

Variation in the CMC of Surfactants with Change in Polymer Concentration

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ABSTRACT

In this work we report the variation of CMC of Brij56 with change in non-ionic semi-flexible polymer, hydroxypropylcellulose (HPC) using tensiometry in aqueous medium. The tensiometric profile of Brij56 in the presence of HPC exhibits two breaks, one is 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 CMC of Brij56 shows first increase with increase in polymer concentration and then shows decrease with further increase in polymer concentration. The change in the CMC of surfactant solutions with change in polymer concentration can be used to predict the behaviour of polymers in the solution. The results of the present study can be used to tune the properties of different solutions in order to make them fit for many formulations.

I. INTRODUCTION

The study of Polymer- Surfactant interactions [1,2] in aqueous solutions are becoming more and more important in recent years, because of their widespread applications. In spite of lot of work is done with polymer surfactant-interactions, complex nature of interactions still remains unknown. Interaction between neutral polymers and surfactants depends on 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. It is found that 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 [3]. The binding of surfactant micelles to a flexible/semi-flexible non-ionic polymer can change the properties of solutions, which can be used to optimize properties of solutions for various industrial purposes.

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. The stock solution of 15mM concentration of Brij-56 was prepared for the experimental work and in case of hydroxypropylcellulose (HPC) a 0.5% stock solution was prepared. All the samples of desired concentration were prepared from the stock solutions.

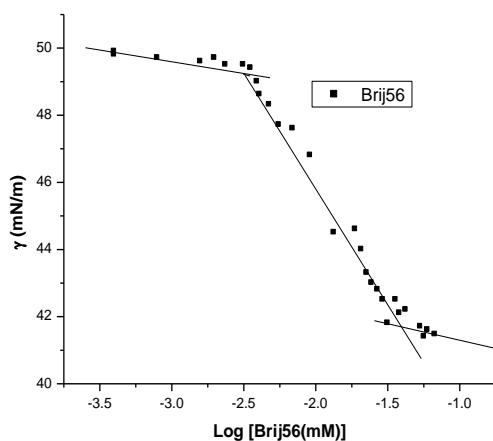
III.DETERMINATION OF CMC AND CAC

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, with the help of ring detachment method using a Kruss-9 (Germany) tensiometer equipped with a thermostable vessel holder that holds the vessel containing the experimental solution to determine surface tension of solutions. During the experiment, temperature was kept constant using BROOKFIELD (TC-102) circulatory water bath. 30 ml polymer solution was placed in the sample vessel and surfactant concentration was varied by adding with a Hamilton microsyringe small instalments of the concentrated stock solution of known surfactant concentration. Measurements were made after thorough mixing, so as to get genuine results.

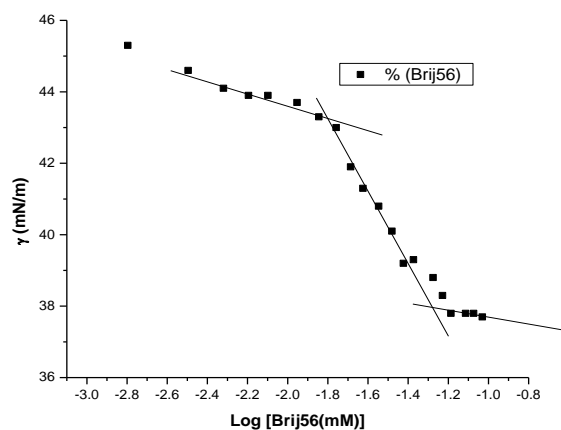
3.1 Surfactant-Polymer Interactions

3.1.1 Polymer with Single Surfactant Systems

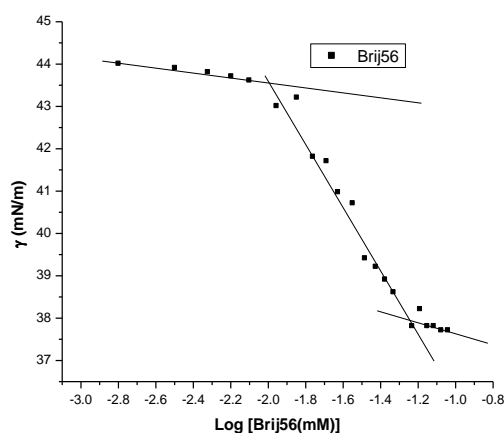
Fig. 3.1 shows the variation of surface tension of polymer solution with varying surfactant concentration. Two break points were obtained first at CAC and another at CMC. The lower concentration break indicates the beginning of formation of polymer-bound micelles while the higher concentration break indicates pure micelle formation [4]. As the surfactant concentration is increased till CAC, γ remains more or less constant signifying



(a)



(b)



(c)

Figure 3.1: Plot between surface tension vs logarithm of: (a) Brij56 concentration in presence of 0.01% HPC.(b) Brij56 concentration in presence of 0.03% HPC.(c) Brij56 concentration in presence of 0.05% HPC

no interaction between Brij56 and HPC adsorbed at the air/solution interface. Above CAC, γ decreases until the interface is saturated or the displacement process is completed. Decrease in γ can be due to specific binding of Brij56 with HPC, thereby increasing its hydrophobicity and hence decreasing the surface tension.

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
2	0.03%	Brij56	0.014	0.064
3	0.05%	Brij56	0.01	0.057

The CMC of Brij56 in aqueous medium has been found to be 0.036mM and in presence of polymer (HPC), CMC of Brij 56 gets altered. It is found CMC of Brij56 is more in presence of HPC probably because some of the surfactant concentration is needed to saturate the polymer. Further, initially with increase in HPC polymer concentration, CMC of Brij56 increases Table (3.1), probably because more and more surfactant concentration is needed to saturate the polymer but a stage is reached when increase in polymer concentration leads to decrease in

CMC of Brij56, probably at this stage the molecules of HPC interact with one another through intermolecular attractions and form polymer aggregates [5] which decreases available sites in polymer for the surfactants and hence CMC decreases.

IV.CONCLUSIONS

- At a given polymer concentration interaction starts between polymer and surfactant only at CAC.
- The HPC molecules start to form aggregates only at a certain minimum polymer concentration.
- The change in properties of polymer-surfactant solutions can be tuned to get desired results and can help to understand protein-surfactant interactions.

REFERENCES

- [1] Goddard, E.D., *Polymer Surfactant Interactions part 1st. Uncharged Water Soluble Polymer and Charged Surfactants, Colloids Surf.* **1986**, 19, 255.
- [2] Hayakawa, K.; and Kwak, J. C. T. *Interactions Between Polymers and Cationic Surfactants, in "Cationic Surfactants,"* Holland, P.; Rubingh, D. (Eds.) Marcel Dekker, New York, **1991**, vol.37, p.226.
- [3] Winnik, F. M.; Winnik, M. A and Tazuke, S. *J. phys. Chem.* **1987**, 91, 594
- [4] Mir, M. A.; Dar, A. A.; Amin, A.; Rather, G. M. *J. Molecular Liquids* **2009**, 150, 86.
- [5] Winnik, F. M. *Macromolecules* **1987**, 20, 2745.