ORIGINAL ARTICLE

Kinetics of the diazotization and azo coupling reactions of procaine in the micellar media

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Abstract The kinetics of the diazotization reaction of procaine in the presence of anionic micelles of sodium dodecyl sulfate (SDS) and cationic micelles of cetyltrimethyl ammonium bromide (CTAB), dodecyltrimethyl ammonium bromide (DDTAB) and tetradecyltrimethyl ammonium bromide (TDTAB) were carried out spectrophotometrically at λ_{max} = 289 nm. The values of the pseudo first order rate constant were found to be linearly dependent upon the [NaNO$_2$] in the concentration range of 1.0×10^{-3} mol dm^{-3} to 12.0×10^{-3} mol dm^{-3} in the presence of 2.0×10^{-2} mol dm^{-3} acetic acid. The concentration of procaine was kept constant at 6.50×10^{-5} mol dm^{-3}. The addition of the cationic surfactants increased the reaction rate and gave plateau like curve. The addition of SDS micelles to the reactants initially increased the rate of reaction and gave maximum like curve. The maximum value of the rate constant was found to be 9.44×10^{-3} s^{-1} at 2.00×10^{-3} mol dm^{-3} SDS concentration. The azo coupling of diazonium ion with β-naphthol (at λ_{max} = 488) nm was found to linearly dependent upon [ProcN$_2^+$] in the presence of both the cationic micelles (CTAB, DDTAB and TDTAB) and anionic micelles (SDS). Both the cationic and anionic micelles inhibited the rate of reactions. The kinetic results in the presence of micelles are explained using the Berezin pseudophase model. This model was also used to determine the kinetic parameters e.g. k_m, K_s from the observed results of the variation of rate constant at different [surfactants].

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1. Introduction

In diazotization, the aromatic primary amine is converted into a diazonium compound by reacting with sodium nitrite in aqueous acid solution. During the course of reaction, the tautomerization takes place with the loss of water leading to the formation of diazonium ion. The diazonium ion is stabilized by delocalization of the positive charge at the ortho and para carbon atoms of the ring. The reaction is used for making
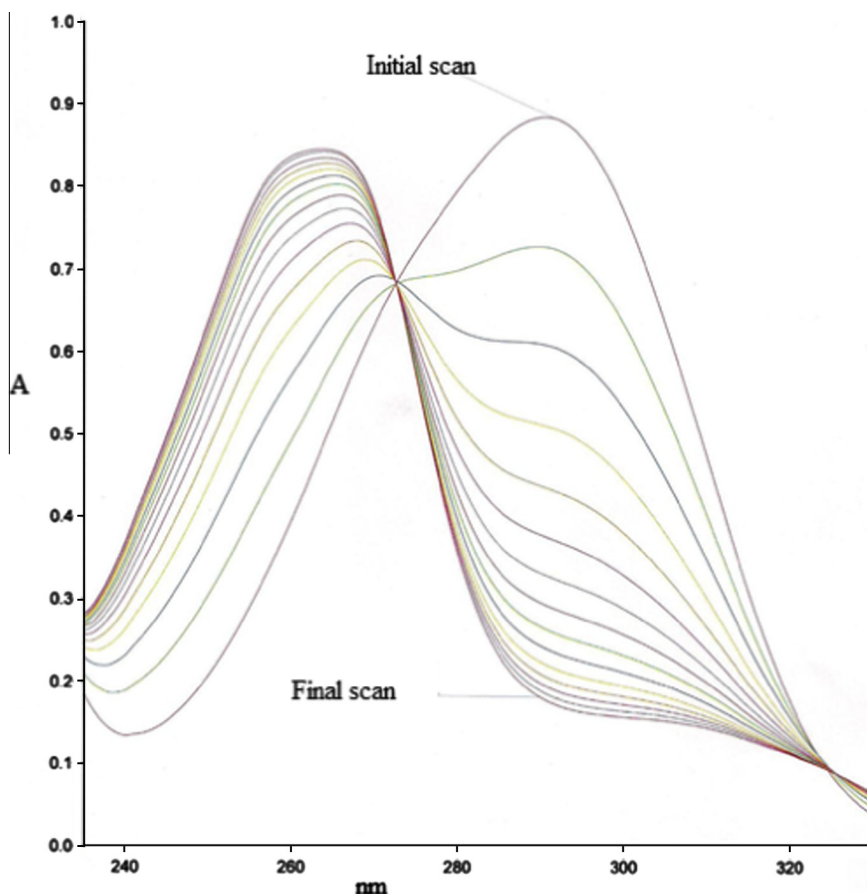
Figure 1 Repetitive scan for the diazotization reaction of procaine with sodium nitrite. Reaction conditions; [Procaine] $= 6.50 \times 10^{-5}$ - mol dm^{-3}, [nitrite] $= 3.00 \times 10^{-3}$ mol dm^{-3}, [acetic acid] $= 3.0 \times 10^{-3}$ mol dm^{-3}, Temperature $= 25.0 \pm 0.1$ °C.

azo dyes used for dying and printing of textiles, for converting amino group in aromatic compound into halogen group, nitrile group or hydroxyl group. The azo pigments are also used for varieties of coloration – paints, printing inks, cosmetic colors etc. The applications of azo dyes in high technology fields include electronic devices, linear and nonlinear optics, reprography, sensors and biomedical uses (Gregory, 1991; Fraleoni-Morgera et al., 2005; Viscardi et al., 2003; Zollinger, 2003). The work described in this paper is the extension of the ongoing research program for exploring the catalytic or inhibitive effect of micelles on the rates of diazotization and azo coupling reactions (Al-Lohedan et al., 1982, 1993; Al-Lohedan, 1990, 1995; Al-Lohedan and Kirby, 1995; Al-Blewi et al., 2013). The surfactant molecules aggregate to form micelles above certain concentration called critical micellar concentration (cmc). The surfactant aggregates above cmc are considered to be microreactor and provide different micro environment than the bulk aqueous medium and thereby, influence the reaction rates. Most of the polar and ionic substances accumulate in the micellar surface region i.e. within the Stern layer and Guoy-Chapman layer while the hydrophobic substances reside in the interior of micelles (Al-Shamary et al., 2012; Broxton et al., 1987; Fendler and Fendler, 1975; Khan, 2007; Rosen, 2004). The alteration in the reaction rates by the micelles describes the nature of binding between the reactive substrates and micelles. In the present work, the diazotization of procaine by sodium nitrite in the presence of acetic acid has been carried out in order to investigate the nature and strength of binding of procaine with cationic and anionic surfactant molecules.

2. Experimental

2.1. Materials

Procaine hydrochloride (99%, Sigma, USA), sodium dodecyl sulfate (SDS, 99%, BDH, England), sodium bromide (99%, BDH, England), and cetyltrimethyl ammonium bromide (CTAB, 99%, Aldrich) were used without further purification. Dodecyltrimethyl ammonium bromide (DDTAB) and Tetradecyltrimethyl ammonium bromide (TDTAB) were synthesized in the laboratory. DDTAB was synthesized by adding 1-bromododecane (0.1 mol) to trimethylamine (0.1 mol) dissolved in 100 ml isopropyl alcohol. The mixture was refluxed for 48 h. Isopropyl alcohol was removed by distillation and the remaining solvent was evaporated by using rotary evaporator. The dried product was recrystallized from absolute alcohol – dry ethyl ether. TDTAB was synthesized by using 1-bromotetradecane instead of 1-bromododecane and following the same procedure as for DDTAB. Sodium hydroxide of Anal R grade was used during the experiments. Deionized double-distilled water (specific conductance: $1–2 \times 10^{-6}$ Ω^{-1} cm^{-1}) was used as a solvent.