

NOTE

Kinetics of Oxidation of Rosaniline Hydrochloride by Potassium Peroxydisulphate in Mixed Micelles of Binary Surfactant System

HITENDRA M. JOSHI and T.N. NAGAR*

Department of Chemistry, South Gujarat University, Surat-395 007, India.

The kinetics of oxidation of rosaniline hydrochloride (R—HCl) has been studied in binary combinations of cationic/nonionic and anionic/nonionic surfactant systems at 30°C. The pre-micellar environment of single C₁₆TABr catalyses the reactions whereas single sodium dodecyl sulphate (SDS) and nonionic surfactants, viz., Triton X-100, Triton X-102, Tween-20 and Tween-80 strongly inhibit the reaction rate of R—HCl. The values of rate constant in mixed micellar solutions (C₁₆TABr + Tween-20, C₁₆TABr + Tween-80) are less than the single cationic surfactant but are higher than the single nonionic surfactant; while the value of rate constant in mixed micellar solutions (SDS + Triton X-100, SDS + Triton X-102) is less than that in single anionic as well as in nonionic surfactant.

Key Words: Kinetics, Oxidation, Rosaniline hydrochloride, Potassium peroxydisulphate, Mixed micelles, Surfactant.

Mixtures of surfactants often exhibit synergism in their physico-chemical properties, thus allowing particular applications. Mixed surfactant systems have received considerable attention both in theoretical and applied studies because of their technological and commercial applications. The effect of macromolecules in micellar systems^{1,2} and the importance of surfactant/polymer mixed micelles in the oil recovery industry, pharmacy and medicine is well known. Many reports have been published in recent years dealing with solution properties of mixed surfactants containing ionic-nonionic or mixed ionic micelles^{3,4}. However, there have been a very few studies analyzing the influence of mixed surfactant systems on reaction processes^{5,6}. Often, the mixture may exhibit a superior behaviour compared to the pure surfactant components. Kinetics of hydroxamic acid in mixed micelles of binary surfactant system has been reported⁷. The influence of CTAB/poly(propylene glycol) (PPG) (m.w. = 425,1000) mixed micelles in the basic hydrolysis of crystal violet has also been studied⁸. We have earlier reported the kinetics of oxidation of malachite green, brilliant green, acid green-16 and acid green-9 dyes in micellar systems⁹. In this paper we have employed the influence of binary combination of cationic/nonionic and anionic/nonionic surfactants on oxidation of rosaniline hydrochloride by potassium peroxydisulphate.

R—HCl was purified by dissolving in dimethyl formamide and precipitating with the help of trichloroethylene¹⁰. Potassium peroxydisulphate (Ranbaxy) and surfactants (Sigma Chemicals) were used without any purification and their fresh solutions were used. The solutions were prepared in fresh doubly distilled water

throughout the experiment. The reaction progress was followed colorimetrically (EQ-650 Digital type) by using a filter of 530 nm. Under these conditions Beer's law was obeyed by the dyes which had absorption maxima in same range.

The oxidation of R—HCl (TPM) dye is of first order in $S_2O_8^{2-}$ ion. The influence of cationic ($C_{16}TABr$), anionic (SDS) and nonionic (Triton X-100, Triton X-102, Tween-20 and Tween-80) surfactants on the oxidation of R—HCl dye was studied at fixed concentration of $S_2O_8^{2-}$ ion.

The rate constant of the reaction increases with an increase in concentration of single cationic surfactants, whereas there is a decrease in anionic and nonionic surfactant with an increase in concentration. The rate constants for the oxidation of R—HCl dye in presence of combined surfactant solutions (1 : 1) are shown in Table-1 and Fig. 1.

TABLE-I
INFLUENCE OF MIXED MICELLAR SYSTEM (ANIONIC/NONIONIC) ON THE OXIDATION OF ROSANILINE HYDROCHLORIDE

[Rosaniline Hydrochloride] = 2.0×10^{-5} M, $[K_2S_2O_8] = 7.5 \times 10^{-2}$ M

Mixed system [surfactant] $\times 10^5$ M	K_{obs} (min^{-1})		
	SDS	SDS + TX-100 (1 : 1)	SDS + TX-102 (1 : 1)
0.00	0.0515	0.0515	0.0515
2.00	0.0489	0.0381	0.0325
4.00	0.0460	0.0349	0.0278
6.00	0.0422	0.0315	0.0241
8.00	0.0374	0.0275	0.0223
10.00	0.0345	0.0250	0.0215

The rate constant for the dye in [anionic/nonionic] decreases with an increase in concentration. It may be pointed out that the values of rate constants are lower than the single anionic surfactants. The mixed micelle formed by anionic and nonionic surfactants behaves as a ionic micelle having a negative charge. The inhibition reaction in the mixed anionic/nonionic micelles may be explained in terms of proximity effect of approaching $S_2O_8^{2-}$ ion in mixed micelles. The dye gets more incorporated in the mixed micelle and $S_2O_8^{2-}$ repelled electrostatically having a similar charge on the mixed micelle. Thus separating the reactants from one another and hence the observed inhibition of the reaction rate than the individual ionic surfactants.

The values of rate constant for R—HCl dye in [cationic/nonionic] systems are less than the single cationic surfactant. The rate constant increases with the concentration in the single pure cationic surfactant. However, in mixed micelle environment the rate constant decreases with the increase in the concentration of mixed surfactant cationic/nonionic (1 : 1). The values of rate constants are higher than the single nonionic surfactant solutions. In the mixed micelle the decrease in the rate may be due to the greater solubilization of the dye in the core of the mixed micelle, thereby separating the dye from the $S_2O_8^{2-}$ ion. Hence an inhibition in the rate has been observed.

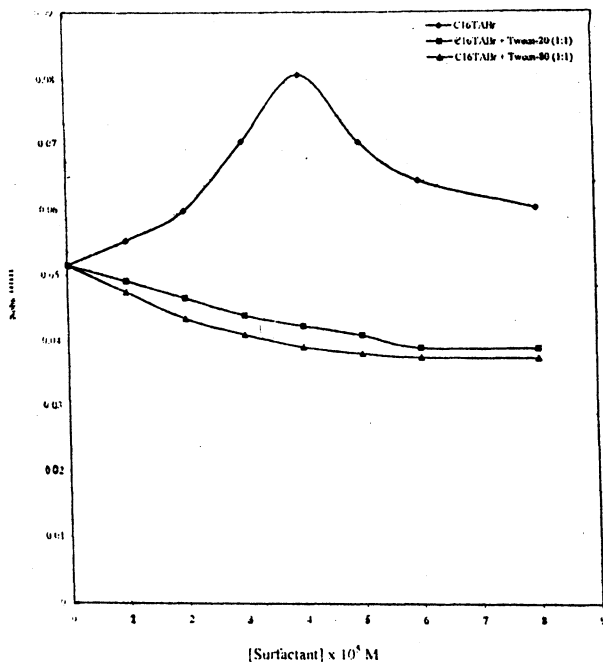


Fig. 1. Influence of mixed micellar system (cationic/non-ionic) on the oxidation of rosaniline hydrochloride. [rosaniline hydrochloride] = 2.0×10^{-5} , $[K_2S_2O_8] = 0.0.75$ M.

REFERENCES

1. G. Karlstrom, A. Carlsson and B. Lindman, *J. Phys. Chem.*, **94**, 5005 (1990).
2. E.D. Goddard, *Colloids Surf.*, **19**, 255 (1986).
3. S. De, V.K. Aswal, P.S. Goyal and S. Bhattacharya, *J. Phys. Chem.*, **101**, 5639 (1997).
4. A. Shiloach and D. Blankshtein, *Langmuir*, **14**, 161B (1998).
5. Z. Xiancheng, L. Qilin, H. Yingke, W. Aian, Q. Ziming, L.G. Anzuo and H. Qizhong, *J. Dis. Sci. Tech.*, **17**, 101 (1996).
6. D.M. Davies and S.J. Foggo, *J. Chem. Soc., Perkin Trans.*, **2**, 247 (1998).
7. K. Ghosh and A. Pandey, *J. Indian Chem. Soc.*, **76**, 191 (1999).
8. M.L. Sierra and E. Rodenas, *J. Phys. Chem.*, **97**, 12387 (1993).
9. H.M. Joshi and T.N. Nagar, *Research J. Chem. Environ.* (communicated).
10. K. Karmarkar, P.P. Kulkarni and M.P. Savasani, *Ind. J. Tex. Res.*, **13**, 45 (1988).

(Received: 16 January 2002; Accepted: 10 June 2002)

AJC-2761