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Influence of Anions and Micelle and Submicellar Aggregates on the Alkaline Hydrolysis of Malachite Green: Tensiometric, Spectrophotometric, and Kinetic Investigations

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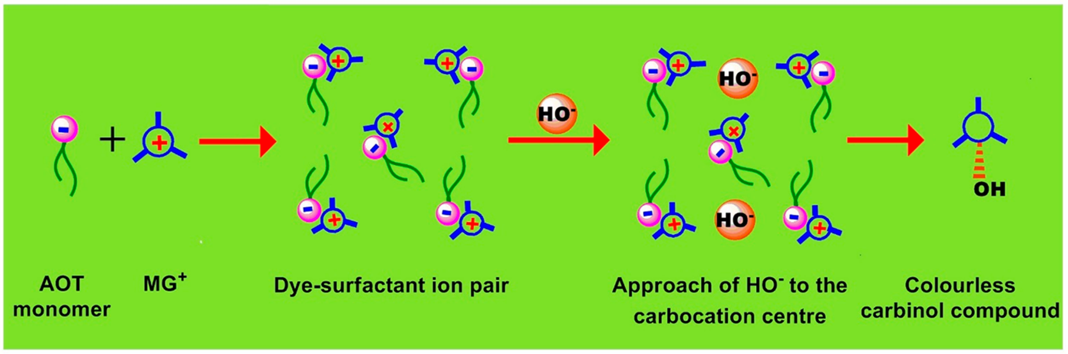

ABSTRACT: The influence of mono- and bivalent anions and micelle/submicellar clusters of different ionic and nonionic surfactants on the hydrolysis of malachite green (MG^+) was studied in the presence of low alkali concentrations. Large polarizable I^- ion and bivalent SO_4^{2-} ion show specific interaction toward MG^+ with the formation of dye−anion ion-pair resulting in a retardation of the reaction rate. Tensiometric studies for anionic surfactants sodium dodecyl sulfate (SDS) and dioctyl sodium sulfosuccinate (AOT) in the presence of dye indicate the formation of ion-pair micelles which subsequently break down to form normal micelles. A change of the absorbance value accompanied by a red shift in the electronic spectra with increase in surfactant concentration also evidenced the formation of ion-pair. The observed rate inhibition by the anionic surfactants and the interaction behavior/nature of binding between the dye and surfactant in the premicellar region have been analyzed in terms of different kinetic models. The Piszkiewicz cooperativity index (n) suggests 1:1 association between the anionic surfactant monomer and MG^+ in the submicellar cluster. A catalyzing effect for the cationic surfactant, cetyltrimethylammonium bromide (CTAB), was noticed in the post-CMC region leading toward a limiting reaction rate, and the Menger−Portonoy pseudophase model was employed to explain the behavior with evaluation of the binding parameter. The nonionic surfactant poly(oxyethylene) (20) sorbitan monolaurate (Tween 20) exerts inhibition effect on the hydrolysis reaction which may be explained qualitatively by the dearth of HO^- ions in the vicinity of the micelle-bound dye and quantitatively in light of the pseudophase model. Different equilibrium constants and binding constant parameters suggest appreciable binding between the dye and surfactant monomer/micelles owing to electrostatic/hydrophobic interactions.

1. INTRODUCTION

Triarylmethane dyes are the chemical compounds containing triphenylmethane moiety. These are classified into different groups depending on the nature of the substituents on the aromatic ring. Malachite green is an important water-soluble cationic dye of the triphenylmethane family,[1] chemically known as 4-{[4-(dimethylamino)phenyl](phenyl)methylidene}-*N*,*N*-dimethylcyclohexa-2,5-dien-1-iminium chloride. It finds use as a dyestuff in the pigment industry.[2] It controls fungal attacks, protozoan infections, etc., in a wide variety of fish and hence is used as an antimicrobial agent in aquaculture.[3] Further, it possesses some antibacterial[3] properties and is also used as a biological stain for microscopic analysis of tissue samples.[4] Malachite green is a carbocation dye stabilized through delocalization of the positive charge via conjugation among the aromatic rings, and thus it may be expected that different anions, as well as the ionic surfactants, if present in the system,

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