

Micellar Effect on the Reaction of Acid Violet-49 with Hydroxide Ion: Influence of Salts and Organic Solvents

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Cationic micelles of cetyl trimethylammonium bromide (CTAB) are known to increase the rate of reaction of triphenylmethyl carbonium ions with the hydroxide ion whereas the anionic micelles of sodium dodecyl sulphate (SDS) inhibit this rate. The addition of monohydric alcohols, *viz.*, methanol, ethanol, *n*-propanol, *n*-butanol and solvents like acetone decrease the cationic micellar catalysed rate of carbinol formation while on the other hand increase the anionic micellar inhibited rate. The influence of electrolytes in the presence of CTAB has also been analysed.

INTRODUCTION

Organic reactions in aqueous solutions of surfactants undergo either rate acceleration or inhibition and this behaviour has been attributed to electrostatic and hydrophobic interactions between the substrate and surfactant aggregates. Some investigations on the influence of organic solvents on the micelle catalysed inhibited reactions have been reported.¹⁻⁴ The solvent assisted dyeing has been developed for the industry, and several fundamental discussions and mechanisms of solvent dyeing have been reported⁵. This paper describes the effect of various organic solvents and the electrolytes on the kinetic reaction of alkaline fading behaviour of acid violet-49 in presence of ionic surfactants.

EXPERIMENTAL

Acid Violet-49 was obtained from Colourtex India Ltd. and purified by dissolving in dimethylformamide and then precipitating with the help of trichloroethylene⁶. The cationic surfactant cetyl trimethylammonium bromide (CTAB) (BDH) and anionic surfactant sodium dodecyl sulphate (SDS) (BDH) were purified before use. Solvents like methanol, ethanol, *n*-propanol, *n*-butanol and acetone were BDH analytical grade chemicals and were purified prior to use by standard procedures⁷. All the inorganic salts, *viz.*, KCl, KBr, KNO₃, K₂SO₄, NaCl and BaCl₂ were used of E. Merck and used without further purification.

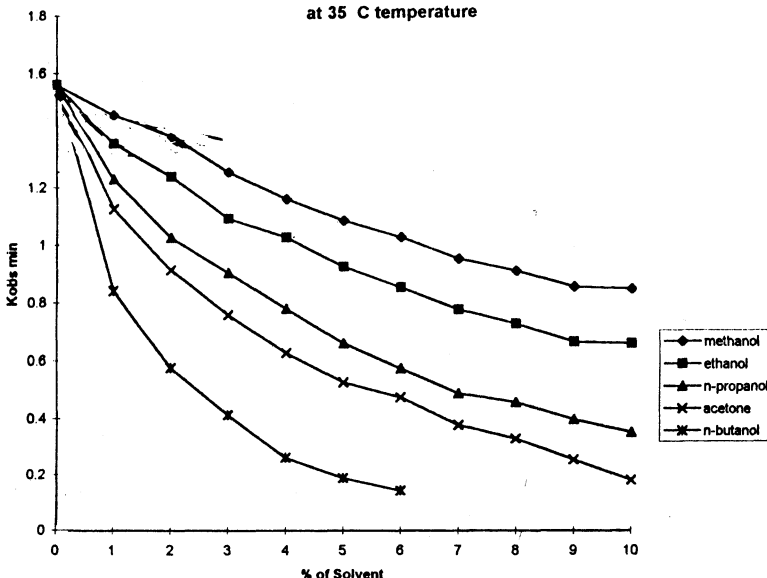
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RESULTS AND DISCUSSION

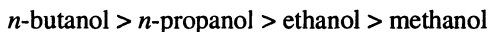
Effect of solvents on the C₁₄ TAB catalysed alkaline fading reaction of triphenylmethyl carbonium ions

The data for the effect of various solvents on the alkaline fading reaction of Acid Violet-49 with hydroxide ion in micellar media of C₁₄ TAB at fixed concentration [0.0025 M] are shown in Fig. 1.

Fig. 1 : Effect of organic solvents on C₁₄ TAB (0.0025 M) catalysed reaction of Acid Violet - 49 (3 x 10⁻⁵ M) with hydroxide ion (1.5 x 10⁻³ M) at 35 °C temperature



It may be seen from these data that the addition of *n*-butanol, acetone, *n*-propanol, ethanol and methanol to the reaction system reduces the overall catalysis by C₁₄ TAB. It may be noted that *n*-butanol is more effective than methanol in reducing the overall catalysis of these reactions by C₁₄ TAB. The alcohol with longer alkyl chain is more effective as shown in Fig. 1. The order of effectiveness of alcohols is as follows.



Similar effect of various solvents on the alkaline fading reaction of carbonium ions was investigated at fixed [CTAB] and in each case the rate constant decreases with increase in percentage concentration of the solvents.^{8,9}

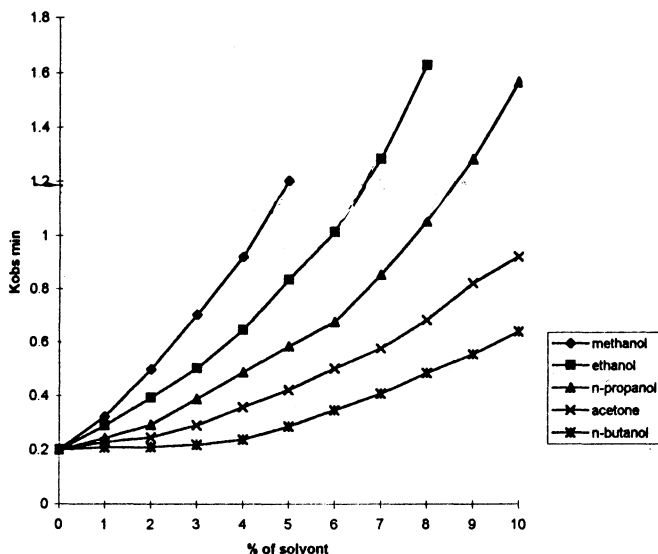
Effect of solvents on the SDS inhibited alkaline fading reaction of triphenylmethyl carbonium ions

The influence of organic solvents, *viz.*, methanol, ethanol, *n*-propanol, acetone, *n*-butanol, on the SDS inhibition reaction of Acid Violet-49 was investigated at fixed concentration of [surfactant], [reactant] and the [substrates] while varying the solvent composition in the reaction system. The studies were performed in

each case at fixed [SDS] which corresponded to saturation concentration (0.005 M) of the surfactant in the rate versus [surfactant] profile for these reactions.^{8,9}

The results for the alkaline fading reaction of Acid Violet-49 are graphically presented in Fig. (2). It may be observed from these kinetic data that the addition of solvents to micelle affected reaction markedly diminishes the overall inhibi-

Fig.2 Effect of organic solvents on SDS (0.005 M) inhibited reaction of Acid Violet - 49 (3.0×10^{-5} M) with hydroxide ion (0.1 M) at 35 C temperature.



tion caused due to the presence of SDS. The effectiveness of an alcohol to reduce the extent of overall inhibition is found to increase with the increasing carbon chain length of alcohol molecules.

methanol < ethanol < n-propanol < acetone < n-butanol.

Several factors might be visualized which could explain the observed effects of solvents on chemical reactions in micellar media. Bruice and Cordes¹⁰ have interpreted the effects of alcohol on the reaction of ethyl *ortho*-benzoate with H⁺ ion in the presence of SDS by considering the following factors:

1. replacement of the substrate by solvent molecules from the micellar phase.
2. changes in the aggregation properties of the surfactant, and
3. modification in the electrostatic stabilization of the transition state of the reaction in the presence of solvents.

It may be pointed out that the ideas concerning the solvent effects on chemical reactivity have undergone drastic amendments since the classical concept of solvent as a continuous dielectric medium.¹¹⁻¹³ Evidences indicate that the selective solvation of the reactants and the motion of solvent species constitutes an important and integral part of the motion of reacting species along the reaction coordinates at the transition state. This is particularly true for ionic reactions as a result of the accompanying motion of solvent molecules.

Influence of electrolytes on the C₁₄TAB catalysed fading of Acid Violet-49 by Sodium Hydroxide at 30°C

The plots of rate constant versus concentration of electrolyte, (*viz.*, KCl, KBr, KNO₃ and K₂SO₄) are shown in Fig. (3) at fixed concentration of C₁₄TAB (0.0025 M). It is found that the rate constant decreases with increase in salt concentration of the anion.

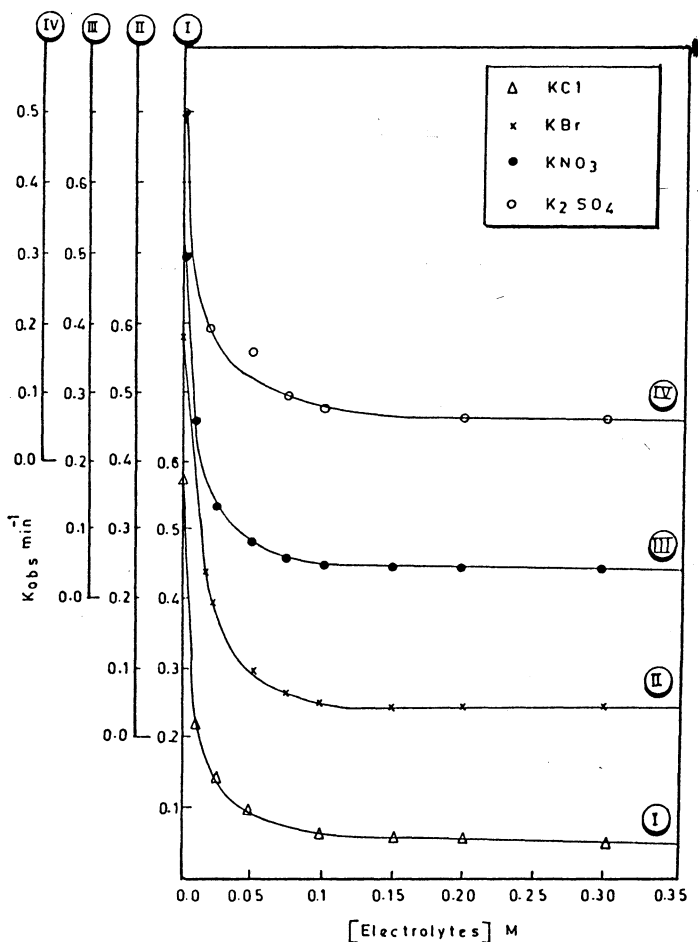


FIG. 3

INFLUENCE OF ELECTROLYTES ON C₁₄TAB CATALYSED ALKALINE FADING OF AV AT 30° C TEMPERATURES.

$$[AV] = 3 \times 10^{-5} \text{ M}, [NaOH] = 1 \times 10^{-3} \text{ M}, [C_{14}TAB] = 2.5 \times 10^{-3} \text{ M}.$$

For reactions between a molecule and an anion catalysed by a cationic micelle, electrolyte inhibition is relatively independent of the nature of added cation but increases strikingly with decreasing charge density of the added anion, whereas for cation-molecule reactions catalysed by anionic micelles. It is found that the rate retardation is maximum at an $[\text{anion}] = 0.2 \text{ M}$ and the order of retardation with respect to anion is $\text{NO}_3^- > \text{Br}^- > \text{SO}_4^{2-}$. This behaviour can be rationalised by assuming a competition between the reactant and the anion for the bonding site in the micelle. This phenomenon is explicable in terms of the greater affinity of the low charge density anions for the micelle.¹⁴

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REFERENCES

1. A.K. Reddy and S.S. Katiyar, *Tetrahedron*, **37**, 585 (1981).
2. A. Bunton and L. Robinson, *J. Am. Chem. Soc.*, **90**, 5979 (1968).
3. J. Blandamer and D.J. Reid, *J. Chem. Soc. Faraday Trans.*, **71**, 2156 (1975).
4. B. Dunlop and E.H. Cordes, *J. Phys. Chem.*, **73**, 361 (1969).
5. Peters and C.B. Stevens, *J. Soc. Dyers Colourists*, **72**, 241 (1956); M. Karholm and J. Lindberg, *Text. Res. J.*, **26**, 258 (1956).
6. K. Karmakar, P.P. Kulkarni and M.P. Savasani, *Indian J. Tex. Res.*, **13**, 45 (1988).
7. I. Vogel, *A Text Book of Practical Organic Chemistry*, Longmans, London (1959).
8. H. Patel and S.S. Katiyar, *Nat. Sci., Acad. Lett.*, **1**, 143 (1978).
9. A. Bunton, C.H. Paik and H.R. Romsted, *J. Am. Chem. Soc.*, **100**, 5420 (1978).
10. B. Dunlop, and E.H. Cordes, *J. Phys. Chem.*, **73**, 361 (1969).
11. J. Blandmer, in: V. Gold and D. Bethell (Eds.), *Advances in Physical Organic Chemistry*, Vol. 14 E.J. Fendler (Eds.), Acad. Press, New York (1977).
12. D. Ritchie, *J. Am. Chem. Soc.*, **97**, 1170 (1975).
13. S. Katiyar, *Trans. Faraday Soc.*, **66**, 2305 (1970).
14. K. Reddy and S.S. Katiyar, in: L. Mittal and *Solution Behaviour of Surfactants*, Plenum Press, New York, Vol. 2, p.1017 (1982).

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