



# The clouding behaviour of PEO–PPO based triblock copolymers in aqueous ionic surfactant solutions: A new approach for cloud point measurements

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## ABSTRACT

The cloud points (CP) of 1 g/dl solutions of polyethylene oxide–polypropylene oxide (PEO–PPO) based triblock copolymers (Pluronics<sup>®</sup> P84, L64, L44 and Reverse Pluronics<sup>®</sup> 10R5, 25R4, 17R4) were measured as a function of their molecular weight and added ionic surfactant. For identical PEO/PPO ratios, copolymers with lower molecular weight show a larger increase in the cloud point in the presence of surfactants than polymers with higher molecular weight. The opposite trend has been observed for reverse Pluronics. The cloud points of polymers with different PEO/PPO ratios have also been reported. An increase in the size of the middle PEO block in reverse Pluronics has a more significant effect on cloud points than molecular weight increment. Ionic surfactants produced marked increases in the cloud points of copolymer solutions. The effect was much larger for surfactants with higher hydrophobicity. Cationic surfactants with different chain lengths were used to examine the surfactant–polymer interaction. A novel approach for normalising the cloud points to their relative values has been carried out to see the clear effect of ionic surfactants. Tri component systems, comprising polymers, cetyltrimethylammonium bromide (C<sub>16</sub>TABr) surfactant and salt (NaBr), have also been studied to see the effect of salt on the phase separation behaviour of solutions within the framework of our new cloud point approach.

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## 1. Introduction

The aggregation and phase behaviour of ethylene oxide–propylene oxide (EO–PO) based block copolymers have attracted a great deal of attention [1–11]. The study of various kinds of triblock copolymers in aqueous solution, including PEO–PPO–PEO (Pluronics<sup>®</sup>) and PPO–PEO–PPO (commonly known as Reverse Pluronics<sup>®</sup>) type block copolymers, has led to the conclusion that triblock copolymers can form various micellar structures [12] (see Fig. 1).

Due to differences in the solubility of the constituent blocks, these copolymers show self-assembly characteristics in an aqueous medium. This aggregation process is accentuated at higher temperatures as both blocks lose solubility. Below the critical micellar temperature (CMT), both the PPO and the PEO blocks are soluble in water, which leads the polymers to remain as unimers in solution. At the critical micellar concentration (CMC), aggregates form having the PPO block as the hydrophobic core and the hydrated PEO blocks as the corona [7]. At a temperature called the cloud point (CP), the PEO blocks also become insoluble, and the copolymer becomes phase separated from the water. Different mechanisms have been proposed to explain this clouding phenomenon (lower critical solution temperature) in aqueous solutions of such

polyethers. These mechanisms are based on the conventional dehydration of the PEO moiety, hydrogen bonding between the ethereal oxygen atoms of the PEO molecule and water molecules, and the polar–nonpolar conformations of PEO [13]. The cloud point of a non-ionic surfactant depends on its molecular architecture. Increasing hydrophobicity (due to PPO block size increase) decreases the CP, while increasing the hydrophilicity shows the reverse trend in the CP. Several studies have been reported to predict/calculate cloud points [12,14,15]. Liu et al. have calculated theoretically the effect of the hydrophobic block on the cloud points of various triblock copolymers [12]. The cloud point of non-ionic surfactants can be conveniently decreased or increased by the use of different additives. Several studies have been conducted on the effect of neutral salts [15,16], hydrotrops [17–19] and ionic surfactants [11,20] on the CP of triblock copolymers.

The interaction of water-soluble polyethylene oxide based surfactants with ionic surfactants, such as sodium dodecyl sulphate (SDS), has been extensively reported [21–23]. Mixed micelles of these surfactants exhibit remarkable differences from those of the individual components, and are thus widely used in industrial formulations. The interaction of PEO–PPO copolymers with SDS has been widely studied using several techniques [24,25]. Lad et al. [26] made a detailed study of the clouding and aggregation behaviour of Pluronics in the presence of anionic surfactants. Hecht and Hoffmann [27] undertook a study of the mixed system comprising

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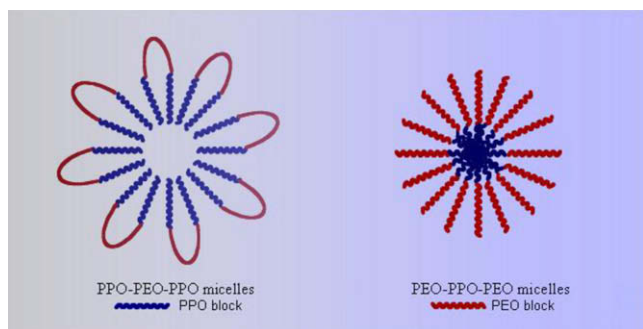
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Pluronic F127 and ionic surfactants [SDS/C<sub>16</sub>TABr]. From scattering and thermal studies, these authors proposed a mechanism involving penetration and interaction of ionic surfactant with micelles or monomers of polymers. Their investigation also suggested that the packing of the complex is loose and depends on the nature of the head group of the hydrocarbon surfactant.

This paper reports the effect of alkyltrimethylammonium bromides (C<sub>n</sub>TABr where *n* = 10, 12, 14, 16, 18) on the clouding behaviour of PEO–PPO–PEO (P84, L64, L44) and PPO–PEO–PPO (10R5, 17R4, 25R4) copolymers. To see the effect of changes in molecular weight, we have chosen copolymers such that the ratio of PEO to PPO remains equal. This leads to the same HLB values for the respective classes of polymer. To see the effect of different ratios of PPO/PEO, we have chosen 10R5 from Aldrich, which has a different HLB value than those of the other reverse Pluronics. All details of the copolymers are shown in Table 1. A new approach for normalising the cloud points is developed so as to see clearly the effect of the ionic surfactants or other additives. This approach may help to simplify the comparison of different cloud point studies on many non-ionic surfactants, including polymeric surfactants. We have also used the salt NaBr to see the counter effect of ionic surfactants and the resultant changes on the cloud points of the polymers.

## 2. Materials and methods

Pluronic® P84, L64, L44 and Reverse Pluronics® 10R5, 17R4, 25R4 were obtained from BASF, Mount Olive, NJ, USA, and were used as received. Details of all polymers are listed in Table 1. AR grade sodium bromide (NaBr) was obtained from Fluka. Cationic surfactants dodecyltrimethylammonium bromide (C<sub>10</sub>TABr), dodecyltrimethylammonium bromide (C<sub>12</sub>TABr), tetradecyltrimethylammonium bromide (C<sub>14</sub>TABr), cetyltrimethylammonium bromide (C<sub>16</sub>TABr), octadecyl-trimethylammonium bromide (C<sub>18</sub>TABr) were highly pure samples obtained from Sigma, Fluka, or Aldrich. Their purity was checked by the absence of a minimum in the surface tension-concentration plot. This also gives the critical micelle concentration. Doubly distilled water from an all PYREX™ glass apparatus was always used to prepare solutions for the CP determination.



**Fig. 1.** Schematic representations of PPO–PEO–PPO and PEO–PPO–PEO micelles in aqueous solutions.

**Table 1**

Physical properties of different block copolymers.

Name	Structure	Avg. mol. wt.	% PEO	PEO/PPO ratio	CP, °C	CP, °C (literature)
P84	E <sub>19</sub> P <sub>43</sub> E <sub>19</sub>	4200	40	0.67	74 °C	74 °C [3]
L64	E <sub>13</sub> P <sub>30</sub> E <sub>13</sub>	2900	40	0.67	57 °C	58 °C [3]
L44	E <sub>10</sub> P <sub>23</sub> E <sub>10</sub>	2200	40	0.67	65 °C	65 °C [3]
10R5	P <sub>09</sub> E <sub>23</sub> P <sub>09</sub>	2000	50	0.97	65 °C	65 °C [29]
17R4	P <sub>14</sub> E <sub>24</sub> P <sub>14</sub>	2650	40	0.65	45 °C	46 °C [30]
25R4	P <sub>19</sub> E <sub>33</sub> P <sub>19</sub>	3600	40	0.66	39 °C	40 °C [31]

## 2.1. Cloud points

The cloud points were measured at a fixed concentration of the copolymer (1 g/dl) in the absence and presence of varying amounts of added cationic surfactants and salt. This was done by gently heating the solutions in thin 20 ml glass tubes immersed in a water bath, which was continuously well stirred with a magnetic bar. The heating rate of the samples was adjusted to 1 °C/min. The first appearance of turbidity was taken as the cloud point. The CP values were reproducible to within 0.5 °C.

## 3. Results and discussion

### 3.1. Results

Dehydration of the PEO moiety, hydrogen bonding between the ethereal oxygen atoms of the PEO molecule to water molecules, and polar–nonpolar conformational changes in the PEO molecule all provide effective mechanisms for understanding the phase separations and structural transitions in block copolymer systems. PEO–PPO based triblock copolymers do show stable cloud points at different concentrations [3,6]. The polymer solutions transform into a two-phase system above the CP. Micellization for these polymers is strongly dependent on the concentration of polymer and the temperature. An increase in the temperature shifts micelle formation markedly to lower concentrations. The micelles often grow particularly large at temperatures near the cloud point [28]. These large structures can easily be tuned by the addition of ionic surfactants. Table 1 lists the CPs of all the triblock copolymers studied (1 g/dl aqueous solution), including those measured by us, and those values previously reported. Different copolymers have different CPs. Hence it is very hard to correlate the results when various polymers interact with additives. To simplify the science we have converted all the cloud points to a relative form by dividing the observed CP by the value of the cloud point without any additives.

$$\text{Relative CP} = \frac{\text{CP}_{\text{Ci}}}{\text{CP}_{\text{Co}}}$$

where CP<sub>Co</sub> = cloud point with zero concentration of additive in the polymer solution. CP<sub>Ci</sub> = cloud point with a particular concentration of additive in the polymer solution.

The effect of cationic surfactants on the CP of 1 g/dl aqueous solution of L44 and 10R5 is shown in Figs. 2 and 3, respectively.

This technique allows us to compare the behaviour of different polymers removing the complication of their lower or higher cloud points. In Fig. 2 we have used 1 g/dl solution of L44 Pluronic, which has a cloud point 65 °C. The CP values in the presence of cationic surfactants have been divided by 65 °C to get relative values. For 1 g/dl 10R5 solution, with a CP of 65 °C, shown in Fig. 3, the same process has been applied.

It is clear from the plots that addition of cationic surfactants has a remarkable effect on the CPs of both copolymers. The CPs rise up to 100 °C in the presence of trace amounts of surfactant much less than the CMC. This effect of increasing the CP was stronger for surfactants with longer hydrophobic tails. The increase in the cloud

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