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# Colloids and Surfaces A: Physicochemical and Engineering Aspects

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## Dye-surfactant interaction in aqueous pre-micellar and micellar environments in the alkaline fading of di-positive methyl green carbocation

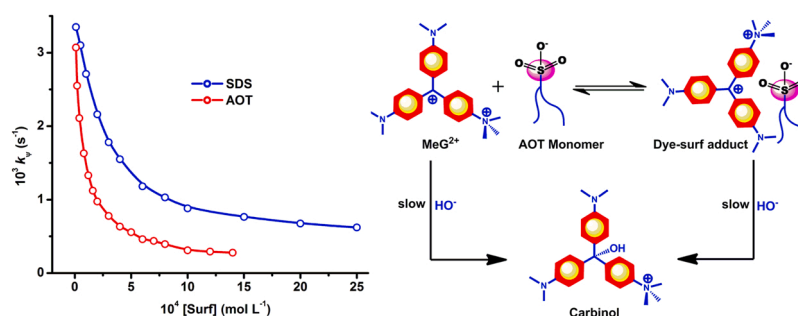
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## HIGHLIGHTS

- Dye-surfactant interaction in pre-micellar and micellar media.
- Ion-pair micelle formation.
- Spectral change showing equilibrium distribution of stereo isomers.
- 1:1 dye-surfactant pre-micellar adduct leading to rate inhibition.
- Post micellar catalysis by Brij35 and inhibition by CTAB.

## GRAPHICAL ABSTRACT

Premicellar rate inhibition by the anionic surfactants SDS and AOT occurs owing to the formation of 1:1 dye-surfactant pre-micellar adduct through electrostatic interaction before the slow hydrolysis step.



## ARTICLE INFO

## Keywords:

Methyl green  
Hydrolysis  
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Dye-surfactant adduct  
Binding parameters

## ABSTRACT

The alkaline fading of di-positive methyl green carbocation ( $\text{MeG}^{2+}$ ) has been studied in different aqueous pre-micellar and micellar environments of anionic, cationic as well as non-ionic surfactants. Mono- and di-negative anions like halides and sulphate have been found to show an inhibiting effect on the fading reaction owing to the formation of dye-anion ion-pair adduct before hydrolysis. The binding strength of the dye-anion ion-pair adduct is in the order:  $\text{SO}_4^{2-} > \text{I}^- > \text{Br}^- > \text{Cl}^-$  which rationalizes the same order of inhibition of the rate. A substantial change in the electronic spectra of  $\text{MeG}^{2+}$  in the presence of anionic surfactants, sodium dodecyl sulfate (SDS) and dioctyl sodium sulfosuccinate (AOT), in the pre-CMC region indicates a change in the equilibrium distribution of the two stereo isomers of the dye owing to the formation of  $\text{MeG}^{2+}$ -surfactant ion-pair and ion-pair micelle. The pre-micellar rate inhibition of the fading reaction by SDS and AOT occurs due to the formation of 1:1  $\text{MeG}^{2+}$ -surfactant ion-pair (where  $\geq 85\%$  of  $\text{MeG}^{2+}$  remain associated) through electrostatic interaction before hydrolysis. The cationic surfactant cetyltrimethylammonium bromide (CTAB) shows a retarding effect in the post-micellar region as the  $\text{HO}^-$  ion experiences both electrostatic repulsion and steric hindrance to approach the carbocation centre of the dye, embedded in the micelle. The polar hydroxyl group and the polyoxyethylene groups present in the moiety of the non-ionic surfactant Brij35 assist to increase the local concentration of  $\text{HO}^-$  and  $\text{MeG}^{2+}$  in the palisade layer resulting in a catalyzing effect on the fading reaction in the post CMC region. Both pre- and post-micellar rate effects have been analyzed quantitatively by different

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