

Surface activity of Hydroxypropylcellulose in Presence of Brij56.

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ABSTRACT

The interaction of non-ionic semi-flexible polymer, hydroxypropylcellulose (HPC) with non-ionic surfactant (polyoxyethylene(10) cetyl ether (Brij56) has been studied using tensiometry in aqueous medium. The tensiometric profile of Brij56 in the presence of HPC exhibit two breaks, first at critical aggregation concentration (CAC) corresponding to onset of interaction with HPC and the second at C_1 corresponding to saturation of the interface. The interaction of Brij56 with HPC solution is discussed in terms of competition between surfactant-surfactant and surfactant-HPC interactions. The results of the present study may prove fruitful in optimizing the properties of surfactant-polymer mixtures relevant for many formulations.

Keywords-*Brij56, CAC, HPC,*

I. INTRODUCTION

The study of Polymer- Surfactant interactions [1,2] in aqueous solutions has attracted significant interest in recent years because of their widespread applications and relatively complex behaviour. Though lot of work has been done with polymer- surfactant systems but the complex nature of polymer-surfactant interactions are still not fully recognised. It is easy to understand electrostatic interactions between charged polymer and ionic surfactants [3], but the situation is quite complex between the neutral polymer and surfactants. Interaction between neutral polymers and surfactants depends on several factors such as nature of surfactant head group, the nature of the polar groups embedded in the polymer backbone, and polymer hydrophobicity [1]. It has been observed that anionic surfactants interact more strongly with neutral polymers than cationic surfactants. Besides the electrostatic interactions between the polar head groups of surfactant and natural polymer such as hexadecylpyridinium chloride-PVP systems, the respective hydrophobic interactions also play a significant role in determining the surfactant-polymer interactions as observed in the presence of poly (vinyl methyl ether), and hydroxypropyl cellulose [4]. The binding of surfactant micelles to a flexible/semi-flexible non-ionic polymer has been demonstrated to cause characteristic changes in the hydrodynamic properties of the polymer solution hence make them fit for various industrial applications.

II. MATERIALS AND METHOD

The non ionic amphiphile polyoxyethylene(10)cetyl ether (Brij-56) surfactant was received from Fluka, and the neutral polymer used hydroxypropylcellulose (HPC) was from Aldrich. All products were used as received. 15mM concentration stock solution of Brij-56 was prepared for the experimental work. In case of hydroxypropylcellulose (HPC) a 0.5% stock solution was prepared. The stock solutions were utilized to prepare the samples of desired concentration. All solutions were prepared in triple distilled water and polymer solutions were prepared in weight by volume percentage.

III. DETERMINATION OF CMC AND CAC

The CMC and CAC values of surfactant solution were determined from the plot of surface tension (γ) vs. logarithm of surfactant concentration ($\log C_t$) as shown in Fig. 3.1. Surface tension measurements were made by the ring detachment method using a Kruss-9 (Germany) tensiometer equipped with a thermostable vessel holder that holds the vessel containing the experimental solution. Water at constant temperature from a thermostatic circulatory bath is circulated through the double walled vessel holder to maintain the experimental solution at constant temperature. BROOKFIELD (TC-102) circulatory bath was used in the present study. 30 ml polymer solution was placed in the sample vessel and constant temperature water from the thermostatic bath circulated into the vessel holder for 30 minutes to allow the sample to acquire the set temperature. Surfactant concentration was varied by adding with a Hamilton microsyringe small instalments of the concentrated stock solution of known surfactant concentration, not to affect the concentration of the polymer in the sample vessel. Measurements were made after thorough mixing and temperature equilibration at 25°C ($\pm 0.1^\circ\text{C}$) by circulating water from a thermostat through the vessel holder. The accuracy of measurements was within 0.1 dyne cm^{-1} .

3.1 Surfactant-Polymer Interactions

3.1.1 Polymer with Single Surfactant Systems

Fig. 3.3 show the variation of surface tension of surfactant solution with surfactant concentration in presence of polymer (HPC). Two break points are prominent in these tensiometric plots. The lower concentration break corresponds to critical aggregation concentration (CAC) marking the beginning of formation of polymer-bound micelles while the higher concentration break, C_1 corresponds to the concentration at which saturation of polymer by the bound micelles occurs (also known as polymer saturation point, psp) and hence marks the beginning of polymer free Micellization [5]. Up to CAC,

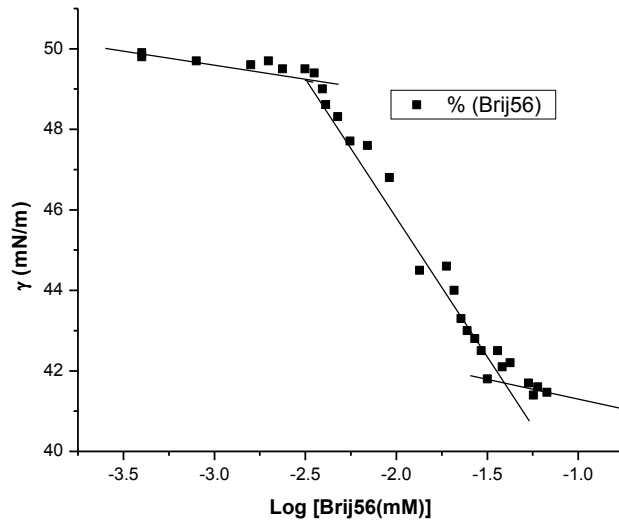


Figure 3.1: Plot between surface tension vs logarithm of: (a) Brij56 concentration in presence of 0.01% HPC.

γ remains more or less constant signifying that Brij56 cannot interact with the HPC adsorbed at the air/solution interface. Therefore, CAC signifies the onset of interaction/ displacement at the air/solution interface. Above the CAC, γ decreases until the interface is saturated or the displacement process is complete to yield C_1 . Decrease in γ can either be due to specific binding of Brij56 with HPC, thereby increasing its hydrophobicity or competitive adsorption between the HPC and Brij56. Constancy in γ up to the CAC suggests the absence of specific interactions between Brij56 and HPC.

Further competitive adsorption not only depends on the nature of the surfactant, but also on the concentration of the surfactant in the bulk [6]. This is because at low concentrations, the surface activity of Brij56 is lower than the surface activity of HPC, but above the CAC their surface activity becomes higher than that of the polymer (Fig. 3.1), and hence are preferentially adsorbed at the interface. Below the CAC, HPC restrains the adsorption of Brij56 on the interface.

Table 3.1:- CAC and CMC of Brij56 in Presence of HPC.

S. No.	Polymer concentration	Surfactant	CAC (mM)	CMC (mM)
1	0.01%	Brij56	0.003	0.040

The CMC of Brij56 in aqueous medium is 0.036mM and in presence of polymer (HPC), CMC of Brij 56 gets changed. The CAC and CMC data of single surfactant + polymer systems are collected in Table 3.1. As seen by comparison, the CMC of Brij56 gets increased in presence of the polymer (HPC), this is probably because in presence of polymer HPC, Brij56 interacts with HPC therefore making free solubilised surfactant concentration less than required to form micelles. Increase in CMC of Brij56 clearly shows appreciable interaction between HPC and Brij56 hence such interactions can be used to tune the properties of polymer solutions as desired.

IV. CONCLUSIONS

At lower surfactant concentrations, Hydroxypropylcellulose predominantly occupies the surface, indicating higher surface activity of the polymer.

The CMC of Brij56 in presence of HPC is more compared to value obtained for the said surfactant in the absence of polymer.

This study is expected to provide some insight to understand protein- surfactant interactions.

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