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Studies on Kinetics of Hydroxylation of *p*-Rosaniline Hydrochloride by Sodium Hydroxide in Micellar Environment

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Basic hydrolysis of *p*-rosaniline hydrochloride in presence of solution of anionic surfactant, *e.g.*, sodium dodecyl sulphate (SDS), cationic surfactant, *e.g.*, hexadecyl trimethyl ammonium bromide (C_{16}TABr) and non-ionic surfactant, *e.g.*, triton X-100 has been studied. C_{16}TABr is known to increase the rate of reaction of triphenyl methyl carbonium ions with the hydroxide ion, where as the anionic micelles of SDS and non-ionic of TX-100 inhibit this rate. At lower concentration of NaOH, reaction rate increase rapidly with cationic surfactant concentration and with increasing hydroxide ion concentration, an inhibition effect is observed for all surfactant concentrations studied. The addtion of monohydric alcohol, *viz.*, ethanol, *n*-propanol, *n*-butanol and solvent like acetone and ethylene glycol decreases the cationic micellar catalysed rate of carbinol formation and on the other hand increase the anionic micellar inhibited rate. The effectiveness of these solvents in reducing the extent of overall inhibition by sodium dodecyl sulphate has been found to follow the order: ethylene glycol < *n*-propanol < *n*-butanol. These trends are discussed with reference to the probable factors that are responsible for the change in the reaction rate in the presence of organic solvents. The effect of polyethylene glycol has also been investigated in the presence of C_{16}TABr. Effect of various salts, *viz.*, KCl, KBr, KNO_3, K_2SO_4 and NaCl has also been studied on this reaction.

Key Words: Kinetics, Hydroxylation, *p*-Rosaniline hydrochloride, Micellar environment.

INTRODUCTION

The interaction between dye molecular and other molecular entities is of paramount importance in both dye and medicine industries. Micellar catalyses have useful biochemical models for numerous processes which occur on or involve amphipathic surface[1]. Studies of chemical reaction in micellar media have led to the development of new methods and to the improvement of existing synthetic and analytical procedure[2]. The present work is an investigation of the reaction of *p*-rosaniline hydrochloride (Fig. 1) by sodium hydroxide in micellar forming substances *viz.*, cationic, anionic and non-ionic surfactants in presence of solvents, salts, polymers and at different temperatures.

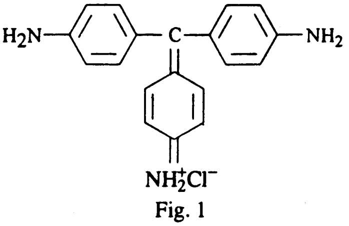

Fig. 1

EXPERIMENTAL

The surfactants, CTAB and SDS (BDH) were purified before use. Triton X-100 and *p*-rosaniline hydrochloride (BDH) were used as such. Inorganic salts of BDH or E. Merck AnalaR grade and polyethylene glycol [m.w. 400 and 4000] of Aldrich were used. The solvents were (BDH) analytical reagents. All solutions were prepared in triply distilled water and used within ten days of their preparation.

All the kinetics runs were carried out under pseudo first-order conditions, The reaction between *p*-rosaniline hydrochloride and sodium hydroxide was followed colourimetrically by observing the absorbance at 540 nm at different time intervals in absence and presence of varying concentrations of surfactant.

RESULTS AND DISCUSSION

The values of rate constant are almost constant with respect to the substrate in presence of surfactants indicate that the reaction with OH^- in micellar environment of CTAB, SDS and TX-100 follows pseudo first-order kinetics.

The pseudo first-order rate constants for these reactions do not vary linearly with cationic surfactant concentrations, as the reaction is an aqueous phase. The pseudo first-order rate constant in presence of CTAB for different surfactant concentration is represented in Fig. 2, increase with increase in cationic surfactant concentration passes through a maximum and decrease at high concentration.

A perusal of figures shows that with the addition of $C_{16}TABr$ at concentration well below the CMC (CMC value for the $C_{16}TABr$ is 2.6×10^{-4} M), the k_{obs} value

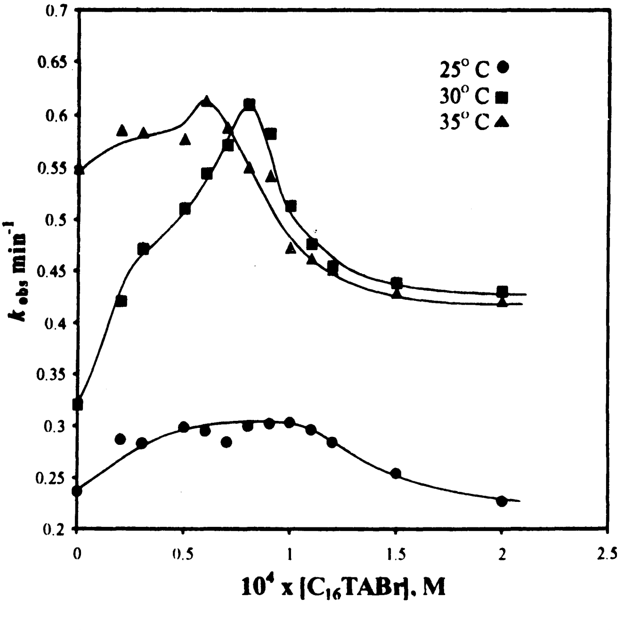

Fig. 2. Influence of varying $[C_{16}TABr]$ on the fading of *p*-rosaniline hydrochloride by sodium hydroxide at different temperatures. [*p*-rosaniline hydrochloride] = 2.5×10^{-5}M, [NaOH] = 4.0×10^{-3} M

increase up to CMC and thereafter it decreases. The rate increase below the CMC may be due to mixed micelle formation of the dye molecule and surfactant molecules. In CTAB micelle, the surface is positively charged which attracts the OH— and is expected to repel the dye cation. The dye molecule has also both hydrophobic and polar portions. Thus CTAB micelles can bind the large hydrophobic groups of the dye and the OH^- on its ionic coat. In this way both the reactant are brought into close proximity and the rate is enhanced and at the higher concentration decrease with the increase in CTAB concentration. When micellization starts the dye molecule may be solubilized in the micelles and with the increase in the concentration of cationic surfactant produces unreactive counter ions Br^-, that displaces micellar OH^- ions in the proximity of the bound dye molecules. This could account for the decreasing rate above the CMC of the surfactant.

In the case of SDS the decrease in k_{obs} with increase in [surfactant] (Fig. 3) can be explained in terms of incorporation of the dye cation into the anion aggregate and non-approachability of nucleophilic OH^- to the micelle bound dye cation due to electrostatic repulsion.

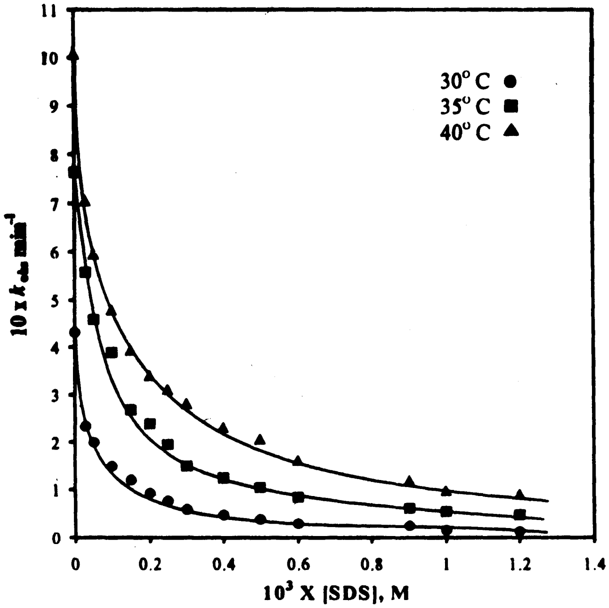

Fig. 3. Influence of varying [SDS] on the fading of *p*-rosaniline hydrochloride by sodium hydroxide at different temperatures. [*p*-rosaniline hydrochloride] = 2.5×10^{-5}M, [NaOH] = 4.0×10^{-3} M

In case of TX-100 the rate decreases rapidly up to 1.0% (v/v) and then becomes constant with the increase in the surfactant concentration (Fig. 4). It has been found that nonionic surfactants have good affinity for TPM dyes, to form complex, the nonionic surfactant does not carry any ionisable groups so that the binding has to be accomplished by inter molecular forces, possibly consisting of mixed micelles, involving both dye and surfactant. The fast decrease in the rate may be due to the strong complex formation between the dye and surfactant. The decrease in the rate constant in case of TX-100 may be due to the neutral surface of the nonionic micelles, the oxygen of polyethylene group creates a negative surface which attracts the positively charged dye cation but repels the attacking OH^- ion.

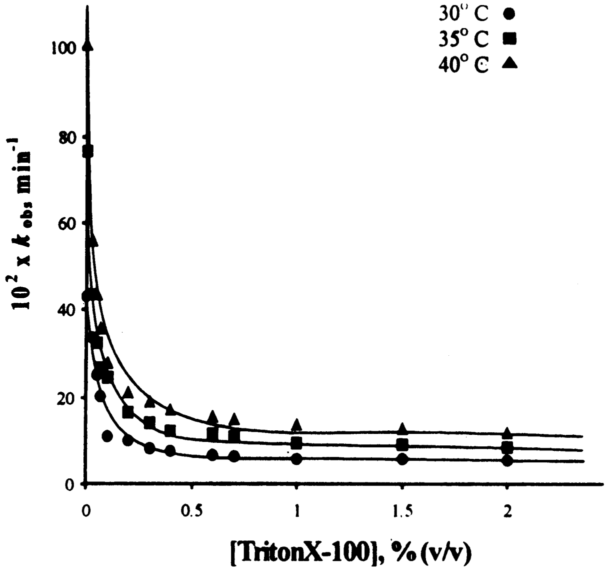

Fig. 4. Influence of varying [Triton X-100] on the fading of *p*-rosaniline hydrochloride by sodium hydroxide at different temperatures. [*p*-rosaniline hydrochloride] = 2.5×10^{-5}M, [NaOH] = 4.0×10^{-3} M

Effect of solvents on the SDS inhibited reaction

The influence of organic solvent, *viz.*, ethanol, *n*-propanol, *n*-butanol, acetone and ethylene glycol on the SDS inhibited reaction on triphenyl methyl carbonium ions was examined at fixed [surfactant], [reactant] and the [substrate] while varying the solvent percentage in the reaction system. The studies were performed in each case, at fixed [SDS] which corresponded to saturation plots of rate constant against solvent composition are shown in Fig. 5. The value of rate constant increase with the volume percentage of the solvent. The overall inhibition is due to the SDS micelles is decreased by the addition of solvents. The effectiveness of an alcohol reduce the extent of overall inhibition is found to increase with the increase carbon chain length of alcohol molecules[3]: ethylene glycol < acetone < ethanol < n-propanol < n-butanol.

Effect of solvents on the CTAB catalysed reaction

A decrease in reaction rate is observed with the increase in the concentration of the solvents (Table-1). A perusal of the figure shows that the alcohol with

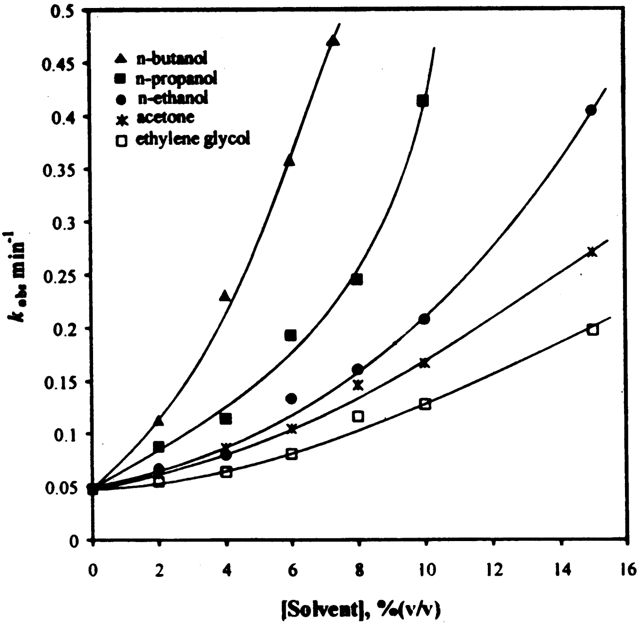

Fig. 5. Effect of organic solvent on SDS inhibited reaction of *p*-rosaniline hydrochloride with hydroxide ion at 30°C t[*p*-rosaniline hydrochloride] = 2.5×10^{-5}M, [NaOH] = 0.1 M, [SDS] = 4.0×10^{-3}M

longer alkyl chain is more effective in decreasing the rate for various solvents

TABLE-1
EFFECT OF SOLVENTS ON THE REACTION RATE ALKALINE FADING OF *p*-ROSANILINE HYDROCHLORIDE IN PRESENCE OF C_{16}TABr at 30°C.

[*p*-rosaniline hydrochloride] = 2.5×10^{-5} M; [NaOH] = 3.0×10^{-3} M
[C_{16}TABr] = 0.9×10^{-4}M

Solvent % (v/v)	k_{obs} (min^{-1})				
	Ethanol	*n*-Propanol	*n*-Butanol	Ethylene glycol	Acetone
0.0	0.1805	0.1805	0.1805	0.1805	0.1805
2.0	0.1671	0.1536	0.1437	0.1229	0.1172
4.0	0.1498	0.1224	0.1074	0.1233	0.0936
6.0	0.1405	0.1102	0.0886	0.1605	0.0778
8.0	0.1279	0.0988	0.0700	0.1508	0.0604
10.0	0.0987	0.0827	0.0618	0.1409	0.0507
15.0	0.0799	0.0564	0.0468	0.1128	0.0418
20.0	0.0668	0.0397	0.0320	0.0979	0.0278

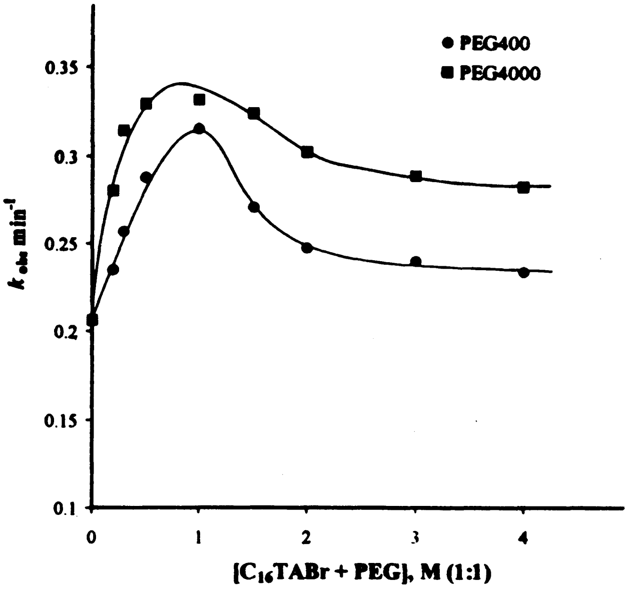

Fig. 6. Rate constant for the alkaline fading of *p*-rosaniline hydrochloride at different surfactant/polymer ratio 1 : 1 at 30°C [*p*-rosaniline hydrochloride] = 2.5×10^{-5}M, [NaOH] = 3.0×10^{-3}M

as follows: acetone > n-butanol > n-propanol > ethanol > ethylene glycol. However it may be pointed out that ethylene glycol shows an anomalous effect. The rate decreases initially up to 2% than increase up to 6% of the ethylene glycol concentration and there after decrease with the increase in the ethylene glycol concentration. Ethylene glycol has been observed for the fading of setoglaucin[4].

Effect of polyethylene glycol (PEG-400 and PEG-4000)/ cationic surfactant (CTAB) mixed micelles on basic hydrolysis of *p*-rosaniline hydrochloride

The pseudo first-order rate constants for basic hydrolysis of *p*-rosaniline hydrochloride at different CTAB/PEG (400, 4000) molar ratio 1 : 1, and hydroxide ion concentrations is given in Fig. 6. The pseudo first-order rate constant increase with the increase in surfactant concentration (CTAB/PEG-400, CTAB/PEG-4000) and becomes almost constant at higher concentration of surfactant.

It is observed that the value of rate constant are lower in case of cationic surfactant/PEG than the cationic micelles in aqueous solution. The retarding effect in the rate constant may be due to the incorporation of PEG in the cationic micelles to form mixed micelles.

The value of rate constant decrease with the increase in Br- concentration for CTAB/PEG is tabulated in Table-2

TABLE-2
PSEUDO FIRST-ORDER RATE CONSTANT FOR THE ALKALINE HYDROLYSIS OF *p*-ROSANILINE HYDROCHLORIDE AT DIFFERENT SURFACTANT/POLYMER CONCENTRATION RATIO 1 : 1

[*p*-rosaniline hydrochloride] = 2.5×10^{-5} M; [NaOH] = 2.0×10^{-3} M

C_{16}TABr + PEG(400), (1:1) M × 10^4	$10 \times k_{obs}$ min^{-1}	C_{16}TABr + PEG(4000), (1:1) M × 10^4	$10 \times k_{obs}$ min^{-1}
0.0	0.2066	0.0	2.0660
0.2	0.2347	0.2	2.8027
0.3	0.2567	0.3	3.1412
0.5	0.2876	0.5	3.2921
1.0	0.3148	1.0	3.3087
1.5	0.2704	1.5	3.2350
2.0	0.2473	2.0	3.0169
3.0	0.2395	3.0	2.8830
4.0	0.2339	4.0	2.8200

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