueous solution [1]. Thus, $\Delta H^\circ_{\text{mic}}$ for the micellization process in water is typically positive.

Finally, the standard entropy of micellization can be obtained from

$$
\Delta S^\circ_{\text{mic}} = \frac{(\Delta H^\circ_{\text{mic}} - \Delta G^\circ_{\text{mic}})}{T}
$$

The system entropy is increased during self-assembly due to the release of water molecules which are constrained by the presence of hydrophobic moieties prior to these moieties packing into a micelle core. This makes the overall change in entropy typically positive.

We have used cmc data obtained from pyrene fluorescence spectroscopy in order to calculate values of $\Delta G^\circ_{\text{mic}}$, $\Delta H^\circ_{\text{mic}}$, and $\Delta S^\circ_{\text{mic}}$. These data can be used to obtain insight into how the surfactant molecular characteristics influence their self-assembly properties.

The Gibbs free energy of micellization for each Lutensol® surfactant family is plotted versus $N_{\text{EO}}$ in Figure 5.3. The value of $\Delta G^\circ_{\text{mic}}$ becomes more positive as the average degree of ethoxylation increases. The trend in $\Delta G^\circ_{\text{mic}}$ deviates slightly from that of cmc vs $N_{\text{EO}}$ due to the relationship between the Lutensol® molecular weight and structure (where the published molecular weights for some of the XL-series surfactants are different than their degree of ethoxylation and alkyl chain length would suggest).

The enthalpy and entropy of micellization are plotted vs $N_{\text{EO}}$ in Figure 5.3. Both quantities increase linearly for the XP-series. However, non-monotonic relationships are observed between $\Delta H^\circ_{\text{mic}}$, $\Delta S^\circ_{\text{mic}}$, and $N_{\text{EO}}$ for the PO-containing XL- and ES-series surfactants. Generally, however, it can be said that both the enthalpy and entropy of micellization increase as $N_{\text{EO}}$ increases.
The total free energy of micellization can be devolved into the following contributions: free energy due to transfer of the alkyl chains from water to the micelle core, $\Delta G(C)$, free energy due to the PEO block, $\Delta G(\text{PEO})$, and free energy due to the PPO block, $\Delta G(\text{PPO})$. These are summarized below for the XP-series (eq. 4) and the XL- and ES-series (eq. 5) surfactants.

$$\Delta G^\circ_{\text{mic}} = \Delta G(C) + \Delta G(\text{PEO}) \quad (4)$$

$$\Delta G^\circ_{\text{mic}} = \Delta G(C) + \Delta G(\text{PPO}) + \Delta G(\text{PEO}) \quad (5)$$

Identifying the contributions of different surfactant moieties provides a mechanistic approach to understanding self-assembly behavior. The effects of the alkyl chain and PEO are well known for the role they play in the micellization of $\text{C}_i\text{EO}_j$ surfactants [4, 27]. The contribution of PPO however is less straightforward to rationalize. PPO homopolymer has a Py-scale value between that of alkanes and (hydrophilic) PEO homopolymer [14]. Its contribution towards $\Delta G^\circ_{\text{mic}}$ was shown to be positive and variable depending on the chemical structure of linear alkyl propoxy ethoxylate surfactants [16]. In this sense, PPO acted against micellization. On the other hand, PPO has been shown to promote lower cmc and cmt values in $\text{EO}_j\text{PO}_n\text{EO}_j$ block copolymers (Pluronics) [28]. Clarifying the contribution of the PO units in the Lutensol$^\circledR$ surfactants will be useful to understanding the micellization behavior of the XL-series and for drawing comparison to other surfactants.

The free energy requirement for moving one mole of alkyl chain from water to the micelle interior can be estimated from the following empirical equation [13]:

$$\Delta G(C) = -3.0(N_C-1) - 9.6 \quad (6)$$

where $N_C$ is the number of carbon atoms in the alkyl chain.
The value of \( \Delta G(\text{PEO}) \) can then be calculated as:

\[
\Delta G(\text{PEO}) = \Delta G_{\text{mic}}^\circ - \Delta G(\text{C})
\]  

(7)

where \( \Delta G_{\text{mic}}^\circ \) is based on our cmc data at room temperature, and \( \Delta G(\text{C}) \) comes from Equation 6. Equation 7 is valid for surfactants without PO units. For the XL- and ES-series, subtracting \( \Delta G(\text{C}) \) from \( \Delta G_{\text{mic}}^\circ \) gives the combined contribution of the EO and PO units. To separate the PEO and PPO free energy contributions, the \( \Delta G(\text{PEO}) \) values found for the XP-series surfactants were applied to the corresponding PO-containing XL-series surfactants of the same average degree of ethoxylation. The free energy contribution of the PO moiety was then calculated using Equation 5. Note that this method could not be used for XL-100, XL-140, or the ES-series surfactants, since we did not have non-PO-containing surfactant homologues available to calculate \( \Delta G(\text{PEO}) \). In any event, by our estimation, XL-100 and XL-140 have close to zero PO content. The free energy contributions to micellization of the alkyl chain, PEO block, and PO moiety are listed in Table 2 at both 22 and 50 °C.

5.3.3. Role of the PEO Block

Poly(ethylene oxide) is hydrophilic and well-solvated in aqueous solution, forming hydrogen bonds with neighboring water molecules. During the micellization process, these bonds must be disrupted as the unimers relocate into the micellar structure, leading to an increase in the enthalpy. Enthalpy contributions firstly arise from the formation of cavities in the water structure to accommodate the hydrophobic moieties of the surfactant [1]. For surfactants with a longer PEO block, the number of hydrogen bonds with neighboring water molecules is increased, and the enthalpy contribution becomes higher. The net effect of the increasingly positive enthalpy is
to increase the Gibbs free energy of micellization (Figure 5.3), which is manifested in higher cmc values for Lutensol® surfactants with longer PEO blocks (Figure 5.2). The free energy contribution of the PEO block for each surfactant is listed in Table 2. Recall that the same values of ΔG(PEO) are used for both the XP- and XL-series as described above. The positive values of ΔG(PEO) increase slightly as N_{EO} increases, a feature reflected in ΔG°_mic. However, the free energy contribution per EO unit decreases exponentially as N_{EO} increases, with an apparent plateau forming at 8 EO units (Figure 5.4). This can be rationalized by considering that EO units far away from the micelle core (i.e., longer PEO block) will be more solvated (hydrated) and participate less in the micelle corona packing [16].

As mentioned earlier, the difference between the cmc at 50 °C and the cmc at 22 °C increases as the PEO block becomes longer. This is expressed in Figure 5.2 as the ratio of cmc_{50°C}/cmc_{22°C} plotted against N_{EO}. The trend in Figure 5.2 is approximately linear for all three surfactant families with the exceptions of the data points corresponding to XL-80 and ES 8928-D. These data points appear to be outliers, perhaps impacted by impurities or possibly extra PPO monomer. In the XP-series, the cmc_{50°C}/cmc_{22°C} ratio decreases from 0.92 to 0.73 as N_{EO} increases from 3 to 9; in the XL-series, the ratio decreases from 0.86 to 0.53 as N_{EO} increases from 5 to 14. This temperature effect stems from the dehydration of the PEO block as the temperature is increased [14, 29], owing to higher fluctuation of hydrogen bonds [10]. As the temperature increases, the hydration number of the EO units decreases, leading to a decrease in the cross-sectional area of the surfactant head group and a reduction in steric repulsion [30]. This gives rise to more negative values of ΔG°_mic. The number of water molecules dehydrated for C_iEO_j surfactants has been estimated as 0.02 per EO unit per °C [30]. The free energy
contribution of the PEO block is smaller for each surfactant at 50 °C, consistent with reduced steric repulsion of the head groups upon self-assembly into micelles.

5.3.4. Role of the PO Linker

Poly(propylene oxide) homopolymers are less polar than water and PEO as indicated by their relative positions on the Py Scale (which varies slightly based on molecular weight) [14]. This makes the hydrophobicity of PO somewhere between that of the branched C_{10} alkyl chain and the PEO block of the Lutensol® surfactants. Applying the analysis method described in the preceding section leads to small and negative free energy contributions (Table 2) for the PO moieties in XL-50, -70, -80, and -90, indicating that PO prefers to be nearer to the “oily” micelle core instead of water. In this sense, PO promotes micellization. The negative free energy contribution of PO may explain the offset to lower cmc values for the XL-series surfactants compared with the XP-series.

The free energy contribution of the PO moiety is largest for XL-80 (-2.6 kJ/mol at 22 °C). The calculated values suggest that PO plays a smaller role in the micellization thermodynamics than the PEO block and the Guerbet-based alkyl chain. The contribution of the PO moiety becomes more negative as the temperature is increased, reflecting the temperature sensitivity of PO solution properties. In a fashion similar to the free energy contributions of each EO unit, the contribution of each PO unit decreases exponentially as N_{PO} increases (Figure 5.4).

5.3.5. Comparison with Linear C_{i}EO_{j} and C_{i}PO_{n}EO_{j} Surfactants

The physicochemical properties of purified and technical grade PEO-containing amphiphiles with linear alkyl chains have been extensively studied and reported [9, 16, 31, 32]. The
micellization of these amphiphiles in water is entropically driven, with the main enthalpy contributions emanating from the hydrophilic PEO block. Molecules with longer hydrophilic portions begin to self-assemble at higher concentrations than those where the hydrophobic portion is dominant. On the other hand, the logarithm of the cmc decreases linearly as the alkyl chain length increases (for C\textsubscript{i}EO\textsubscript{j} surfactants) [4, 12]. By comparing the Lutensol\textsuperscript{®} surfactants under study here with compositionally similar surfactants with linear alkyl chains, we can gain further insight into how molecular characteristics control solution behavior.

The cmc of linear alkyl chain C\textsubscript{i}EO\textsubscript{j} and the XP-series Lutensol\textsuperscript{®} surfactants are plotted in Figure 5.5 versus the ratio N\textsubscript{C}/N\textsubscript{EO}, where N\textsubscript{C} is the number of carbons in the alkyl chain. The cmc values for all three surfactant types plotted (branched Lutensol\textsuperscript{®} C\textsubscript{10}, linear C\textsubscript{10}, and linear C\textsubscript{12}) decrease as the PEO block shortens. However, the XP-series surfactants display higher cmc values than both the C\textsubscript{12} and C\textsubscript{10} linear alkyl chain surfactants, presumably owing to the single branch of the Guerbet alcohol. The difference approaches almost one order of magnitude in direct comparison to linear C\textsubscript{10} surfactants. Surface tension measurements comparing C\textsubscript{16} linear and branched Guerbet ethoxysulfate surfactants also indicated [20] higher cmc values for the branched surfactant. The difference was attributed to steric hindrance to micellization conferred by the branch in the Guerbet chain [20].

In Figure 5.5 the cmc values of XL- and ES-series PO-containing surfactants are plotted along with linear C\textsubscript{13}PO\textsubscript{12}EO\textsubscript{j} surfactants versus N\textsubscript{C}/N\textsubscript{EO}. It has been previously reported [16] that the PPO block of the linear alkyl chain C\textsubscript{13}PO\textsubscript{12}EO\textsubscript{j} surfactants can be viewed as hydrophilic on the basis of its (positive) free energy contribution to micellization. A comparison between the linear alkyl chain C\textsubscript{12}EO\textsubscript{j} (Figure 5.5, top panel) and C\textsubscript{13}PO\textsubscript{12}EO\textsubscript{j} surfactants (Figure 5.5, bottom panel)
yields a similar conclusion: despite the latter surfactant containing one more carbon atom in its alkyl chain, its cmc values are higher than the non-PO containing C\textsubscript{12}EO\textsubscript{j} surfactant. In the case of Lutensol\textsuperscript{®}, however, we have determined the opposite to be true. The free energy contribution of PO is negative, supported also by the lower cmc values displayed by XL-series surfactants compared with the XP-series with the same N\textsubscript{EO}. A steeper slope in cmc vs N\textsubscript{C}/N\textsubscript{EO} for the XL-versus the XP-series in Figure 5.5 is also observed, attributable to the hydrophobic nature of the PO unit.

In order to compare the free energy contributions of each surfactant moiety between linear and branched surfactants, the standard enthalpies and entropies of micellization are plotted in Figure 5.6a and 5.6b versus the ratio N\textsubscript{C}/N\textsubscript{EO}. Data for linear alkyl chain C\textsubscript{i}EO\textsubscript{j} [9, 10] and C\textsubscript{13}PO\textsubscript{12}EO\textsubscript{j} [16] were computed from cmc data at different temperatures available in the literature. The overall enthalpies and entropies of micellization are lower for the branched surfactants studied here compared with compositionally similar linear surfactants. It can be seen in Figure 5.6a that, while the absolute enthalpy values between linear and branched surfactants are offset, the trends with composition are roughly the same. As the PEO block length increases the enthalpy also increases, consistent with the view of hydrogen bond breaking and bending between the EO units and water molecules during self-assembly. The same trend is found for the Guerbet alkyl chain XL and ES-series surfactants, and linear C\textsubscript{13}PO\textsubscript{12}EO\textsubscript{j} surfactants, in Figure 5.6b. While the slope for the XL-series surfactants is not steep, and appears to plateau, the slopes for the ES-series and linear surfactants are significantly steeper. Both families of surfactants have longer PEO blocks compared with the XL-series. Despite having alkyl chains of similar length, the standard entropy of micellization is smaller for the branched surfactants compared with linear ones. In Figure 5.6a, the relationship between entropy and N\textsubscript{C}/N\textsubscript{EO} is quite flat. On the other hand, a stronger
relationship exists for the linear alkyl chain C$_{13}$PO$_1$EO$_j$ and ES-series surfactants in Figure 5.6b. The difference in compositional dependence between the XL- and ES-series surfactants is interesting, considering that the alkyl chain lengths are similar and both surfactant families contain PO and EO units.

Figures 5.6c and 5.6d present the enthalpy and entropy of micellization normalized by $N_{EO}$ plotted versus $N_C/N_{EO}$. Compared with linear C$_i$EO$_j$ surfactants, the enthalpy change per EO unit is flat for XP-series surfactants. This is the result of a very gradual change in the enthalpy of micellization with increasing length of the PEO block, a characteristic that seems unique to the branched surfactant. In Figure 5.6d, the enthalpy change per EO unit is non-monotonic for the XL-series surfactants, with XL-80 being an outlier possibly attributable to impurities. While $N_{PO}$ is not known for the ES-series, differences in $N_{PO}$ of these surfactants or impurities may explain the non-linear relationship between $\Delta H^\circ_{mic}/N_{EO}$ and $N_C/N_{EO}$.

### 5.3.6. Isothermal Titration Calorimetry

Curves of $\Delta H$ versus concentration for the titration of micellar solutions of XP-30, XL-90, and XL-140 into pure water at 20 °C are plotted in Figure 5.7. The sigmoidal curve can be broken into three distinct portions [23]. The lower plateau at low surfactant concentration covers a region where the micellar titrant is diluted (following the injection into the sample cell) to a concentration that is less than the cmc. The large heat evolved is a result of demicellization of the titrant. As the surfactant concentration in the sample cell increases, the slope of the $\Delta H$ curve increases, passes through an inflection point, and reaches an upper plateau. The inflection point signifies the cmc, while the upper plateau represents a concentration regime above cmc where the surfactant concentration in the sample cell becomes closer to that of the titrant and, as a
result, the enthalpy exchange is small upon injection and mixing. The negative enthalpy values on the y-axis of Figure 5.7 reflect the demicellization of the surfactant. Put another way, the micellization process captured by ITC is endothermic, in agreement with the ΔH data obtained from the analysis of cmc values. The span of the curves from the lower to the upper plateau increases as the surfactant PEO block becomes longer, indicating an increase in the enthalpy of micellization. The data are in good agreement with those calculated from cmc data obtained from fluorescence spectroscopy. The discrepancy in ΔH°_{mic} values between the two methods is likely attributable to the assumption used for calculating ΔH°_{mic} from fluorescence experiments that enthalpy is independent of temperature in the range studied (per eq. 2).

### 5.3.7 Cloud Point

The separation of ethoxylated nonionic surfactant-aqueous solutions into a turbid mixture of water-rich and surfactant-rich phases occurs above a lower critical solution temperature, identifiable as the cloud point (CP) [1]. As the solution temperature is increased, hydration of the PEO block becomes more entropically unfavorable, ultimately leading to expulsion of water and strong attraction between EO units [33]. The CP depends strongly on the molecular characteristics of the surfactant [1, 34]. Amphiphiles with longer PEO blocks display higher CP values, owing to their higher state of hydration. The CP decreases sharply as the PEO block shortens. On the other hand, the alkyl chain length plays a minor role. However, the Guerbet alkyl chain structure of Lutensol® surfactants makes comparison with linear alkyl chain C_{i}EO_{j} worthwhile.

The cloud point of the Lutensol® and other linear alkyl chain surfactants in water as a function of the ratio of the number of carbon atoms in the alkyl chain to the average number of EO units in
the head group is presented in Figure 5.8. The cloud point of all of the PEO-containing surfactants increases sharply as the as PEO block increases in length. The XL-series displays a local maximum, followed by a decrease and finally a sharp increase, as \( N_{\text{EO}} \) increases. Similarly to trends in micellization thermodynamics, XL-80 appears here as an outlier. The ES-series cloud point quickly exceeds 100 °C as \( N_{\text{EO}} \) increases, consistent with the phase behavior of molecules with long PEO blocks. It is interesting to note that the trend of cloud point with \( N_{\text{EO}} \) bears resemblance to that of \( \Delta H^\circ_{\text{mic}} \) vs \( N_{\text{EO}} \) in the case of the XL-series. In comparison, compositionally [9] similar surfactants with linear alkyl chains display linear monotonic relationships between cloud point and \( N_{C}/N_{\text{EO}} \). While alkyl chain length plays a role, it is the entropic effect of PEO hydration which more strongly dictates the temperature at which phase separation occurs. Nonetheless, \( \text{C}_{10}\text{EO}_j \) surfactants exhibit lower cloud points than XP-series surfactants at low \( N_{\text{EO}} \) values, perhaps indicating a subtle role of the alkyl chain chemical structure.

### 5.3.8. Relative Viscosity

The relative viscosity of aqueous Lutensol® solutions is plotted in Figure 5.9 versus concentration normalized by the surfactant cmc. Normalizing the data in this manner facilitates interpretation of the change in relative viscosity below and above the surfactant cmc. The relative viscosity is indicative of the solute (surfactant in this case) contribution to the solution viscosity. In this sense, we can make some qualitative descriptions about the structure of the system at different concentrations. This can include micelle formation and micelle shape transitions [35]. For all of the surfactants tested here, the relative viscosity initially decreases with concentration before increasing again.
XP-50 and XL-100 (top panel of Figure 5.9) display apparent changes in slope. The change in slope for XL-100 near the cmc is stronger compared with XP-50, which can be attributed to its higher molecular weight. A similar, positive slope in XL-140 is observed. However XL-140 never attains a relative viscosity value of 1.0 (water), even above cmc. In the bottom panel of Figure 5.9, data for the higher molecular weight ES 8298-series surfactants are plotted. Significant changes in the relative viscosity are observed for all three surfactants in the vicinity of 0.5 cmc, perhaps indicative of premicellar aggregates. This is also observed in XL-140 (top panel). A lack of large relative viscosity change in the case of the XP-50 and XL-100 could be due to the fact that they have relatively short PEO blocks, resulting in small assemblies with a low impact on solution viscosity. The surfactant with the longest PEO block evaluated, ES 8928-C, shows a strong and linear increase in the relative viscosity with concentration, possibly due to a micelle shape transition such as sphere to ellipsoid [35].
5.4. Conclusions

The aqueous solution properties of a homologous series of single-branched PEO-based surfactants have been evaluated. The surfactant alkyl chain, based on a C-10 Guerbet alcohol, contains a branch on the β carbon relative to a PEO block of varying length. The Geurbet alkyl chain structure differentiates the behavior of the surfactants examined here from linear PEO-containing surfactants. The XP- and XL-series surfactants studied are technical grade and commercially produced by BASF under the trade name Lutensol®. The ES-series surfactants are laboratory compounds. The alkyl ethoxylate (XP-series) surfactants compositionally resemble \( C_iEO_j \) surfactants, while the alkyl alkoxyate (XL- and ES-series) surfactants resemble \( C_iPO_nEO_j \) surfactants.

Lutensol® surfactants with longer PEO blocks displayed both higher cmc values and temperature sensitivity. Alkyl alkoxylate surfactants showed slightly higher temperature sensitivity than alkyl ethoxylates. The cmc values of the XL-series surfactants were lower compared with the XP-series of the same average degree of ethoxylation. This is likely due to the presence of the PO unit(s), which were established to behave as hydrophobic on a free energy basis. The value of \( \Delta G(PPO) \) was calculated by subtracting the free energy contributions of the alkyl chain and the PEO block from the overall Gibbs free energy of micellization (eq. 5) obtained from dye solubilization experiments. The standard enthalpies and entropies of micellization were found to be positive for all surfactants studied.

The cmc values of the single-branched alkyl chain Lutensol® surfactants were approximately one order of magnitude higher than linear-alkyl-chain \( C_iEO_j \) and \( C_iPO_nEO_j \) surfactants with the same number of carbons in the alkyl chain. The steric hindrance associated with packing a branched,
as opposed to linear, alkyl chain into the micelle core is likely the cause. Pyrene fluorescence studies on linear and branched Guerbet ethoxy-sulfates demonstrated that the branched surfactant micelle presented a higher micropolarity, indicative of a less-well-packed micelle [36]. Meanwhile, the standard enthalpies and entropies of micellization of the Lutensol® surfactants were lower for the single-branched surfactants than their linear counterparts.

The cloud point and relative viscosity data provide qualitative information about the surfactant solutions. Linear C_{10}EO_j surfactants have lower CP values than XP-series surfactants at high values N_C/N_{EO}. Changes in the relative viscosity versus the surfactant concentration normalized by cmc reveal strong shifts in the solution structure for higher PEO-length surfactants commencing below the cmc.

Branched Guerbet alkyl chain surfactants show distinct interfacial behavior, particularly in the modulation of surface tension [20]. This makes them attractive candidates for formulations with a wide array of applications, including emulsification and surface wetting. Effective formulation may be accomplished when the performance of a surfactant in a given environment is understood. The data presented here on Guerbet-based Lutensol® XP-, XL-, and ES-series surfactants connect surfactant molecular characteristics with their aqueous self-assembly properties. In particular, developing knowledge of how the branched alkyl chain and PO units contribute to micellization is important for achieving desired performance. The mildly hydrophobic PO units included in the surfactant head group may act as a molecular linker [37] with implications on solubilization and emulsification.
Acknowledgements

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Conflict of Interest

The authors declare that they have no conflict of interest.
References for Chapter 5


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**Table 5.1.** Lot numbers, molecular weight, and average number of EO units ($N_{EO}$) of Lutensol® surfactants. The molecular weight and $N_{EO}$ data are obtained from the BASF technical bulletin for XP- and XL-series surfactants [21, 22].
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<td>ES 8928-D</td>
<td>-36.6</td>
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<td>16.6</td>
</tr>
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**Table 5.2.** Free energy contributions to micellization in water for each surfactant component (kJ/mol). Refer to section *Thermodynamics of Micellization and Surfactant Composition* for details on how values of ΔG the alkyl chain, PEO block, and PO unit(s) were calculated.
Figure 5.1. Pyrene $I_1 / I_3$ values calculated from fluorescence spectroscopy plotted versus the logarithm of the Lutensol surfactant concentration. Left column: 22 °C, right column: 50 °C. Top row: XP-series, middle row: XL-series, bottom row: ES 8928-series. Note that the concentration axis range is shifted higher for the ES 8298-series. For XP- and XL-series: (●) 3 EO units, (■) 5 EO units, (▲) 7 EO units, (▼) 8 EO units, (◆) 9 EO units, (◇) 10 EO units, ( ○) 14 EO units. For ES 8928-series: (○) A, (□) B, (△) C, (▽) D.
Figure 5.2. Cmc of aqueous surfactant solutions plotted versus the average number of EO units ($N_{EO}$). Top panel: 22 °C. Middle panel: 50 °C. Bottom panel: ratio of the cmc at 50 °C to the cmc at 22 °C plotted versus $N_{EO}$. (●) XP-Series, (■) XL-Series, and (▲) ES 8928-series.
Figure 5.3. Variation of (top panel) $\Delta G^\circ_{\text{mic}}$, (middle panel) $\Delta H^\circ_{\text{mic}}$, and (bottom panel) $\Delta S^\circ_{\text{mic}}$ with $N_{\text{EO}}$. (●) XP-Series, (■) XL-Series, and (▲) ES-Series in water at 22 °C.
Figure 5.4. Free energy contributions of each (●) EO unit plotted versus \( N_{EO} \) (bottom axis) and each (□) PO unit plotted versus \( N_{PO} \) (top axis) for the XL-series. Note that we have assumed that the free energy contribution of the entire PEO block is the same for XP and XL surfactants of the same \( N_{EO} \). The surfactants in the series \( \Delta G^\circ (PO)/N_{PO} \) (□) are labeled inside the graph to make clear which surfactant each data point represents. We have omitted XL-80, XL-100, and XL-140 from this plot as the calculated values for XL-100 and XL-140 were near zero, while the value for XL-80 is known to be inaccurate.
Figure 5.5. Comparison of the critical micellization concentration of homologous series of nonionic surfactants in water. Top panel: (●) XP-series at 22 °C, (○) linear C$_{10}$EO$_j$ at 25 °C [9], and (▃) linear C$_{12}$EO$_j$ at 20-25 °C [10]. Bottom panel: (■) XL-series and (▲) ES 8928-series at 22 °C, and (▲) linear C$_{13}$PO$_{12}$EO$_j$ at 25 °C [16]. Lines drawn to guide the eye.
Figure 5.6. Standard entropies (empty symbols) and enthalpies (filled symbols) of nonionic surfactant micellization in water (top). Standard entropy per EO unit (empty symbols) and enthalpy per EO unit (filled symbols) of micellization in water (bottom). Panels a and c contain data on aqueous (⚫, □) XP-series, (▲, △) linear C$_{10}$EO$_{j}$, and (■, □) linear C$_{12}$EO$_{j}$ surfactant systems. Panels b and d contain data on aqueous (▽, ▽) XL-series, (♦, ◊) ES 8928-series, and (◀, ◆) C$_{i}$PO$_{n}$EO$_{j}$ (j = 8, 17, and 34) surfactant systems.
Figure 5.7. Plots of $\Delta H$ versus surfactant concentration for the titration of micellar aqueous solutions of (●) XP-30, (▲) XL-90, and (▼) XL-140 into pure water at 20 °C from isothermal titration calorimetry.
Figure 5.8. Cloud point data for the (●) XP-, (□) XL-, and (▲) ES-series Lutensol® surfactants (1% w/w) in water, and (▽) linear C₆, (○) linear C₁₀, linear C₁₂ (◇) alkyl ethoxylate surfactants in water (data for linear surfactants from ref [9]). Error bars for the XP, XL, and ES series surfactants represent one standard deviation based on three measurements. Lines are drawn to guide the eye. Data points above the dashed line at 100 °C indicate that the cloud point was above 100 °C; data points below the dashed line at 20 °C indicate that the cloud point was below room temperature.
Figure 5.9. Relative viscosity of aqueous surfactant solutions plotted versus surfactant concentration normalized by the surfactant cmc (measurement at 25 °C). Top panel: (●) XP-50, (■) XL-100, (▲) XL-140. Bottom panel: (○) ES 8928-A, (□) ES 8928-B, and (▲) ES 8928-C.