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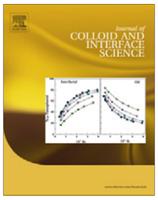

Micellization of amphiphilic block copolymers in binary and ternary solvent mixtures

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ABSTRACT

Amphiphilic block copolymers of the poly(ethylene oxide)–poly(propylene oxide) (PEO–PPO) family (commercially available as Pluronics or Poloxamers) are well-known for self-assembling in water (selective solvent for PEO) into micelles with a PPO-rich core and a hydrated PEO corona. The micellization of two PEO–PPO–PEO block copolymers (Pluronic P105: $EO_{37}PO_{56}EO_{37}$ and Pluronic F127: $EO_{100}PO_{65}EO_{100}$) has been studied in binary mixed solvents consisting of water and one of the following organic solvents: ethanol, glycerol, D(+)-glucose monohydrate, propylene carbonate, or triacetin, and also in ternary mixtures of water with 50/50 wt% ethanol + glycerol or 50/50 wt% ethanol + propylene carbonate. Glycerol, glucose, propylene carbonate and triacetin were found to promote micellization when added to water. Glycerol and glucose interact favorably with water, and reduce the block copolymer critical micelle concentration (cmc) by dehydrating the PEO–PPO interface as well as changing the bulk solvent properties. Propylene carbonate and triacetin act by locating at the PEO–PPO interface and increasing its hydrophobicity. The addition of ethanol to water provides better solvent conditions for the block copolymers compared to plain water, and disfavors the formation of micelles. In the case of ternary solvents consisting of water, ethanol (that prevents micelle formation), and glycerol or propylene carbonate (that favor micelle formation), the observed changes in the cmc are subtle. For Pluronic P105, the cmc increase is greater for ethanol + propylene carbonate (50/50 wt%) than for ethanol + glycerol (50/50 wt%). For Pluronic F127, the cmcs remain the same as in plain water, i.e., the effects of the two organic solvents compensate each other. The difference between the free energy of micellization in plain water and that in solvent mixtures varies linearly with the cosolvent concentration, and collapses into a single line for each solvent mixture type when normalized with the number of the block copolymer PO units (N_{PO}), indicating that the micelle core is mainly affected by varying solvent condition for different PEO/PPO ratios.

1. Introduction

Amphiphilic molecules tend to associate in solution into discrete assemblies called micelles [1,2]. The amphiphile concentration at which the micelles start to form is called the critical micellization concentration (cmc) and it represents a very important characteristic of a surfactant, especially in consideration of its practical uses [1,2]. In the past decade or so, many researchers have studied the micellization of polymeric amphiphiles, particularly those composed of water-soluble poly(ethylene oxide) (PEO) blocks and water-insoluble poly(propylene oxide) (PPO) blocks [3–11]. These block copolymers are commercially available as Pluronics, Poloxamers or Synperonics. Due to their characteristic surface modifying properties, these non-ionic polymeric amphiphiles find widespread applications in emulsification, detergency, foaming, lubrication, dispersion stabilization, etc. [12–16], and more specialized applications in pharmaceutical formulations, drug solubilization, dental care products, bioprocessing, and nanomaterials synthesis [17–20].

The solvent quality is a controlling factor in the cmc and the structure of the micelles formed by PEO–PPO block copolymers. The addition to water of electrolytes [21–23] or polar organic solvents [22–25] provides extra degrees of freedom in directing the solution properties for various applications. The presence of polar organic solvents also affects the overall phase behavior, for example, the concentration range of stability of various types of lyotropic liquid crystals formed by PEO–PPO block copolymers in water [26–29].

Organic additives to aqueous surfactant solutions can be classified into cosolvents and cosurfactants [30,31]. Cosurfactants denote weakly amphiphilic polar organic molecules that cannot form micelles alone. Cosurfactants act at low concentrations; they adsorb at the outer portion of the micelle (at the water–micelle

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core interface) and favor micellization of the surfactant. Cosolvents affect the micellization at much higher concentrations. Cosolvents are not necessarily amphiphilic in nature and may not interact with micelles. Instead, cosolvents affect the cmc via modification of water–surfactant interactions due to changes of the properties of the mixed solvent. A given molecule can often act as both cosurfactant and cosolvent. For example, it has been reported that ethanol acts as cosurfactant and reduces the cmc at low concentration, whereas at high concentration it increases the cmc, indicating its role as cosolvent [32].

It is known that PEO–PPO–PEO block copolymers can self-assemble in mixtures of water and nonaqueous polar solvents [6,11,23–25,33–35]. The ability of nonaqueous polar solvents and oils to modify the block copolymer self-assembled structure can be ascribed to the preference of the solvents to locate in different domains of the microstructure depending on their relative polarity [36]. We have an interest in our research group in understanding the effect on self-assembly of solvents having polarity intermediate to that to oils and water. Among such solvents, propylene carbonate and triacetin are hydrophobic, having positive log *P* (octanol–water partition coefficient) values, with triacetin being more hydrophobic (higher log *P* value) than propylene carbonate [37]. Both of them are approved for use in pharmaceutics, thus the present study can have a direct impact on such formulations [37,38]. Propylene carbonate is also used as an electrolyte in rechargeable lithium batteries [39]. Propylene carbonate and triacetin were found to locate at the interface between PEO-rich and PPO-rich domains in lyotropic liquid crystals formed at high concentrations of PEO–PPO block copolymers [37]. However, the micellization of PEO–PPO–PEO block copolymers in aqueous solutions of these solvents has not yet been investigated. Such information would contribute to the fundamental understanding of solution thermodynamics related to the influence of hydrophobic solvents on the micellization of amphiphiles in aqueous solutions. Moreover, it would be useful to explore the self-assembly of amphiphiles in mixtures of three solvents; one being water, and the other two organic solvents that are known to affect the micellization process in an opposite manner. Such multicomponent mixtures occur frequently in formulations for, e.g., food grade micro-emulsions [40,41], liquor [42–44], and biological molecules [45–47].

In this work, we examine the micellization of Pluronic P105 and F127 PEO–PPO–PEO block copolymers in binary mixtures of water with one of the following solvents: ethanol, glycerol, D(+)-glucose monohydrate, propylene carbonate or triacetin. We first discuss the role of hydrophilic solvents (glycerol and glucose), followed by the role of hydrophobic solvents (propylene carbonate and triacetin), and finally the role of ethanol. We also consider the influence of ternary solvent mixtures of water and 50/50 wt% ethanol + glycerol or 50/50 wt% ethanol + propylene carbonate. The cmc, the free energy of micellization and the free energy contribution due to the addition of cosolvent for Pluronic P105 and F127 in the above mentioned mixed solvents are reported. To the best of our knowledge, this is the first report on the micellization of PEO–PPO block copolymers in mixtures of water with propylene carbonate or triacetin, and also in ternary solvent mixtures.

2. Materials and methods

The Pluronic P105 and F127 PEO–PPO–PEO block copolymers were obtained from BASF Corp. (Mount Olive, NJ) and were used as received. Pluronic P105 has a molecular weight of 6500 and contains an average of 56 PO units and 2*36 EO units, whereas Pluronic F127 has molecular weight 12,600, 70 PO units and 2*100 EO units.

Water of Milli-Q quality (18 MΩ cm) was used as the primary solvent. Ethanol (200 Proof) was obtained from Pharmo-Aaper (Brookfield, CT). Glycerol (99.8% pure) and propylene carbonate (98% pure) were obtained from Fisher Scientific (Fair Lawn, NJ). 99.5% pure D(+)-glucose monohydrate was purchased from Fluka Chemicals (Milwaukee, WI) and 99% pure triacetin was purchased from Sigma Chemicals (St. Louis, MO). The solubility of propylene carbonate and triacetin in water was reported to be 17.5 and 8 wt%, respectively [48,49]. Our studies have been therefore limited to using up to 15 v/v% of propylene carbonate and up to 6 v/v% of triacetin in water. All solvents were used as received. Table 1 lists the physicochemical properties of the solvents used in this study.

For the determination of cmc in binary solvents, organic solvents were first mixed with water to achieve the desired (v/v%) concentration (the composition reflects the volumes prior to mixing). Ternary mixtures were prepared by mixing previously prepared 50/50 wt% ethanol + glycerol and 50/50 wt% ethanol + propylene carbonate binary mixtures with water to the desired final (v/v%) concentration. The block copolymer was dissolved in the solvent mixture and then diluted to the desired concentration (ranging from 0.0001% to 10% w/v). The experiments were carried out within a few days of sample preparation.

A dye solubilization technique was employed to determine the onset of the amphiphile micellization [4]. Below the cmc, the UV–Vis absorption of 1,6-diphenyl-1,3,5-hexatriene (DPH) is very low. Above the cmc, the concentration of solubilized DPH increases with the total micelle concentration and its absorption intensity rises. A stock solution of 740 μM DPH in methanol was prepared; 25 μL of the DPH/methanol solution is added to 3 mL of copolymer solution. The solutions were left in the dark to equilibrate for at least 3 h (and no more than 24 h) before the spectroscopic analysis was performed.

UV–Vis absorption spectra of the DPH/amphiphile/solvent samples were recorded in the 300–500 nm range using a Hitachi U-1800 UV–Vis spectrophotometer. Three peaks characteristic of DPH were observed, with the maximum intensity peak at 356 nm. The spectroscopic experiments were carried out at a constant temperature of 25 ± 1 °C. The DPH absorption intensity at 356 nm was plotted vs. the amphiphilic block copolymer concentration and the critical micelle concentration was obtained from the first inflection point of this curve (data not shown here).

3. Results and discussion

3.1. Micellization in binary solvent mixtures

3.1.1. CMC in binary mixtures of water with hydrophilic solvents

The most hydrophilic (as attested by their log *P* values) among the organic solvents used in the study are glycerol and glucose. Table 2 lists the cmc values of Pluronic P105 and F127 following the addition of glycerol and glucose to water. Both glycerol and glucose favor PEO–PPO–PEO block copolymer micelle formation. For example, addition of 40% glycerol to water causes the cmc of Pluronic P105 to decrease from 0.31 w/v% to 0.01 w/v%, and that of Pluronic F127 to decrease from 0.71 w/v% to 0.016 w/v%. In order to compare the solvent effect on the micellization of the two different block copolymers we normalized the cmc with the cmc_0 (i.e., cmc in plain water), and plotted cmc/cmc_0 against cosolvent concentration in Fig. 1. The log (cmc/cmc_0) decreases linearly with glycerol and glucose concentration, with a rate that is higher for glucose (higher negative slope). The observed difference between the influence of glycerol and glucose can be attributed to the difference of their individual properties.