

# Aggregation and clouding behavior of aqueous solution of EO–PO block copolymer in presence of *n*-alkanols

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## Abstract

The aqueous solution behavior of an ethylene oxide–propylene oxide triblock copolymer Pluronic® P123 [(EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub>] was investigated in the presence of various *n*-alkanols (C<sub>1</sub>–C<sub>6</sub>) by cloud-point, viscosity, dynamic light scattering (DLS) and spectroscopic (FTIR, NMR) measurements. For lower alkanols (methanol, ethanol and 1-propanol), the cloud-points (CPs) increased with increase in alkanol concentration. The reverse effect was found for higher alkanols (C<sub>4</sub>–C<sub>6</sub>) where both the CPs and critical micelle temperatures (CMTs) decreased with increase in concentration. This behavior is explained in terms of a co-operative association of higher alkanols and block copolymers by replacing water molecules in the PPO core and inducing micellar growth in aqueous P123 solution. Lower alkanols are likely to be good solvents for both PEO and PPO blocks and the effect on PPO blocks predominates indicating an increase in CP and CMT with increase in alkanol concentration.

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## 1. Introduction

In the past two decades, a great deal of effort has been devoted to the study of physico-chemical properties of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) PEO–PPO–PEO block copolymers (commercially available under the trade names Poloxamers or Pluronics) in aqueous solutions. Poly(propylene oxide) shows phase separation from

water at relatively low temperature (around 15 °C), whereas poly(ethylene oxide) remains soluble in water even up to 100 °C. The block copolymers consisting of a central PPO block flanked by two PEO blocks thus display thermosensitive amphiphilic properties. The interesting features of PEO–PPO–PEO block copolymers are their temperature dependent self-association in aqueous solutions and rich phase behavior [1–12]. At low polymer concentration and low temperature, these block copolymers dissolve in water as unimers. The process of self-association is induced when the block copolymer concentration is above the critical micelle concentra-

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tion (CMC) and the temperature exceeds the critical micellization temperature (CMT). The structure of PEO–PPO–PEO block copolymer micelles is well described by the core-corona model in which a spherical core composed of PPO is surrounded by a corona composed of Gaussian chains of strongly hydrated PEO [2–12]. The segment density profiles of the predicted micelles with a mean-field lattice theory indicate that there is a finite concentration of water in the micellar core and that there is a diffuse interface between the core and corona [13,14]. Small-angle neutron scattering (SANS) studies have established that the micellar core cannot consist of PPO only but contains significant quantities of water. The water content of the micellar core decreases with increasing temperature in the transition region, with a corresponding increase of the micelle aggregation number [15–17].

Water is typically used as a solvent for PEO–PPO–PEO block copolymers. The solvent quality is a controllable factor in the CMC, CMT and structure of the micelles [18–21]. The addition of polar cosolvents provides an extra degree of freedom in tailoring the solution properties for specific applications, for example, in the formulation of aqueous preparations of water-insoluble drugs and cosmetics and as templates in the synthesis of mesoporous materials [22,23]. Gold nanoparticles of different morphologies such as sphere, rod, triangles and hexagonal arrays have been synthesized in micelles comprising different block copolymer mixtures [24]. The addition of cosolvents can modulate the swelling behavior of the different blocks of the polymer and hence alter the phase behavior to a great extent. The rich phase behavior observed in ternary mixtures of block copolymer, water and additives provide new pathways for morphological control that suits specific applications. The cosolvent effects on the self-assembled microstructure are related to changes in the mean interfacial area occupied by the PEO blocks, its preference to locate in different microdomains and ability to modify the interfacial curvature by swelling different blocks of the copolymer to different extents [25,26]. The published information about the mechanism of the cosolvent effect is limited, though the theories of solubilization go a long way to meeting the needs of the experiments. Short chain alcohols such as methanol and ethanol are good solvents for both PEO and PPO blocks of the polymer and hence prevents the onset of micellization [27]. It is reflected as an increase in CMT, CMC and cloud-points of the block copolymers. On the

other hand, medium chain alcohols such as pentanol promote the micellization in block copolymers and the effect is more pronounced with higher homologues [21,28]. Apart from these reports, a comprehensive study of the effect of variable chain length aliphatic alcohols on the self-assembly behavior of block copolymers is still lacking. Our aim is to provide information concerning the alcohol effect on the association behavior of PEO–PPO–PEO block copolymers in aqueous solutions. With this objective, we investigated the effect of alkanols of different chain lengths ( $C_1$ – $C_6$ ) on the self-assembly behavior of P123 block copolymer micelles.

## 2. Experimental materials

Pluronic P123 was obtained from BASF Corp, Parsippany, New Jersey. Alkanols viz methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol employed in this study were of analytical reagent grade. All chemicals were used as received and triple distilled water from an all Pyrex glass apparatus was used to prepare aqueous solutions.

## 3. Methods

### 3.1. Cloud-point

Cloud-points were measured by visually observing the temperature at which the copolymer solution becomes turbid on heating and clear on cooling. Heating and cooling rates of 1–2 °C per minute near the cloud-point were maintained. The process was repeated several times and the average temperature was taken as the CP. The results were reproducible within  $\pm 0.5$  °C.

### 3.2. Viscosity

The solution viscosity measurements were carried out using an Ubbelohde suspended level capillary viscometer. The viscometer was always suspended vertically in a thermostat at  $25 \pm 0.1$  °C and was cleaned and dried every time before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch.

### 3.3. Dynamic light scattering

DLS measurements were carried out at 90° scattering angle on solutions using Autosizer 4800

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