



# Influence of ionic liquids on the critical micellization temperature of a tri-block co-polymer in aqueous media



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## ABSTRACT

To explore the role of additives in controlling the critical micellization temperature (CMT) of a block copolymer in aqueous solution, in the present work, a series of ionic liquids (ILs) containing the same cation, 1-butyl-3-methylimidazolium,  $\text{bmim}^+$  and commonly used anions such as  $\text{SCN}^-$ ,  $\text{BF}_4^-$ ,  $\text{I}^-$ ,  $\text{Cl}^-$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{HSO}_4^-$  were chosen for study with a triblock copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), (PEG-PPG-PEG) in aqueous solution. The present results suggest that the ability of ILs for decreasing the polymer CMT is mainly a result of not only from charge and size of anions of the ILs, but also due to the weak ion-ion pair interactions within IL. The present study provides important information that can be helpful to tune the IL- or temperature-sensitive copolymer CMT and micelle shapes which are crucial for understanding the drug delivery mechanisms.

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## 1. Introduction

Triblock copolymers (commercially known as Pluronics<sup>®</sup> or Poloxamers<sup>®</sup>) have attracted considerable attention both in terms of fundamental research and for a diverse range of practical applications [1,2]. By analogy with classical simple nonionic surfactants, Pluronics<sup>®</sup> can self-assemble into nanostructures in aqueous solution due to minimization of the unfavorable interactions between hydrophobic groups and water molecules [3,4]. The process of self-assembly predominantly occurs in aqueous amphiphilic polymer solutions by changing the temperature [5,6], light [6,7] and pH [8,9]. Further, self-assembly can also be attained by inclusion of a third component (additive) such as ionic salts [10], ionic liquids (ILs) [11], surfactant [12] and co-solvents [13–15]. Owing to important and inherent potential applications amphiphilic polymers are important in various fields such as detergency, dispersion, stabilization, emulsification, lubrication, drug delivery [16,17]. The micelles of Pluronics<sup>®</sup> have a core dominated by hydrophobic portion and a corona comprising the hydrated hydrophilic portion at their characteristic temperature called the critical micellization temperature (CMT) [18].

The hydrophobic core of the micelle carries the hydrophobic drug to the targeted place, while the hydrophilic corona enhances

the stability of the micelles [19]. Because of this, the study of Pluronics<sup>®</sup> has substantial deal of significance in scientific and industrial communities. In this regard, till date, the majority of studies have focused mainly on CMT of Pluronics<sup>®</sup> in the presence of salts [20], surfactants [21–24], alcohols [25], urea [26] and IL [27]. In particular, the alkali-metal anions such as  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{F}^-$  and  $\text{Cl}^-$  act as structure makers for water molecules leading to an increase in their self-hydration and decrease in hydration of polymer in aqueous medium [28]. On the other hand, salts of  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$  and  $\text{SCN}^-$  act as structure breakers for water molecules leading to decrease in their self-hydration and an increase in hydration of polymer in aqueous medium [28]. Based on their ability of water structure making or breaking in protein aqueous solution in 1888, Franz Hofmeister arranged these anions in a series known as Hofmeister series and is as follows  $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{SCN}^-$  [29].

ILs are typically composed by organic cations and organic/inorganic anions existing as liquids at ambient room temperature [30]. Because of their unique properties such as negligible vapor pressure, high reactivity, favorable solvation behavior and high thermal stability, ILs are good candidates for replacing the traditional organic solvents [30,31]. Due to their rich applications in various chemical industries, research of ILs is at great pace from the last decade. ILs are often referred as “designer solvents” because of their tunable physical properties such as polarity, viscosity, miscibility and density [31–35].

In recent years, the use of ILs to tune the aggregation of copolymer is greatly intensified [36–39]. However, the action of IL may be

Abbreviations: ILs, ionic liquids; CMT, critical micellization temperature; LCST, lower critical solution temperature;  $\text{bmim}^+$ , 1-butyl-3-methylimidazolium.

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different on aggregation of copolymers based on the type of anion or cation of IL being used. In this context, the suppression of lower critical solution temperature (LCST) of poly(*N*-isopropylacrylamide), PNIPAM was observed over the addition of 1-benzyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) in aqueous medium [11]. Surprisingly, in contrast to this, the same polymer exhibits upper critical solution temperature (UCST) in hydrophobic IL, 1-ethyl-3-methylimidazolium bis (trifluoromethane sulfone) imide (EMITFSI) [44]. In another instance, Zheng et al. [27] claimed through FTIR results that 1-butyl-3-methylimidazolium bromide [bmim][Br] decreases the CMT of Pluronic P104 when the [bmim][Br] concentration was above 1.232 mol/L. However, from these results one can understand that the aggregation process of the copolymer can be tuned by the ILs.

Indeed, the physical properties of ILs are unique. Obviously, an interesting aspect of ILs is that the physicochemical properties of ILs can undergo huge changes on a slight variation in their constituted ions. In this regard, it is much interesting to explore the behavior of anions of ILs especially in terms of structure making and/or breaking of water in polymer aqueous media. In spite of vast utilization of ILs in polymer science, there is a huge scarcity of knowledge regarding ability of IL in controlling the solubility of copolymer in aqueous solution. Moreover, as far as our knowledge, there has been no attempt in open literature to explore the effect of anions of ILs on the solubility of copolymer in aqueous media. In the present study, various ILs including 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim]HSO<sub>4</sub>), 1-butyl-3-methylimidazolium acetate ([bmim]Ac), 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-butyl-3-methylimidazolium iodide ([bmim]I), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF<sub>4</sub>) and 1-butyl-3-methylimidazolium thiocyanate ([bmim]SCN) have employed to identify the effect of anions of ILs on the solubility of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEG-PPG-PEG) (commercially known as Pluronic® F-108) through CMT studies in aqueous solution. The ILs induced modulations in CMT of Pluronic® F-108 aqueous solution have monitored through fluorescence spectroscopy, viscosity ( $\eta$ ), UV-vis spectroscopy, dynamic light scattering (DLS) and scanning electron microscope (SEM) measurements. The primary goal of the present work is bringing the idea about the influence of a Hofmeister series of anions of ILs on temperature-sensitive block copolymer in aqueous medium.

## 2. Materials and methods

### 2.1. Materials

The Pluronic® F-108, ILs and pyrene were purchased from Sigma-Aldrich Chemicals Co. and used without further purification. The polymer molecular weight ( $M_n$ ) is ~14,600 with a PEG content of 82.5%. Sample solutions were prepared by using the high purity of water with a resistivity of 18.3 M $\Omega$  cm. and which was obtained from a NANO pure water system (Rions India, India). All the sample solutions were prepared gravimetrically.

### 2.2. Sample preparation

By using Mettler Toledo balance with a precision of  $\pm 0.0001$  g, the required amount of pyrene and Pluronic® F-108 was weighed for stock solutions. Aliquots of these solutions were mixed and prepared the sample solutions at desired concentration of polymer. The final polymer concentration for all measurements maintained at 7 mg/mL. The weighed amounts of ILs at various concentrations (5, 10 and 15 mg/mL) were added directly to the aqueous polymer solution. In fluorescence measurements the concentration of probe

was kept at  $6 \times 10^{-7}$  M for avoiding the probe interference in measurements. Prior to the measurements, each sample was filtered with 0.45  $\mu$ m disposable filters (Millipore, Millex-GS) through a syringe.

### 2.3. Fluorescence intensity measurements

Fluorescence intensity measurements of pyrene in Pluronic® F-108 aqueous solution in the presence of ILs were carried out using a Cary Eclipse fluorescence spectrophotometer (Varian optical spectroscopy instruments, Mulgrave, Victoria, Australia) with an intense Xenon flash lamp as light source. All intensity measurements were performed at excitation wavelength ( $\lambda_{ex}$ ) of 335 nm. Emission spectra were recorded with slit width of 5/5 nm and the PMT voltage of 720 V. Scan speed was kept at 1200 nm min<sup>-1</sup>. Quartz cuvette (QC) containing sample was placed in multi cell holder, which is electro-thermally controlled at precise temperature regulated by peltier. The temperature control of the peltier thermo stated cell holders is extremely stable over time, with a typical precision of  $\pm 0.05$  °C. Each sample solution left for 30 min in undisturbed condition at all desired temperatures to get the thermodynamic equilibrium.

### 2.4. Viscosity measurements

The viscosities ( $\eta$ ) of Pluronic® F-108 aqueous solution in the presence of ILs have measured by using a sine-wave vibro viscometer (model: SV-10 A&D Company Limited, Japan) with uncertainty of 1%. The  $\eta$  of sample solutions was collected in the wide temperature range by using the circulating temperature control water bath (LAUDA alpha 6, Japan) with accuracy of temperature of  $\pm 0.02$  °C. The sine-wave vibro viscometer equipped with two gold sensor plates measures the  $\eta$  of sample by detecting the driving electric current necessary to resonate the two sensor plates at a constant frequency of 30 Hz and amplitude of less than 1 mm. All  $\eta$  measurements of the sample were collected at heating rate of 1 °C/30 min after allowing to the thermodynamic equilibrium. All of the viscometer accessories were cleaned and dried each time before each measurement.

### 2.5. UV-vis absorption measurements

UV-vis absorption spectra of the pyrene-containing Pluronic® F-108 aqueous solution in the presence of ILs were recorded with a UV-vis spectrophotometer (UV-1800, SHIMADZU Company, Japan) and collected from a 1 cm path length quartz cuvette at room temperature. The entire absorbance wavelength readings were made within the range of 190–500 nm.

### 2.6. Hydrodynamic radius ( $R_h$ ) measurements

Hydrodynamic radius ( $R_h$ ) of Pluronic® F-108 aggregates in the presence of ILs has measured from DLS measurements by using the Zetasizer Nano ZS90 (Malvern Instruments Ltd., UK), equipped with He-Ne (4 mW, 632.8 nm). In built thermostatic sample chamber enables to maintain the desired temperatures within a temperature range of 2–90 °C with a great accuracy. This instrument measures the movement of particles under Brownian motion and converts this motion into size by using the Stokes-Einstein equation as follows

$$R_h = \frac{kT}{6\pi\eta D} \quad (1)$$

where  $k$  is the Boltzmann's constant,  $T$  is absolute temperature,  $\eta$  is viscosity, and  $D$  is diffusion coefficient. All data were obtained by

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