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The origin of *anomalous* positive heat capacity change upon micellization of Pluronic triblock copolymer F108 in aqueous solutions: Effect of PEO-PPO diblock impurities

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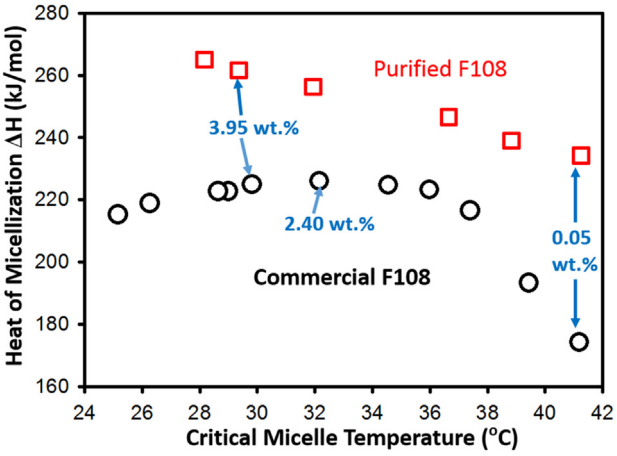
HIGHLIGHTS

- Heat of micellization of commercial Pluronics abnormally increases with temperature.
- Impurities of commercial Pluronic F108 would form aggregates.
- Impurity aggregates would dissociate and integrate into micelles upon micellization.
- Heat of micellization of F108 increases with temperature after removing impurities.
- Heat of micellization of F108 may enhance by 25.6% after removing impurities.

GRAPHICAL ABSTRACT



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ABSTRACT

It is well understood that the heat of micellization is monotonically decreased along with increasing temperature. However, it was found (Langmuir 2008, 24, 13858.) that the heat of micellization for Pluronic triblock copolymer in aqueous solutions abnormally increases along with the temperature at high Pluronic concentration region. The origin of this ***anomalous*** positive heat capacity change upon micellization of Pluronic F108 in aqueous solutions was explored by using differential scanning calorimetry, chromatography and dynamic light scattering. The impurities of commercial Pluronic F108, used as received, in aqueous solution form large aggregates at the temperatures well below its critical micelle temperature (CMT). At high F108 concentrations (>2.4 wt.%), the aggregates almost completely dissociate and then integrate into micelles, resulting in *anomalous* positive relationship of heat of micellization (ΔH) with critical micelle temperature (CMT). By contrast, at low F108 concentrations (<2.4 wt.%), the aggregates do not, or only partly, participate the micellization. When the impurities of F108 are separated and removed by using high performance liquid chromatography, the ΔH of purified

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F108 aqueous solutions monotonically decreases along with an increase in CMT. That is, a typical linear relationship of ΔH vs. CMT is resumed. It is interesting to find out that the ΔH of 0.05 wt.% purified F108 aqueous solution (234.1 kJ/mol) is higher than that of unpurified F108 (174.2 kJ/mol) by 25.6%.

1. Introduction

The tri-block copolymers, poly(ethylene oxide) (PEO)-poly(propylene oxide) (PPO)- poly(ethylene oxide) (PEO), are commercially named as Pluronics (BASF) or Poloxamers (ICI) and have been widely used in various fields such as drug delivery, bioseparation, emulsification, and synthesis of nanoparticles [1–5]. Due to their significant applications, numerous studies have been done on their rich self-assembling behavior in aqueous solutions. These copolymers are synthesized by ethoxylation of polypropylene glycol using base-catalyzed polymerization. Even in an ideal synthesis, a distribution of polymer length and side products, such as homopolymers and diblocks, should be expected. Although for practical purpose, it is common to use samples as received from the manufacturer without further purification, the effect of polydispersity and impurities of copolymers were not always appreciated and misinterpretations were often found in the literature. While many anomalous aggregation behaviors of the copolymers have been observed and directly attributed to the impurities, there are only a few reports on the effect of these impurities on the micellization, which sometimes even showed conflicting results and interpretations [6–19].

Zhou and Chu used dynamic light scattering (DLS) and nuclear magnetic resonance (NMR) to study an reported anomalous association behavior of Poloxamer 184 (or Pluronic L64) in a temperature region between unimer and micelle regions [6]. A normal transition can be recovered by using filtration to remove the minor components. The effect was attributed to the composition heterogeneity of the samples. By using DLS for P85 solution, Brown et al. reported that with an increase in copolymer concentration or temperature, the observed large aggregates were gradually diminished [14]. They attributed the impurities to the small amount of relatively hydrophobic diblock copolymers, which can be separated by using high performance liquid chromatography (HPLC). Similar results were also reported for L64 [19]. Kositza indicated that when L64 was purified by stirring in hexane, the DLS peak of the large aggregates disappeared. It can then reappear by adding small amounts of L61 which has the same PPO length. These aggregates were suggested to be a mixture of mainly hydrophobic impurities and some L64. Trathnigg and Gorbunov used liquid chromatography under critical conditions to characterize F68 and F108 copolymers [9,10]. The distributions of the PEO and PPO block lengths were reported. Both F68 and F108 do not contain any PPO homopolymers but have some PEO homopolymers.

Linse applied a mean-field lattice theory to model the effects of polymer impurities and polydispersity on the micellization [11,12]. It was predicted that the diblock impurities and polydispersity reduce the critical micelle temperature (CMT), but the latter has a stronger effect than the former. At the CMT, the diblock impurities and the longer copolymers aggregate more readily than the short copolymers. The PPO homopolymer also slightly reduced the CMT, whereas the effect of PEO homopolymer was negligible. In a series of pioneering papers, Hvidt, Batsberg, and coworkers reported that Pluronics are inhomogeneous in two respects: a distribution of PPO block lengths (polydispersity) and a 10–25 wt.% amount of impurities, consisting of mostly diblock copolymers with one full PEO block length but rather small PPO block and some double-bond containing contaminants [13,15–17]. The polydispersity of Pluronics was shown to broaden the micellization transitions, and the micellization was first proceeded by copolymers with a relatively long PO chain and gradually with higher EO/PO ratios at increasing temperatures, as predicted by Linse [11,12]. However, these authors concluded that the impurities were not incorporated into the micelles, with one possible exception for 25 wt.% F127 solution. This seems contradictory to the Linse's predictions. Fernandez et al. used DLS, differential scanning calorimeter (DSC), gel permeation chromatography to elucidate the kinetics of Pluronic P103 micellization [18]. They reported that the solutions first formed the large aggregates in the proximity of CMT, resulting from interactions between hydrophobic impurities and P103 copolymers. The aggregates then became proper micelles at higher temperatures. They proposed that the large aggregates were fragmented into two micelles of any size, and these micelles grew by fusion with other micelles or by association with free monomers to form proper micelles. In summary, from the studies mentioned above, it is difficult to determine the effects of impurities on the micellization. The role which the impurities play in micellization process remains obscure and is open for discussion.

It is well accepted that the micellization is entropy-driven, resulting from the destruction of the structured water shell surrounded PPO group. The process normally produces a large amount of endothermic heat which decreases monotonically with an increase in CMT. In a screening study of heat of micellization for Pluronics, F108, F98, F88, F68, and P65, at various concentrations, Tsui et al. found that the heat of micellization, however, increased with increasing CMT at high Pluronic concentrations to reach a maximum and then decreased with further increasing CMT at low Pluronic concentrations [20–22]. It was mentioned that these "unexpected" positive heat capacity changes may be due to the formation of large aggregates prior to micellization. The objective of this article, therefore, is to systematically investigate these positive heat capacity changes and their relationship with impurities. By using DLS, eluent gel permeation chromatography (EGPC), DSC, transmission electron microscopy, and HPLC to characterize Pluronic F108 solution, direct evidences of impurities effects on heat of micellization are presented here for the first time. It is unambiguously concluded that at high Pluronic concentrations, the impurities incorporate into micelles, resulting in positive heat capacity changes, whereas at low concentrations, the impurities only partly contribute to micellization.

2. Experimental

2.1. Materials

The triblock copolymer Pluronic F108 was obtained from BASF. The chemical formula of Pluronic F108 is $(EO)_{132}(PO)_{50}(EO)_{132}$, where the subscripts represent the numbers of PO and EO units. The molecular weight of Pluronic F108 is 14600 g/mol. It was reported that Pluronic F108 sample obtained from BASF contains about 24 wt.% impurities [16]. All aqueous solutions were prepared using double-distilled water followed by a PURELAB Maxima Series (ELGA Lab Water) purification system with a resistivity equal to 18.2 MΩ-cm. Concentrations are given as weight percentage.