



Effect of ionic liquids on microstructures of micellar aggregates formed by PEO–PPO–PEO block copolymer in aqueous solution



Rohit L. Vekariya^a, Debes Ray^b, Vinod K. Aswal^b, Puthusserickal A. Hassan^c, Saurabh S. Soni^{a,*}

^a Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

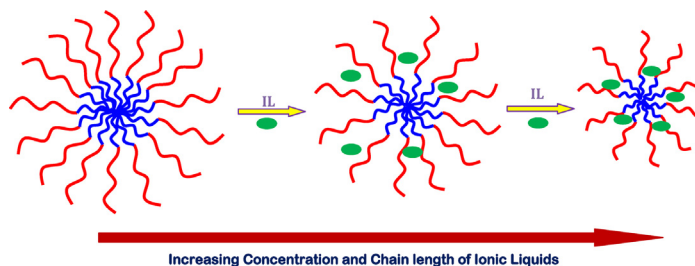
^b Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, Maharashtra, India

^c Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, Maharashtra, India

HIGHLIGHTS

- Aqueous mixed systems of Pluronics® (F127) with various pyridinium based ILs were studied.
- Size and shape for micelles of F127 in aqueous solutions of ILs were measured by SANS and DLS.
- The interactions between PEO/PPO with ILs were checked by ¹H NMR and viscosity.
- Upon addition of ILs, an enhancement in CMC and reduction in micellar size of F127 were found.
- Effect of alkyl chain length, head group, anions and concentration of ILs has been discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Effect of ionic liquids (ILs) viz. pyridinium, picolinium and imidazolium halide on the micellization and the structure of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer, F127 in aqueous solution has been studied by small angle neutron scattering (SANS) and dynamic light scattering (DLS) measurements. The interaction information between ILs and PEO/PPO has been explored by using ¹H NMR and viscosity measurements. The micellar structural parameters are obtained as a function of variation in alkyl chain length, cationic head group and concentrations of ILs by fitting the SANS data with model composed of core–shell form factor and a hard sphere structure factor of interaction. Addition of ILs is found to decrease the micellar core radius, aggregation number and hard sphere radius of F127 micelles. The effect of concentration, chain length and head groups of ILs also have been studied.

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1. Introduction

Amphiphilic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), (PEO–PPO–PEO) triblock copolymers are known as Pluronics® or polaxamer or symperonics (ICI). These interesting types of amphiphilic block copolymers are commercially

* Corresponding author. Tel.: +91 2692 226858x216; fax: +91 2692 236475.
E-mail addresses: soni.b21@yahoo.co.in, saurabhavna@gmail.com (S.S. Soni).

available in a variety of molecular weights and PEO/PPO ratios [1]. The hydrophobic/hydrophilic character of the copolymer in aqueous solution can be altered by varying the solution temperature or modifying the solvent properties, hence they are widely used in many industrial formulations [2,3]. In recent years, the scope of their application is much broader as they used in nanoparticles synthesis [4,5], gene delivery [6], as polymer gel electrolyte [7,8], as templating agents [9], etc. Majority of these applications are associated with the micelles, those are formed in aqueous solution and therefore, micellization of block copolymers has attracted great attention [10]. In aqueous media, above the critical micellization temperature (CMT) or above the critical micellization concentration (CMC) they self associate into micelles with a hydrophobic core containing PO blocks surrounded by outer shell of the hydrated EO blocks [3]. The interesting feature of Pluronics is they self assembled in rich micro-crystalline phases. It is well known that copolymers interact with classical surfactants such as anionic, cationic and nonionic. The Pluronic F127 with aqueous solutions of sodium dodecyl sulphate [10], tetradecyltrimethylammonium bromide [11] and hexaethylene glycol mono-*n*-dodecyl ether [12] were studied. The addition of salts and conventional cationic and anionic surfactants has a strong effect on the micellization, cloud point and CMT [13]. Hecht et al. [14,15] have reported that very small amounts of NaDS interfered with the micelle formation of F127 and when the concentration of added NaDS was sufficiently high the micellization of F127 was completely suppressed [16]. Pluronics–cetyltrimethylammonium bromide (CTAB) supramolecular assemblies, in which the hydrophobic chains of CTAB occupy the hydrophobic core of the Pluronics micelle while the positively charged head groups reside at the micellar core–shell interface has been studied by Sing et al. [17].

Ionic liquids (ILs) received great attention, because of their intriguing properties like negligible vapour pressure, negligible flammability, excellent chemical and thermal stability, electrochemical window and stability over a broad temperature range [18–20]. Due to these interesting properties, ILs have been widely in use in the areas of organic synthesis, catalyst, electrochemistry, polymer electrolyte, etc. Among all reported ILs, due to higher biodegradability, IL composed of alkyl pyridinium cation with variety of anions are used in various applications including as surface active agent [21,22].

In recent years, ILs in combination with polymers have also been used as reaction media for polymer synthesis [23], supported catalyst [24], polymer electrolyte membrane [25], metal ion removal [26], as an electrolyte in dye sensitized solar cell [27], lithium ion batteries [28], etc. Moreover, very recently, water based polymer gel electrolyte received much attention because of the environmental and safety issues [29]. In view of these, it is necessary to study the effect of ILs, their interactions and location of cation/anion fragments in micelles of amphiphilic block copolymers in aqueous solutions.

Association behaviour and surface activity of amphiphilic block copolymers and ILs are very well documented in literature [21,22,30,31]. Some reports are available on self-assembly and micellization behaviour of amphiphilic block copolymer in an IL (where ILs were used as a solvent) [32,33]. But very few literatures are available on effect of IL on aggregation behaviour of triblock copolymers in aqueous medium. To the best of our knowledge, only two reports on the effect of ILs on Pluronic micelles are available in literature [34,35]. Zheng et al. [34] reported aggregation behaviour of Pluronic P104 in presence of 1-butyl-3-methyl imidazolium bromide (BmimBr) in aqueous solution. The variation of CMT, CMC and interaction between hydrophobic part (butyl group of the Bmim⁺) cation with PO block of triblock copolymer were carried out using FTIR, FFTEM, DLS and NMR spectroscopy. Very

recently, Parmar et al. [35] studied interaction between 1-alkyl-3-methyl imidazolium tetrafluoroborate and Pluronic P103 in aqueous solutions using DLS, SANS and NMR studies. From the selective NOESY NMR spectrum, they indicated that there is an interaction between butyl chain of cation and PO group of P103 micelles. Both of these reports are based on the imidazolium based ILs and as far as we aware, no other reports are available on detailed SANS analysis as a function of concentrations, cationic head groups and alkyl chain length on pyridinium cation of ILs on micelles of F127 block copolymer in water. The aim of the present study is to make correlation between variation of concentration, alkyl chain length and cation of IL and micellization of Pluronic F127 in aqueous solutions.

In this paper we report the results on the aggregation behaviour of a block copolymer, Pluronic F127 [(EO)₉₇(PO)₆₉(EO)₉₇] in presence of various ILs in aqueous media as studied by SANS, DLS, NMR and viscosity measurements. SANS and DLS studies were used to determine the size and shape of F127 micelles under the influence of ILs. From NMR analysis, interactions of ILs with micellar core (PPO block) and shell (PEO block) were determined. Effects of head groups, alkyl chain length of cations, anions and concentration of ILs on micellization of F127 in aqueous solution have been discussed.

2. Experimental

2.1. Chemicals and materials

Pluronic F127 (EO₉₇PO₆₉EO₉₇) with average molecular weight 12,600 g mol⁻¹ was purchased from the Sigma–Aldrich, India and used as received. All ILs were prepared by the procedure reported in literature [18,22,36,37] and were characterized by ¹H NMR, TGA, IR methods. All ILs were stored at 60 °C in vacuum prior to use and the water content was measured by Karl–fisher analysis which found less than 0.05% in all ILs. The structures, molecular weight, and CMC of synthesized ILs are given in Table 1. Aqueous solutions of Pluronic and ILs were prepared by weight using an analytical balance in degassed Millipore grade distilled water. For SANS and NMR measurements samples were prepared in D₂O (>99% purity, Sigma–Aldrich).

2.2. Methods

2.2.1. Small angle neutron scattering (SANS)

SANS measurements were carried out on micellar solutions of F127 triblock copolymer in presence of various types of ILs. The SANS measurements were performed using a fixed geometry SANS instrument with a sample-to-detector distance of 1.8 m at DHRUVA reactor, Trombay, India [41]. This spectrometer makes use of a BeO filtered beam which provides a mean wavelength of 5.2 Å and has a wavelength resolution of about 15%. The angular distribution of the scattered neutrons is recorded using a 1 m long one dimensional detector. The accessible wave transfer, *q* range of this instrument is 0.015–0.35 Å⁻¹. The solutions were held in a 0.5 cm path length UV-grade quartz sample holder with tight fitting Teflon stoppers sealed with parafilm. The theoretical approach for analysis of SANS distribution curves is given in supporting documents.

2.2.2. Dynamic light scattering (DLS)

DLS measurements of the solutions were performed using a Malvern 4800 autosizer employing a 7132 digital correlator. The light source was an argon ion laser operated at 514.5 nm with a maximum output power of 2 W. The average decay rate was obtained by analyzing the electric field autocorrelation function *g*¹(*τ*) vs. time data using a modified cumulants method. The data were analyzed as per the theory and equation reported elsewhere [42].

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