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Kinetics of Fading of Acid Dyes by Sodium Hydroxide in Presence of Surfactants

M.S. PATEL, D.M. KOTHWALA and T.N. NAGAR*
Department of Chemistry, South Gujarat University, Surat-395 007, India
e-mail: minesh_63063@yahoo.co.in

Cationic micelles of cetyl trimethyl ammonium bromide ($C_{16}TABr$) increase the rate of reaction of acid dyes with the hydroxide ion. Non-ionic surfactant micelles Triton X-102 have also little enhancing effect, whereas the anionic micelles of sodium dodecyl sulfate (SDS) inhibit the rate. The thermodynamic parameters have been calculated in absence and presence of surfactant solutions.

Key Words: **Kinetics, Acid dyes, Sodium hydroxide, Surfactants**

INTRODUCTION

Studies of chemical reaction in micelles media have led to the development of new methods and to the improvement of existing synthetic and analytical procedures[1-3]. Organic reactions in aqueous solutions of surfactants under go either rate acceleration or inhibition and this behavior has been attributed to electrostatic and hydrophobic interactions between the substrate and surfactant aggregates. The present paper reports the effect of cationic surfactant $C_{16}TABr$, anionic surfactant SDS, and nonionic surfactant Triton X-102, on the reaction of acid dyes [Acid Green-9 (AG-9) and Acid Green-16 (AG-16)] with nucleophile hydroxide ion.

EXPERIMENTAL

The cationic surfactant $C_{16}TABr$ (BDH),anionic surfactant SDS, (BDH) and nonionic surfactant Triton X-102 (Sigma Chemicals, USA) were purified before use. Acid dyes AG-9 (Acid Green-9) and AG-16 (Acid Green-16) were obtained from Colourtex Ind. Ltd. and purified by dissolving in dimethylformamide and precipitating with the help of trichloro-ethylene[4]. The reaction between acid dyes [2.5×10^{-5} M] and NaOH taken as [2×10^{-2} M] to [6×10^{-2} M] was followed colorimetrically by observing the absorbance for AG-9 and AG-16 using a filter 450–520 nm in absence and presence of surfactants at different time intervals, employing photoelectric colorimeter-112 with thermostated cell holder and temperature of cell compartment could be controlled within ±0.1°C

RESULTS AND DISCUSSION

Both the dyes in aqueous media were found to obey Beer's law up to 2.5×10^{-5} M. Cationic surfactant $C_{16}TABr$ micelles affect the pseudo first-order rate constant for the fading of acid dyes. The variation of pseudo first-order rate constant for AG-9 (Table-1) and AG-16 at different concentrations and temperatures for $C_{16}TAB$ are shown in Fig. 1 respectively.

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TABLE-1

-EFFECT OF VARYING [C_{16}TABr] ON THE FADING OF ACID GREEN-9 BY SODIUM HYDROXIDE AT DIFFERENT TEMPERATURES

[Acid green-9] = 2.5×10^{-5} M; [NaOH] = 2.0×10^{-2} M

[C_{16}TABr] × 10^4 M	k_{obs} (min^{-1})		
	25°C	30°C	35°C
0.0	0.0614	0.0882	0.1105
0.4	0.0783	0.1151	0.1305
0.8	0.1036	0.1266	0.1842
1.2	0.1496	0.1658	0.2456
1.6	0.1995	0.2303	0.3838
2.0	0.2840	0.4145	0.5290
2.4	0.3799	0.5757	0.7982
2.8	0.5181	0.6332	0.9872

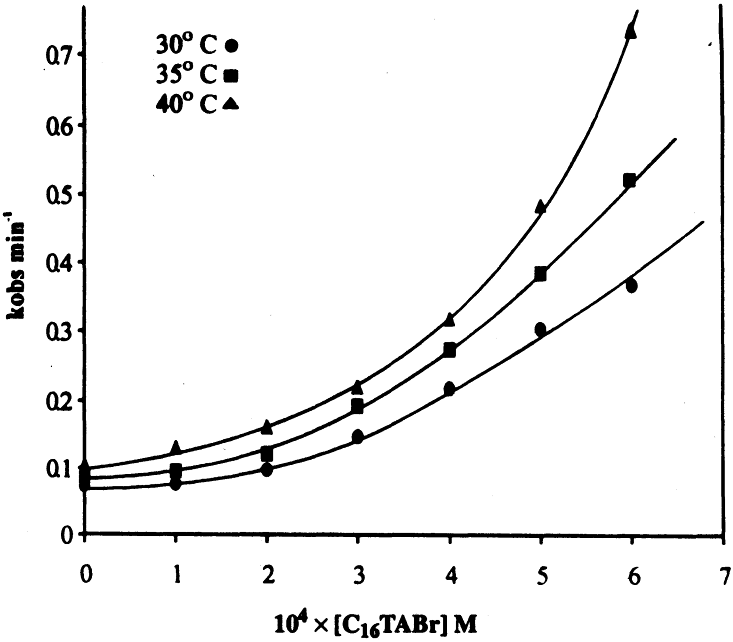

Fig. 1. Pseudo first order rate constant for the alkaline fading of AG-16 at different C_{16}TABr concentrations and temperatures. [AG-16] = 2.5×10^{-5} M; [NaOH] = 0.06 M

The rate of reaction in presence of SDS decreases with increase in concentration and becomes almost constant at higher concentration. Anionic surfactant SDS, inhibited the rate of fading of acid dyes. The range of varying concentrations of SDS on the alkaline fading of AG-9 (Table-2) and on AG-16 at different temperatures are shown in Fig. 2 respectively.

TABLE-2
EFFECT OF VARYING CONCENTRATION OF SDS ON THE ALKALINE FADING OF ACID GREEN-9 AT DIFFERENT TEMPERATURES

[Acid green-9] = 2.5 × 10^{-5} M; [NaOH] =62.0 × 10^{-2} M

SDS M	k_{obs} (min^{-1})		
	25°C	30°C	35°C
0.000	0.2149	0.2533	0.3761
0.010	0.1688	0.2360	0.3608
0.015	0.0921	0.1704	0.2763
0.020	0.0307	0.0431	0.0997
0.025	0.0126	0.0202	0.0311
0.030	0.0105	0.0148	0.0215
0.035	0.0076	0.0119	0.0165

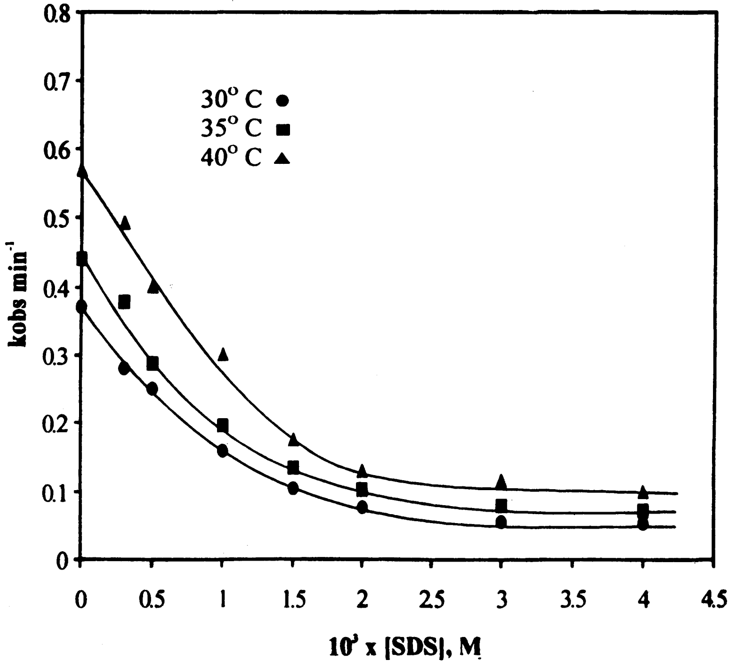

Fig. 2. Pseudo first order rate constant for the alkaline fading of AG-16 at different SDS concentrations and temperatures. [AG-16] = 2.5 × 10^{-5} M; [NaOH] = 0.3 M

Nonionic surfactant Triton X-102 micelles have little enhancing effect on the reaction of fading of acid dyes. The variation of the pseudo first-order rate constant for AG-9 (Table-3) and AG-16 at different TritonX-102 concentration are given in Fig. 3 respectively.

TABLE-3
EFFECT OF VARYING [TRITON X-102] ON THE ALKALINE FADING OF ACID GREEN-9 AT DIFFERENT TEMPERATURES

[Acid green-9] = 2.5×10^{-5} M; [NaOH] = 2.0×10^{-2} M

Triton X-102 % (v/v)	k_{obs} (min^{-1})		
	25°C	30°C	35°C
0.000	0.0614	0.0882	0.1105
0.010	0.0635	0.0898	0.1120
0.015	0.0665	0.0921	0.1150
0.020	0.0710	0.0967	0.1190
0.025	0.0765	0.1030	0.1290
0.030	0.0835	0.1100	0.1380
0.035	0.0940	0.1190	0.1450
0.040	0.1050	0.1290	0.1520

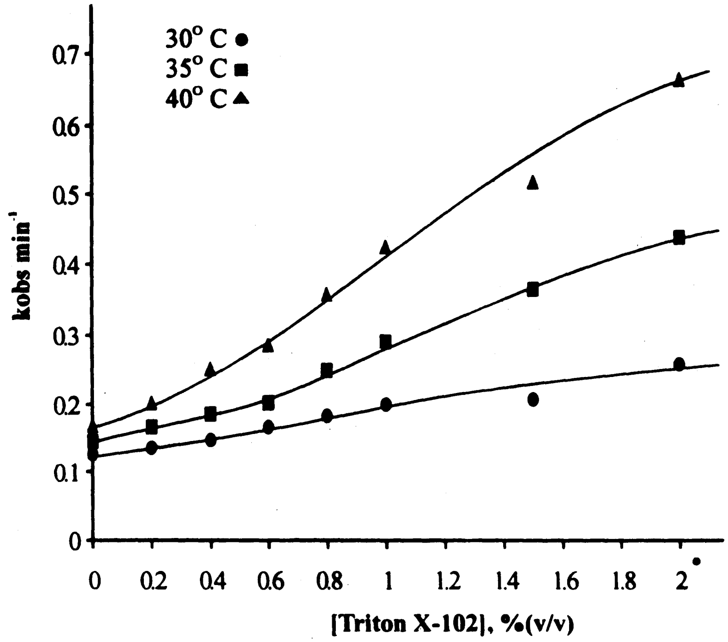

Fig. 3. Pseudo first order rate constant for the alkaline fading of AG-16 at different Triton X-102 concentrations and temperatures. [AG-16] = 2.5×10^{-5} M; [NaOH] = 0.06 M

The pseudo first-order rate constants for the reaction do not vary linearly with cationic surfactant concentration as the reaction is in the aqueous phase. The pseudo first-order rate constants (k_{obs}) increase with increase in cationic surfactant. The increase in rate below the CMC of the cationic surfactant may be due to mixed micelles formation of the dye molecule and surfactant molecules. Considerable evidence[5] is available to show that concentration of reactants into a small bulk at the micellar surface is the major source of enhancement of bimolecular reactions. In case of $C_{16}TABr$ micelle, the surface is positively charged which attracts the OH^-, $C_{16}TABr$ micelle can bind the large hydrophobic groups of the dye and OH^- on its ionic coat, and the rate is enhanced.

Inhibitory effect in presence of SDS, may be due to non approachability of OH^- to the bounded substrate in the anionic micelle of similar charge.

The rate of reaction increase with increase in Triton X-102 concentration. The rate enhancement may be due to the closer proximity of the hydroxide ion and the dye present in the non ionic micelle. The increased rate of formation of triphenylmethanol from TPM dyes with OH^- in nonionic micelle has been reported[6].

The plost of log *k* versus 1/T in absence and presence of surfactants are linear. The values of activation parameters, *viz.*, E_a, frequency factor Z, $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ in aqueous and micellar media are summarized for acid green-9 and acid green-16 in Tables 4(a) and 4(b) respectively. The values of activation energies obtained from the slopes of Arrhenius plots for $C_{16}TABr$ catalysed reaction and for SDS inhibited reaction in aqueous solutions suggest that a decrease in activation energy in presence of $C_{16}TABr$ relative to aqueous medium is one of the factors responsible for the catalysis and higher activation energy in presence of SDS contributes towards inhibition. The value of $\Delta S^{\#}$ in all three systems are negative indicating that the reaction is occurring between ionic species. Micelle do not alter the mechanism of the reaction but only affect the reaction rate.

TABLE-4 (a)

VALUES OF THERMODYNAMIC QUANTITIES FOR THE REACTION OF ACID GREEN-9 WITH OH^- ION IN ABSENCE AND PRESENCE OF $C_{16}TABr$ AND SDS

Activation parameter	E_a# (kJ mol^{-1})	Z (lit mol^{-1} sec^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
In aqueous solutions	56.26	4.39×10^8	−87.89	53.74	80.37
In the presence of $C_{16}TABr$ (2×10^{-4} M)	47.57	6.58×10^7	−103.69	45.05	76.47
In aqueous solutions	42.74	5.90×10^6	−123.72	40.22	77.71
In the presence of SDS (3×10^{-2} M)	54.69	3.97×10^7	−107.88	52.17	84.86

TABLE-4 (b)

VALUES OF THERMODYNAMIC QUANTITIES FOR THE REACTION OF ACID GREEN-16 WITH OH^- ION IN ABSENCE AND PRESENCE OF $C_{16}TABr$ AND SDS

Activation parameter	$E_a\#$ (kJ mol^{-1})	Z (lit mol^{-1} sec^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
In aqueous solutions	38.63	3.3×10^5	–155.97	33.59	80.85
In the presence of $C_{16}TABr$ (4×10^{-4} M)	30.03	3.2×10^4	–175.26	24.99	78.09
In aqueous solutions	31.20	8.8×10^4	–167.00	23.16	76.76
In the presence of SDS (2×10^{-4} M)	56.99	3.8×10^8	–97.360	51.95	81.45

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