Kinetic investigations on alkaline fading of malachite green in the presence of micelles and reverse micelles

Somnath Dasmandal, Harasit Kumar Mandal, Arjama Kundu, Ambikesh Mahapatra *

Department of Chemistry, Jadavpur University, Kolkata 700 032, India

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ABSTRACT

The kinetics of alkaline hydrolysis of malachite green (MG^+) have been studied spectrophotometrically in the presence of cetyltrimethylammonium bromide (CTAB) under pseudo-first-order condition at buffered of pH 11 and 298 K. The rate increases slightly up to the critical micelle concentration of CTAB then increases rapidly for surface catalysis of the micelles. The reaction has also been studied in the water pools of the CTAB/ 1-butanol/heptane/water reverse micelles and found 4–8 times faster over its rate in aqueous phase but the rate decreases exponentially with its water pool (w) size. The CTAB micellar medium has been characterized using steady state emission spectroscopy and tensiometry at the reaction condition for better explanation of the experimental findings. The thermodynamic activation parameters for the hydrolysis reaction have also been determined for comparison of the kinetic behavior in different environments.

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1. Introduction

The chemistry of dyes and their applications to other scientific fields get immense popularity in the modern era. They have played an important role as an effective indicator in the analysis of some elements such as ruthenium (Ru), iodine (I) and osmium (Os) [1]. The recognition of DNA by dye molecules is of paramount importance in biochemistry and molecular biology [2]. Dye sensitization of semiconductors is becoming a promising strategy for solar energy conversion [3]. The principal application of dyes is in the coloration of substrates, typically textiles, where a great quantity of water and dyes are used, with about 50% of the dyes discharged into wastewater, thereby polluting the environment [4]. The wastewater, discharged from textile industries, contains high concentrations of reactive dyes that exert serious threats to sustainability of natural ecosystems [5]. Moreover, the contamination of reactive dyes may present a risk to the aquatic living organisms through bioaccumulation thus entering into their food chain. Toxicity of reactive dyes has been reported at concentrations as low as 5.2 mg L^{-1} [6]. Recently, several methods for dealing with the treatment of textile wastewater like physico-chemical treatment [5], biological oxidation [7], adsorption and advanced oxidation processes (AOPs), e.g. ozonation, photolysis, electrochemical, and sonolysis [8] have been investigated. Usually, these processes lead to the release of more toxic products than the parent compound that prove fatal for the living creatures [9]. Hydrolysis is one of the prime detoxification mechanisms for organic compounds as hydrolysis by-products are normally less toxic to the environment than the parent compound [10].

A number of investigations over the last three decades [11–13] have revealed that the rates of a variety of organic reactions are altered in the presence of dilute aqueous solution of surfactants [14]. One of the most important properties of the aqueous surfactant solution is their ability to solubilize a wide variety of organic molecules, thereby influencing their reactivity. The variation of rate can be explained with the specific interactions between surfactant molecules and reactant species, viz. Coulombic, hydrophobic and charge transfer. All of the interactions can play a significant role in altering the rate of the reaction [15,16]. The surfactant molecules mutate the reaction rate through the formation of aggregates, called micelles. These micelles are capable in changing the rate of the reaction by several ways [17]—decreasing the entropy of reactant species due to their binding with micelles, relative stabilization or destabilization of the reactants due to their preferential interaction with surfactants and promoting the approach of reactants towards the micellar core. The catalytic activity of micelles has been studied for different organic reactions, especially the hydrolysis of esters [18], Schiff bases and carbocationic dyes [19]. That means the micellar effects on the reactivity have frequently been a matter of study. However, a lot of interests have been placed on the study with reverse micelles because of its similarity with the microenvironment in the biological cells [20]. Although the majority of kinetic studies have been carried out in the ternary systems formed by AOT (sodium bis(2-ethylhexyl) sulfosuccinate)/alkane/water microemulsions [21]; nevertheless, only few systematic quantitative studies have been carried out in four component microemulsions [22–24]. Zakharova et al. [25] have shown

* Corresponding author. Tel.: +91 33 2457 2767 (office), +91 33 2432 4586 (residence); fax: +91 33 2414 6223.
E-mail addresses: amahapatra@chemistry.jdvu.ac.in, ambikeshju@gmail.com (A. Mahapatra).

the catalytic effect of reverse micellar systems on the alkaline hydrolysis of phosphonic acid esters. Microemulsions, also called reverse micelles, are pseudo-heterogeneous mixtures of water-insoluble organic compounds, water and a surfactant/co-surfactant mixture. They are transparent, isotropic and thermodynamically stable dispersion systems of 'oil' and 'water'. Two types of reverse micelles are recognized—oil-in-water (o/w) reverse micelles, where the 'oil' resides at the center of the droplet and is surrounded by surfactant and co-surfactant, whereas 'water' is at the droplet center in the water-in-oil (w/o) reverse micelles. The size of liquid drop in the dispersed phase is in the range of 8–80 nm. Due to the dynamic nature of reverse micelles, they can exchange their constituents including water, surfactants or other content [26]. The charged head groups of the reverse micelles make the liquid confined in it different in their physical properties from that of the bulk phase [27,28]. The liquids, entrapped in a very small cavity of nanometer range, play the fundamental role as a medium that controls the structures, functions and thermodynamics of the system which is akin to that of the biological membrane system. One of the most striking features of reverse micelles is the "water pool" which is usually expressed by the molar ratio of water to surfactant i.e., $w = [H_2O]/[Surf.]$ [29–31]. The size of water pool can precisely be controlled by taking different values of 'w'. The parameter 'w' is believed to be the key factor in controlling the most important structural features of the reverse micellar system. In most instances, water-in-oil systems (w/o) have been used and the water droplets have been proven useful as 'minireactors' for various types of reactions.

Malachite green (di[4-dimethylaminophenyl]phenyl cation) is an important water soluble dye. The name of the dye just comes from the similarity of its color. These dyes represent a class of dyes of commercial and analytical importance [32]. The high solubility of the dye in water makes it potential water pollutants. In the textile industry, the removal of the dyes from effluents in an economic fashion is a major problem. Since these wastewaters contain substances that modify the medium, and a study of the dyes fading in the presence of surfactants, which are already present in such water, can contribute to the development of new decontaminating procedures. The kinetic studies of alkaline fading of malachite green thus have extensively been developed [33].

In this article, we have presented some of our interesting results on the study of kinetics of alkaline fading of malachite green in micellar medium and reverse micellar medium of the cationic surfactant CTAB. All of the experimental works have been carried out in buffer medium of pH = 11 at 298 K. The reaction of malachite green with hydroxide ions is a one-step reaction [34] and follows pseudo-first-order kinetics. Rationalizations of the kinetic results with proper explanations have been attempted.

2. Experimental

2.1. Reagents & materials

Malachite green (MG^+), CTAB, sodium carbonate and bicarbonate salts have been used as received from Merck, India. Pyrene has been procured from Sigma-Aldrich and used without further purification. N-Cetyl pyridinium chloride (CPC) has been purchased from Merck, India and recrystallized from methanol/ethanol mixture before use. Highly pure water from Milli-Q Ultra has been used for preparation of aqueous solutions throughout the experiment. Fresh aqueous solution of malachite green has been used for day to day works and it is stored in a dark place. The concentration of malachite green solution has been determined spectrophotometrically using its molar extinction coefficient, $\varepsilon_{616} (MG^+) = 148424$ L mol^{-1} cm^{-1} [35]. The aqueous solution of CTAB and CPC have been prepared with 0.02 mol L^{-1} Na$_2$CO$_3$ = 0.02 mol L^{-1} NaHCO$_3$ buffer solution of pH = 11 (± 0.02). Ethanolic solution of pyrene has been used as a probe. All fluorimetric, tensiometric and kinetic experiments have been carried out at a constant temperature of 298 K and buffer medium of pH = 11.

2.2. Methods

2.2.1. Fluorimetry

Steady-state fluorescence measurements have been performed on a Shimadzu RF-5000 spectrofluorimeter thermostated at 298 K (± 0.1 K). For the determination of critical micelle concentration (CMC) and effective dielectric constant (ε) on CTAB micellar surface, a pyrene solution of concentration 1×10^{-6} mol L^{-1} has been used as a probe. Pyrene has been excited at 332 nm, and its emissions recorded at 375 and 386 nm corresponding to the first and third vibronic peaks respectively, with the use of both excitation and emission slits of 5 nm. The formation of micelle has been attributed by the change in the intensity ratios of the first and third peaks (I_I/I_{III}) from the emission spectra of pyrene. The aggregation number (N) of CTAB in buffer (pH = 11) medium has been determined using the steady-state fluorescence quenching (SSFQ) method where N-Cetyl pyridinium chloride (CPC) has been employed as quencher (Q). For the determination of N, the concentration of CTAB has been kept well above its CMC throughout the experiments.

2.2.2. Tensiometry

Tensiometric measurement has been carried out on a calibrated du Nouy tensiometer (Jencon, India) employing ring detachment technique [36]. A buffer solution of 10 mL has been placed in a thermostated 298 K (± 0.1 K) double walled jacketed glass container where the CTAB solution of desired concentration has been added gradually in a number of steps with the aid of a micro-pipette from Finnpipette. After each addition of surfactant, the mixture has been stirred well using a magnetic stirrer, allowed the mixture to equilibrate and finally the measurement of surface tension (γ) was carried out subsequently. The measured values of surface tension have been found to be reproducible within ± 0.02 dyn cm^{-1}.

2.2.3. Kinetic measurements

The alkaline hydrolysis reactions have been carried out spectrophotometrically on a UV–visible Spectrophotometer (Shimadzu, UV-1800) equipped with a Peltier temperature controller, TCC-240A maintaining a constant temperature of 298 K (± 0.1 K). The kinetics of hydrolysis reactions have usually been performed up to 2–3 half-lives of the reaction. The decrease in absorbance (Fig. 1) at 616 nm has been recorded as a function of time. All the kinetic runs have been carried out under pseudo-first-order conditions with excess amount of alkali over MG^+. The observed pseudo-first-order rate constants (k_{obs}) have been

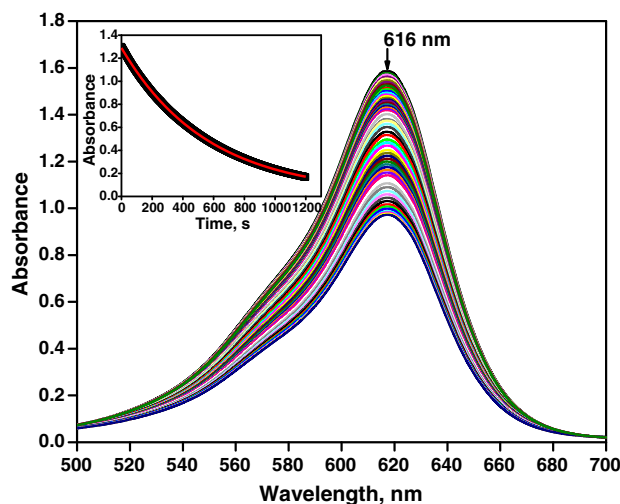**Fig. 1.** UV–vis Spectra of MG^+ and $^-$OH reaction mixture in aqueous buffer medium at different time intervals. [Inset: Change of absorbance as a function of time at 616 nm.] $[MG^+]_0 = 5.77 \times 10^{-5}$ mol L^{-1}, pH = 11, $\mu = 4 \times 10^{-3}$ mol L^{-1} at 298 K.