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Static and dynamic surface tension behaviour of a triblock copolymer and a non ionic surfactant mixture

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HIGHLIGHTS

- Block copolymer-surfactant mixtures exhibit synergistic adsorption.
- Surfactant adsorbs on block copolymer hydrophobic backbone
- Interaction of block copolymer and surfactant is composition dependent.
- Dynamics of the surface tension of polymer-surfactant mixture is dominated by polymer.

GRAPHICAL ABSTRACT
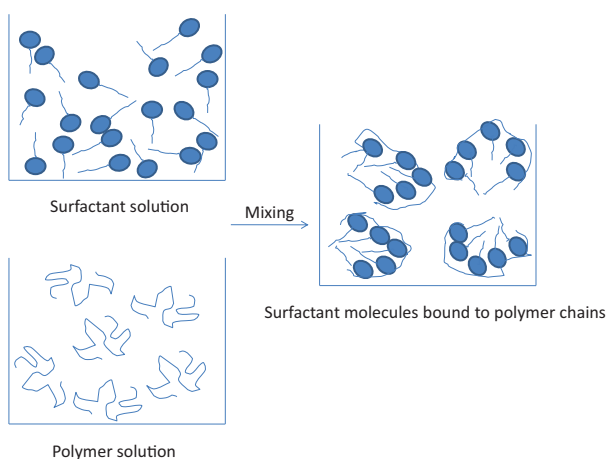
ARTICLE INFO

ABSTRACT

Static and dynamic surface tension measurements have been carried out on mixtures of a commonly used block copolymer Pluronics® P123 and a non-ionic surfactant polyoxyethelene (9) lauryl ether ($C_{12}E_9$) to understand the block polymer-surfactant interactions. The effects of the interaction on the adsorption and micellisation behaviour have also been studied. Three different compositions comprising 3:1, 1:1 and 1:3 molar ratios of Pluronic P123 and $C_{12}E_9$ have been investigated and the results are compared with the data of pure P123 and $C_{12}E_9$ solutions. It has been observed that the nature and magnitude of the polymer surfactant interactions depend on the composition of the mixtures. The mixture containing 3:1 molar ratio of P123 and $C_{12}E_9$ shows synergistic effect with a negative value for the interaction parameter (β), as obtained from the analysis of surface tension data using Rubingh's model. However, for the other two compositions (i.e., 1:1 and 1:3 molar ratios), the equilibrium surface tension data show premicellar adsorption and aggregation of the surfactant molecules on the polymer chain. The dynamic surface tension (DST) results indicate that the strong polymer surfactant interactions, as reflected in the equilibrium surface tension data, do not modify the DST behaviour significantly from that of pure components. This is attributed to the dominant effect of the polymer adsorption at the interface, during the short time scale studied.

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1. Introduction

Polymer surfactant mixtures are often used in a wide range of commercial applications [1–3] e.g., in stabilisation of emulsions and foams in food industry, and for coating processes in photographic industry [4–5]. Mixtures of proteins and surfactants are also common in many biological systems. Thus, it is important to understand the adsorption behaviour of mixed polymer surfactant systems for specific applications. Several other reviews have dealt with the subject [6–9]. There has been a continued interest to understand the adsorption behaviour of polymer surfactant mixtures in terms of composition and structure of polymer surfactant layers at the air–liquid interface. Several complementary techniques have been employed for this purpose; e.g., neutron reflectometry [10], X-ray reflectometry [11,12] ellipsometry [13–21], and atomic force microscopy [22]. Static and dynamic surface tension measurements provide important insight into the mechanism of adsorption at the interface as well as micellisation behaviour of surfactants [23,24]. For polymer surfactant mixtures, the results of static and dynamic surface tension measurements have been reviewed in the recent literature [9,10]. The polymer surfactant mixtures can be grouped into weakly interacting systems such as neutral polymers and charged or uncharged surfactants and strongly interacting systems such as oppositely charged polyelectrolyte-surfactant mixtures. For strongly interacting systems, the equilibrium surface tension as a function of concentration exhibits complex behaviour in the form of discontinuities before CMC. This is interpreted as a manifestation of the surfactant polymer interactions.

Block copolymers are a class of amphiphiles which show surface active properties similar to surfactants. By virtue of its amphiphilic nature, they are adsorbed at the interface and form micelles. Their surface activity is strongly dependent on temperature, leading to the occurrence of a critical micelle temperature (CMT) and critical micelle concentration (CMC). Triblock copolymers of polyethylene oxide and polypropylene oxide, denoted as (PEO-PPO-PEO) are commercially available water soluble polymers which are surface active agents and find wide applications in industry for detergency and as emulsifiers [25–28]. They have the common structure $(PEO)_x$-$(PPO)_y$-$(PEO)_x$. They are commercially available under the name Pluronics and Poloxamers. The PEO blocks constitute hydrophilic part while PPO is the hydrophobic part in these polymers [29]. The static surface tension behaviour of these triblock copolymers has been reported in the literature [30–32]. However reports on the dynamic surface tension behaviour of mixtures of Pluronics and non-ionic surfactants are scanty. Both synergistic and antagonistic behaviour of block copolymer surfactant mixtures are reported, from the equilibrium surface tension measurements. Vieira et al. have reported that the mixed CMC of Pluronic P123 and C_8E_4 is higher than that of either of the pure components, indicating antagonistic behaviour with a positive interaction parameter (β) [33]. On the other hand Couderc et al. have found strong synergistic interaction between $C_{12}E_6$ and both L-64 and F-127 [34,35]. This shows that the mixing behaviour of amphiphilic block copolymers with non-ionic surfactants is quite complex compared to other non-ionic homo polymers.

In this manuscript, we report the static and dynamic surface tension behavior of block copolymer-surfactant mixtures and their effects on the adsorption and micellisation behaviour. Pluronics P123 $[(PEO)_{20}$-$(PPO)_{70}$-$(PEO)_{20}]$ and non-ionic surfactant $C_{12}E_9$ have been used in the present work. Mixtures of P123 and $C_{12}E_9$ with molar ratios of 3:1, 1:1 and 1:3 have been studied. The results have been compared with that of pure P123 and $C_{12}E_9$ data and found to be consistent with the polymer surfactant interaction model, as revealed by other sophisticated techniques like neutron reflectometry and ellipsometry.
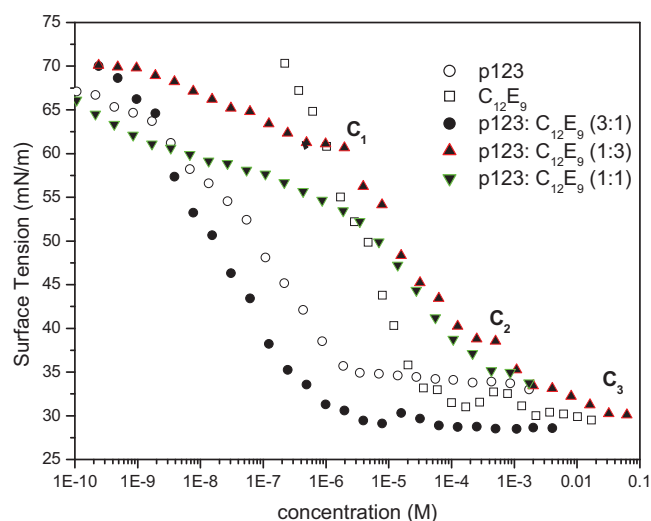

Fig. 1. Plots of equilibrium surface tension of pure P123, C12E9 and their mixtures in molar ratio of 3:1 ,1:1 and 1:3.

2. Experimental

2.1. Materials and methods

Non-ionic surfactant polyoxyethelene (9) lauryl ether ($C_{12}E_9$) (Molecular weight 590/g mol^{-1}) was obtained from Galaxy Surfactants Ltd., Mumbai, India (purity > 98 %) and used as received. The Pluronics P123 (MW ∼5800/g mol^{-1}) was obtained from Sigma–Aldrich Germany (purity > 98.5 %) and used as received. The 1 wt% aqueous solutions of the surfactant and the polymer were prepared in nanopure water (Milli Q Millipore filtration system). The polymer solution was kept in refrigeration for overnight to ensure complete dissolution of the polymer. The 1 wt% solutions were mixed in the molar ratio of 3:1, 1:1 and 1:3 to prepare stock solutions. The stock solutions were diluted to prepare mixtures of varying concentrations spanning below and above CMC. The equilibrium surface tension measurements were carried out by the Wilhelmy plate method using a Kruss K11 tensiometer (Kruss GmbH, Germany). The final surface tension values were the average of 5 readings obtained in a span of 30s. The uncertainty of the measurement was 0.2 mN/m. Dynamic surface tension (DST) measurements were carried out for solutions of different concentrations by maximum bubble pressure method using Kruss BP100 bubble pressure tensiometer (Kruss GmbH, Germany). Hydrophobically modified glass capillary with an inner diameter of 0.2 mm was used for the measurements and the uncertainties in the measurements were +/−0.2 mN m^{-1}. Surface ages of the bubbles were varied from 10 ms to 10 s. The temperatures of the measurements were kept constant at 298 K.

3. Results and discussions

3.1. Equilibrium surface tension of polymer surfactant mixtures.

First, we look upon the equilibrium surface tension behaviour of block copolymer surfactant mixture. Fig. 1 shows the plot of equilibrium surface tension of pure P123, $C_{12}E_9$ and their mixtures in the molar ratio of 3:1, 1:1 and 1:3. The data for pure components are taken from our earlier work [36]. The value of surface tension at the CMC is nearly same for the polymer and the surfactant, being equal to about 35 mN/m. The equilibrium surface tension of the pure components follows the typical behaviour as expected for conventional surfactants. The surface tension decreases with