



Research Paper

Urea induced changes in self-assembly and aggregate microstructures of amphiphilic star block copolymers with widely different hydrophobicity



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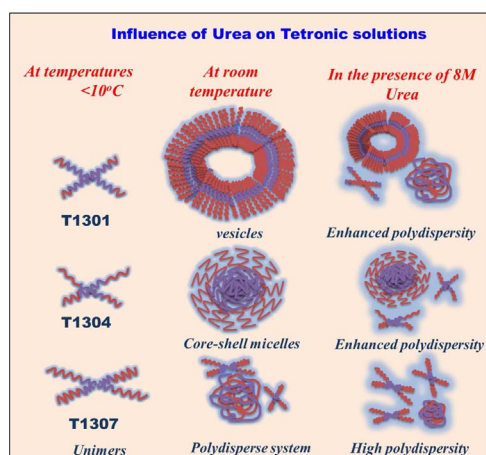
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GRAPHICAL ABSTRACT



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ABSTRACT

The presence of excess of denaturants like urea unfolds proteins and disfavours micellization of surfactants; the mode of interaction of urea has always been a matter of debate. Inspired by this need, the effect of urea on the monolayer and micellar characteristics of three polyethylene oxide/propylene oxide (PEO/PPO) starblock copolymers Tetronics[®] viz. T1301, T1304 and T1307 (with almost same molecular weight of PPO but varying% PEO as 10, 40 and 70%, respectively) in aqueous urea solutions was investigated through scattering/spectral technique and Langmuir film balance.

The three copolymers showed markedly different behaviour. In the absence of urea, the most hydrophobic T1301 forms vesicular structures (few hundred nm), T1304 with moderate hydrophobicity forms spherical micelles (~10–20 nm) with low polydispersity while very hydrophilic T1307 exists as a highly polydispersed system with unimers (~3–5 nm), loose aggregates (~10–20 nm) and clusters (with few hundred nm size). However, the addition of urea (0–8 M) to these copolymer solutions leads to the disruption of any loose aggregates formed which is probably due to its binding with the copolymer chains that enhances the solubility of

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Tetronics[®] and overall polydispersity of the copolymer solutions. In support to our hypothesis, the binding of urea was validated using fluorescence measurements/Langmuir film balance and it was established that urea follows the direct mechanism (as proposed in earlier reports) and the intercalation of urea between the PEO chains leads to the extended conformations as observed by Langmuir film balance. Although, urea had a common denaturing effect on all the three copolymers, the hydrating effect of urea was most evident for copolymers with more hydrophilic character.

1. Introduction

Urea is a peculiarly important stabilizer of water-exposed surfaces that agglomerate at interfaces and disrupts water structure. Thus, it endorses protein unfolding [1], favours demicellization [2,3], and curbs surfactant clouding [3] by promoting the exposure of hydrophobic units to water. Urea has long been employed as a standard tool in (un)folding studies of globular proteins and manifested tuning of membrane protein stability [4]. The mechanism by which urea administers its effect on bio-macromolecules has been a matter of debate. However, it has been shown that urea employs a direct or indirect mechanism to exert its effect [5–7]. The direct mechanism considers that urea develops favourable H–bonding with protein molecules, which empowers it to replace water in the solvent shell around hydrophobic segments resulting in their embellished solubility. The indirect mechanism assumes that urea disrupts the three-dimensional arrangement of water, thereby reducing the energetic cost essential to dissolve hydrophobic segments in bulk solution [8–10]. Though urea is usually considered as a water-structure breaker, actual evidence denotes only a minimal influence of urea on the three dimensional structure of water [11,12].

The commercially available linear (Pluronic[®]) and branched (Tetronics[®]) block copolymers are nonionic surfactants that find applications in several fields [13–15]. In addition to the features shown by their prominent linear analogue, Pluronic[®] which are common ingredients of pharmaceutical micellar systems in reference to their long established temperature-sensitiveness and biodegradability [13,16,17], the unique structure of Tetronics[®] with added versatility endows them with multi-stimuli responsiveness. In recent years, they have found applications in detergency, wetting, emulsification, nano-particle stabilizers, bioprocessing, and pharmaceuticals. The molecular weight and EO/PO ratio of Tetronics[®] plays an influential role on the self-assembly [18]. Moreover, the physicochemical conditions, mainly the pH and the ionic strength of solution, alter the protonation extent of the ethylenediamine central group, disrupting the hydrophobic interactions that dictates the self-assembly. Thus, both structure and stimuli responsiveness has a profound influence on the performance of Tetronic[®] micelles.

Studies based on the effect of urea on the micellar systems date back to several decades [19–22]. Schick [21], demonstrated the disruptive nature of urea on micelles of different *n*-dodecyl sulphates and prompted an increase in the critical micelle concentration (CMC). In line with this, there are several contributions in literature based on the influence of urea on micellar systems of different ionic [19,23–26] and nonionic surfactants [3,27,28]. Indeed, urea has been exposed to increase the CMC of ionic [24,29] and non-ionic [21] surfactants and shrinks the average micellar hydrodynamic radius in case of ionic micelles [30]. Haldar and Chattopadhyay [31] using fluorescence correlation spectroscopy monitored aggregation in sodium dodecyl sulphate and dodecyl trimethylammonium bromide at single-molecule resolution in the presence of urea and other organic additives. The study revealed that presence of urea curbed self – association. Broecker and Keller [32] quantified the influence of urea on micellar behaviour of sugar surfactants and suggested increase in CMC along with a linear drop in micellar size and Gibb's free energy of micellization. Conversely, Kumar et al. [33] observed a decrease in the CMC of sodium dodecyl sulphate for urea concentrations below 1 M. In line with this, Chakraborty et al. [34] from scattering elucidated the stabilizing action

of urea at low concentrations in AOT/*n*-heptane reverse micelles. The disruptive nature of urea has also been examined for Pluronic[®] micelles [28,35–38]. Hatton and co-workers suggested that the presence of urea increased CMC and critical micelle temperature (CMT) values of Pluronic[®] and observed a decrease in the micelle micropolarity and microviscosity [28]. Ma et al. [35] using NMR demonstrated that urea selectively interacts with the PEO blocks and increases the CMT; the effect being more evident in Pluronic[®] with higher PEO content. On the contrary, Zangi et al. [39] using computational analysis deduced that during the denaturation of proteins, urea forms stronger attractive interactions with the hydrophobic core than water and thus enhances the solubility of the core. Recently, Anand and Mukherjee [38] suggested that temperature counteracts the effect of urea. Further, the counteraction is more noticeable in the core region as compared to corona, while the peripheral region is least affected. Also urea decreases the microviscosity in the core and the corona region of F127 micelles.

Though there are several reports in literature on micellar behaviour of Pluronic[®], reports on Tetronics[®] are limited [40–45]. Cavallaro et al. [40] witnessed formation of mixed micelles for Tetronics[®] and fluorinated surfactants by incorporating various perfluoro carboxylic acids and observed improved selectivity for hydrogenated and fluorinated oils. Dreiss and co-workers [43,45] explored the influence of different cyclodextrins on the self-assembly of Tetronics[®] and added to the information available for Tetronics[®] in literature. There are also contributions on the effect of salts [46,47], glucose [48], amino acids [49,50], ionic liquids [51] and alkanols [52,53] on micellar solutions of Tetronics[®], among which few are reported by our group. However, a systematic study shedding light on the influence of urea on Tetronic[®] micelles still lacks. Despite of the available literature on the effect of urea on its linear counterparts, unfortunately, there is no report describing its influence on star shaped EO-PO block copolymer micelles. With this background, we report here, the effect of urea on the micellar properties of three Tetronics[®] viz. T1301, T1304 and T1307 (Table 1) with varying hydrophobicities using plethora of techniques. The information attained from our work will be useful for optimizing the performance of star block copolymers and provides a clear understanding on the influence of urea on Tetronic[®] micelles which can be used in therapeutics/cosmetics and in several industrial processes together.

2. Materials and methods

2.1. Materials

Tetronics[®] T1301, T1304 and T1307 (Table 1; Scheme1), were gift samples from BASF Corp. and used as received. AR grade urea was purchased from Sigma Aldrich (India). The copolymer solutions were prepared by dissolving the weighed amount of copolymer in water and

Table 1
General characteristics of Tetronics[®].

Tetronics [®]	Mol. wt	No. of PO units (a)	No. of EO units (b)	%PEO	HLB	CP (°C)
1301	6800	26	4	10	1–7	16
1304	10500	27	24	40	12–18	76
1307	18000	27	61	70	> 24	> 100

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