

Comparative Study of Pure Micelles and Mixed Micelles in the presence of Polymer

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ABSTRACT

In this work we report the critical aggregation concentration (CAC) of pure surfactants and their mixtures in aqueous medium. The study was carried out with the help of tensiometric technique. Variations in CAC can be interpreted in terms of their ability to interact with polymers. Brij56 has lowest CAC compare to any mixture of Brij56+CTAB examined, showing Brij56 molecules have more tendency to interact with HPC when present in pure form than when present in mixture form. CMC of different surfactant mixtures can be used to guess scattering of surfactants on the polymer molecules. The results of the present study can be used to know the quantitative nature of surfactant-surfactant interaction and surfactant-polymer interactions. This study can also help us in making various formulations of industrial use.

I. INTRODUCTION

Aqueous polymer-surfactant solutions are gaining more and more attention both in view of their technological importance due to their wide spread practical applications, and in fundamental scientific research for understanding the physio-chemical reasons that determine their high performance. The physio-chemical aspects of the problem can be explained using the study of interaction mechanism between the surfactant and the polymer in aqueous media which in turn are exploited to provide the beneficial effects sought from formulations such as paints and coatings, food products, pharmaceuticals, cosmetics, detergent processing and in tertiary oil recovery [1,2].

The mixed micelles are considered to be more versatile than single surfactants in view of their wide industrial applications and hence the evaluation of their physiochemical properties has recently attracted a lot of attention[3,4]. Most of the work on such properties of binary surfactant systems has been focused in pure water only[3-6].

Mixed micelles are often used in technical, pharmaceutical and biological fields, since they work better than pure micelles[7,8]. They have importance in industrial preparation, pharmaceutical and medicinal formulation, enhanced oil recovery process, and so forth, by way of efficient solubilization, suspension, dispersion, and transportation influenced by temperature, pressure, pH, nature of solvent, additives etc[9].

The interactions of surfactant micelles to a 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 cationic amphiphile cetyltrimethylammonium bromide CTAB used was a Sigma product and non ionic amphiphile polyoxyethylene(10)cetyl ether (Brij-56) surfactant was obtained from Fluk. The hydroxypropylcellulose (HPC) was obtained from Aldrich. All products were used as received. Stock solutions of Brij-56 and CTAB were prepared at concentrations of 15mM and 25mM respectively. In case of hydroxypropylcellulose (HPC) a 0.5% stock solution was prepared. The stock solutions were utilized to prepare the samples of various desired concentrations. All solutions were prepared in triple distilled water and polymer solutions were prepared in percentage concentrations.

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. 30 ml polymer solution was placed in the sample vessel and constant temperature water from the thermostatic bath circulated into the vessel holder for 10 minutes to allow the sample to acquire the set temperature. Surfactant mixture concentration or pure surfactant concentration was varied by adding with a Hamilton microsyringe small amounts of the concentrated stock solution of known surfactant mixture concentration, not to affect the concentration of the HPC in the sample vessel. Measurements were made after thorough mixing at constant temperature.

3.1 Surfactant-Polymer Interactions

3.1.1 Polymer with Single Surfactant and Binary Surfactant Systems

The CAC and CMC values of pure surfactants and surfactant mixtures in presence of polymer were also determined by plotting graph between the surface tension (γ) and logarithm of surfactant concentration. The CAC and CMC values so obtained from the graphs are listed in Table 3.1 and 3.2. The tensiometric profiles for single surfactants and Brij56+CTAB binary mixtures in the presence of HPC consist of two breaks, the first break corresponds to the CAC and second break to the CMC. Like CMC of single surfactants, the CMC's of surfactant mixture are also higher in presence of HPC polymer than their corresponding CMC's obtained in absence of polymer. This is possibly due to the fact that some concentration of surfactants is needed to saturate the polymer, especially due to the formation of polymer surfactant complexes. Plots of surface tension versus logarithm of surfactant concentration which indicate said behaviour are shown in Fig. 3.1 and Fig 3.2.

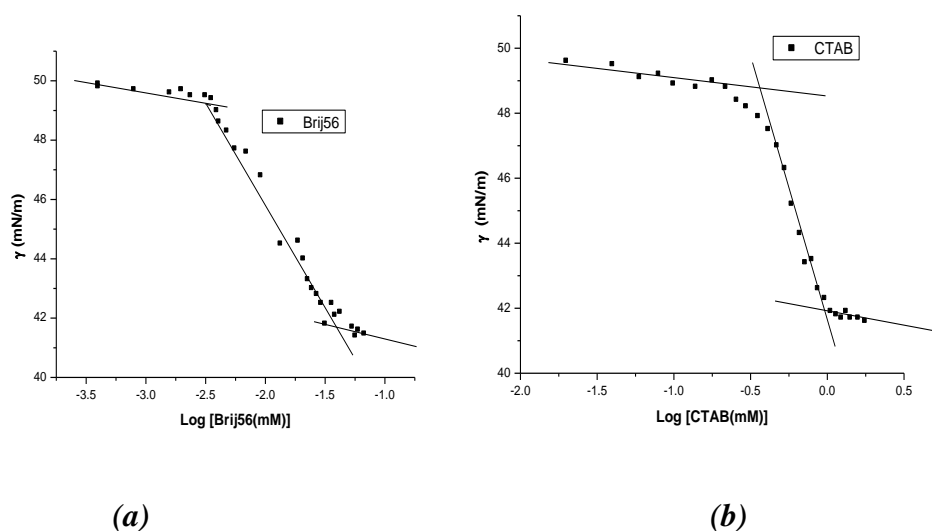


Figure 3.1: Plot between surface tension vs logarithm of: (a) Brij56; (b) CTAB concentration in presence of 0.01% HPC.

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

S. No.	Polymer concentration	Surfactant	CAC (mM)	CMC (mM)
1	0.01%	Brij56	0.003	0.040
		CTAB	0.365	0.957

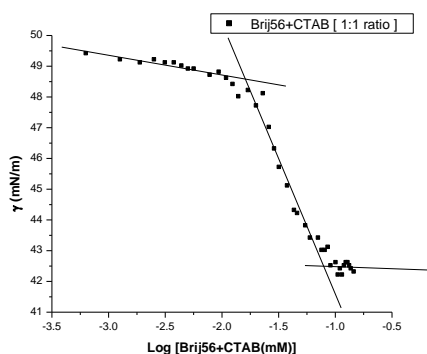


Figure 3.2: Plots of surface tension vs logarithm of surfactant concentration for binary Brij56 & CTAB systems at various mole fractions in presence of 0.01% HPC.

Table 3.2: Variation of CAC and CMC of binary Brij56+CTAB systems with polymer concentration.

S. No.	Mole fraction of Brij56 in the mixture of Brij56+CTAB	0.0% HPC	0.01 % HPC		0.03% HPC		0.05% HPC	
		CMC (mM)	CAC (mM)	CMC (mM)	CAC (mM)	CMC (mM)	CAC (mM)	CMC (mM)
1	0.1	0.095	0.102	0.838	0.116	1.199	0.104	0.436
2	0.3	0.038	0.028	0.073	0.0361	0.1513	0.060	0.134
3	0.5	0.017	0.016	0.080	0.006	0.038	0.017	0.086

Further, from the Table 3.2, it is clear as mole fraction of Brij56 increases, CAC shows almost decrease indicating instability of surfactant mixture molecules in monomeric form in the system and hence show tendency to get attached to polymer. This is probably due to the reason that increase in Brij56 mole fraction in the solution leads to decrease in the entropy of the system, hence to make the system stable interaction of surfactant molecules with HPC occurs at lower concentration. Moreover, increase in mole fraction of Brij56 in the mixture also favours micelle formation probably due to less electrostatic repulsions in the micelle.

Moreover, it is found Brij56 has lowest CAC in presence of HPC than any of its mixture with CTAB, showing its much higher tendency for interaction with HPC, probably its addition decreases the entropy of the system, therefore to stabilise such a system entropy should get increase which is possible if Brij56 gets attached to HPC.

IV. CONCLUSIONS

Surfactant mixture shows same behaviour with HPS as shown by the individual surfactants with the polymer.

As mole fraction of Brij56 increases in the mixture of Brij56 + CTAB, CAC shows decrease in aqueous HPC solution.

Brij56 has lowest CAC than any of its mixture with CTAB in presence of HPC.

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