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Effect of Cetyltrimethylammonium Bromide and Sodium Dodecyl Sulphate on Oxidation of Indigo Carmine with Potassium Peroxy Diphosphate: A Kinetic and Mechanistic Study

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The oxidative kinetic study of Indigo carmine (IC) with potassium peroxydiphosphate (PDP) in absence and presence of cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulphate (SDS) micelles was studied in an aqueous sulphuric acid medium by maintaining the ionic strength at 3.0 mol dm^{-3} using sodium sulphate. The pseudo-zero-order constant was determined from the linear plots of absorbance *versus* time under the conditions [IC] < [PDP]. The reaction obeys zero-order kinetics with respect to varying [IC], first order kinetics with respect to varying [H$^+$] and [PDP] in the absence and in presence of micelles. The reaction rate was accelerated with varying [CTAB] and [SDS] and reached a limiting value. The [surfactant] rate profile has limited nature since the reaction is unimolecular on the micelle surface. The binding constant of peroxy diphosphate was also determined with CTAB and SDS micelles by applying Berezin equation for the kinetic pattern.

Keywords: Indigo carmine, Potassium per diphosphate, Cetyltrimethylammonium bromide, Sodium dodecyl sulphate.

INTRODUCTION

Dyes are extensively used in paper, food, plastic, printing, textile, pharmaceutical industries, *etc*. These dyes in effluent water discharged from industries contaminated the natural streams and other water bodies [1-3]. The products of these dyes are carcinogenic, mutagenic and allergenic [4-7]. The dyes in water bodies have severe hazardous impacts making the water bodies unfit for human and aquatic life [8].

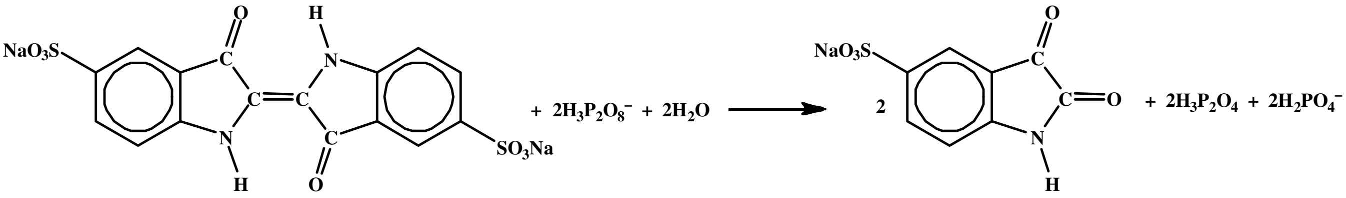
Indigo carmine, an anionic dye, contains cross conjugation or hydrogen chromophore attached to the double-bonded carbon atoms, which exhibit an intense blue colour in the aqueous solution [9,10]. However, this dye is toxic and shows adverse effects on eyes, skin, reproductive, developmental and neuronal systems [11,12].

Researchers investigated several analytical methods to remove Indigo carmine dye from the water effluents [13,14]. Moreover, the kinetics oxidation of Indigo carmine dye can be done by using oxidants like potassium peroxydisulphate [15], sodium metaperiodate [16], *N*-bromosuccinimide [17] and potassium bromate [18]. In present investigation, the authors have shown interest to investigate the kinetics and mechanism of oxidation of Indigo carmine with potassium peroxydiphosphate in aqueous and micellar media.

EXPERIMENTAL

The stock solutions of Indigo carmine (IC), sulphuric acid and sodium sulphate (E-Merck India Pvt. Ltd.) were prepared in triple distilled water and standardized according to the literature [19,20]. The stock solutions of sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) were prepared without purification from their standard samples and their CMC was determined by surface tension method. A stock solution of potassium peroxydiphosphate (PDP, 1.0 × 10^{-1} mol dm^{-3}) was prepared and standardized cerimetrically using *N*-phenyl anthranilic as indicator [21].

General procedure: The oxidation of Indigo carmine with potassium peroxydiphosphate was analyzed using Systronics 106 visible spectrophotometer. The reaction was followed by fixing the wavelength at 620 nm in aqueous and SDS micellar media and at 570 nm in cationic CTAB micellar media [22].



Scheme-I

All the kinetic investigations were performed under pseudo zero order conditions [PDP] >> [IC]. The pseudo rate constants were determined from the linear plots drawn between absorbance *versus* time.

Detection method: The stoichiometric reaction was determined by mole ratio method [16], which is reported as 1:2 (**Scheme-I**). The colourless solution formed after decolourization of Indigo carmine is made alkaline and 4-nitro phenyl hydrazine, magnesium nitrate was added. The formation of blue colour precipitate confirmed the product as isatin-5-monosulphonic acid [23].

RESULTS AND DISCUSSION

The reaction exhibits zero order kinetics with varying [IC] in aqueous and micellar media. Plots drawn between absorbance *versus* time are linear under the condition [PDP] >> [IC] (Table-1). The reaction shows first order kinetics with varying [H^+] in aqueous and micellar media (Table-2), since the plot drawn between of k *versus* [H^+] is a straight line passing through origin (Fig. 1).

TABLE-1
EFFECT OF [INDIGO CARMINE] ON RATE OF REACTION

[IC] × 10^5 (mol dm^{-3})	[H^+] (mol dm^{-3})	[PDP] × 10^2 (mol dm^{-3})	[SDS] × 10^3 (mol dm^{-3})	[CTAB] × 10^3 (mol dm^{-3})	10^3 K_0 (mol dm^{-3} min^{-1})
1.000	0.7	1.0	–	–	4.900
1.500	0.7	1.0	–	–	5.200
2.000	0.7	1.0	–	–	5.100
2.500	0.7	1.0	–	–	5.500
3.000	0.7	1.0	–	–	5.200
1.000	0.7	2.0	5.0	–	5.500
1.500	0.7	2.0	5.0	–	5.700
2.000	0.7	2.0	5.0	–	6.000
2.500	0.7	2.0	5.0	–	6.900
3.000	0.7	2.0	5.0	–	6.200
0.827	0.4	1.0	–	1.0	0.835
1.654	0.4	1.0	–	1.0	0.898
2.480	0.4	1.0	–	1.0	0.855
3.300	0.4	1.0	–	1.0	0.837
4.130	0.4	1.0	–	1.0	0.844

TABLE-2
EFFECT OF [H^+] ION ON REACTION RATE

[IC] × 10^5 (mol dm^{-3})	[H^+] (mol dm^{-3})	[PDP] × 10^2 (mol dm^{-3})	[SDS] × 10^3 (mol dm^{-3})	[CTAB] × 10^3 (mol dm^{-3})	10^3 K_0 (mol dm^{-3} min^{-1})
2.0	0.36	1.0	–	–	2.30
2.0	0.42	1.0	–	–	3.40
2.0	0.48	1.0	–	–	4.30
2.0	0.60	1.0	–	–	5.05
2.0	0.66	1.0	–	–	5.16
2.0	0.72	1.0	–	–	6.75
2.0	0.96	1.0	–	–	7.28
2.0	1.08	1.0	–	–	8.26
1.0	0.30	2.0	5.0	–	1.50
1.0	0.60	2.0	5.0	–	2.50
1.0	0.90	2.0	5.0	–	3.20
1.0	1.20	2.0	5.0	–	6.00
1.0	1.50	2.0	5.0	–	7.20
2.0	0.03	1.0	–	1.0	3.12
2.0	0.06	1.0	–	1.0	9.09
2.0	0.12	1.0	–	1.0	12.4
2.0	0.18	1.0	–	1.0	20.0
2.0	0.24	1.0	–	1.0	24.4
2.0	0.30	1.0	–	1.0	29.8

The reaction also followed first order kinetics with varying [PDP] (Table-3). Plot drawn between k *vs*. [PDP] is a straight line passing through origin (Fig. 2).

The reaction rate was accelerated with varying [SDS] and [CTAB] and reached a limiting value (Table-4, Fig. 3).

The following dissociation equilibria of potassium peroxydiphosphate (PDP) was considered to recognize the nature of the reactive species in the present reaction.

$$H_4P_2O_8 \xrightleftharpoons{K_1} H_3P_2O_8^- + H^+ \qquad (1)$$

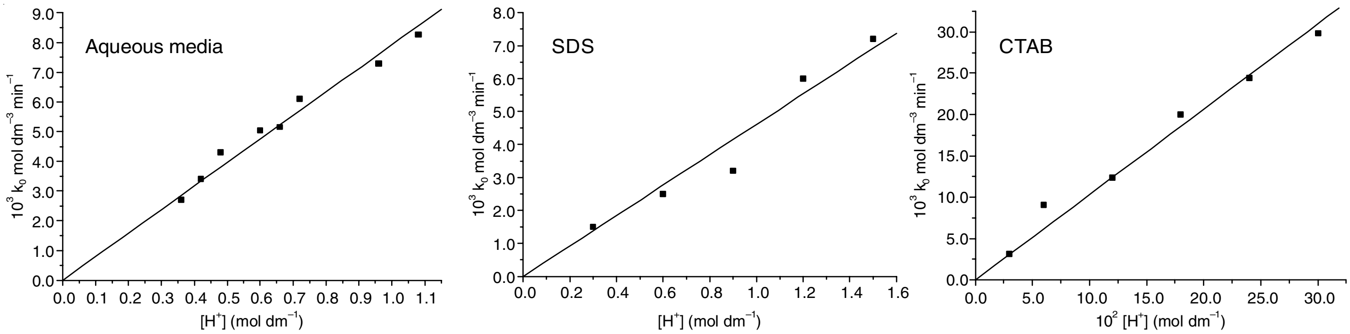


Fig. 1. Effect of hydrogen ion concentration on rate

TABLE-3
EFFECT OF [PDP] ON REACTION RATE

[IC] × 10^5 (mol dm^{-3})	[H^+] (mol dm^{-3})	[PDP] × 10^2 (mol dm^{-3})	[SDS] × 10^3 (mol dm^{-3})	[CTAB] × 10^3 (mol dm^{-3})	10^3 K_0 (mol dm^{-3} min^{-1})
2.0	0.72	0.80	–	–	1.96
2.0	0.72	1.20	–	–	2.25
2.0	0.72	1.60	–	–	2.53
2.0	0.72	2.00	–	–	5.27
2.0	0.72	3.00	–	–	6.82
2.0	0.72	3.50	–	–	7.81
2.0	0.72	4.00	–	–	9.25
2.0	0.72	5.00	–	–	12.3
3.0	0.72	0.50	5.0	–	1.42
3.0	0.72	0.80	5.0	–	2.75
3.0	0.72	1.00	5.0	–	3.50
3.0	0.72	1.50	5.0	–	5.30
3.0	0.72	2.00	5.0	–	6.40
3.0	0.72	0.10	–	0.94	15.0
3.0	0.72	0.25	–	0.94	27.0
3.0	0.72	0.50	–	0.94	41.5
3.0	0.72	0.75	–	0.94	64.7
3.0	0.72	1.00	–	0.94	79.9
3.0	0.72	1.20	–	0.94	88.0

$$H_3P_2O_8^- \xrightleftharpoons{K_2} H_2P_2O_8^{2-} + H^+ \qquad (2)$$

$$H_2P_2O_8^{2-} \xrightleftharpoons{K_3} HP_2O_8^{3-} + H^+ \qquad (3)$$

$$HP_2O_8^{3-} \xrightleftharpoons{K_4} P_2O_8^{4-} + H^+ \qquad (4)$$

TABLE-4
EFFECT OF [SURFACTANT] ON REACTION RATE

[IC] × 10^5 (mol dm^{-3})	[H^+] (mol dm^{-3})	[PDP] × 10^2 (mol dm^{-3})	[SDS] × 10^3 (mol dm^{-3})	[CTAB] × 10^3 (mol dm^{-3})	10^3 K_0 (mol dm^{-3} min^{-1})
2.0	0.48	1.0	0.0	–	0.202
2.0	0.48	1.0	1.0	–	0.385
2.0	0.48	1.0	2.0	–	0.538
2.0	0.48	1.0	3.0	–	0.630
2.0	0.48	1.0	4.0	–	0.655
2.0	0.48	1.0	6.0	–	0.884
2.0	0.48	1.0	8.0	–	0.993
2.0	0.48	1.0	10.0	–	0.971
2.0	0.48	1.0	15.0	–	1.072
2.0	0.48	1.0	20.0	–	1.020
2.0	0.48	1.0	25.0	–	1.050
2.0	0.72	1.0	–	0.0	0.430
2.0	0.72	1.0	–	0.1	2.070
2.0	0.72	1.0	–	0.3	2.150
2.0	0.72	1.0	–	0.5	4.110
2.0	0.72	1.0	–	0.7	5.130
2.0	0.72	1.0	–	0.9	6.720
2.0	0.72	1.0	–	1.1	9.210
2.0	0.72	1.0	–	1.5	10.77
2.0	0.72	1.0	–	2.0	14.87
2.0	0.72	1.0	–	3.0	16.40
2.0	0.72	1.0	–	4.0	16.90
2.0	0.72	1.0	–	5.0	17.00

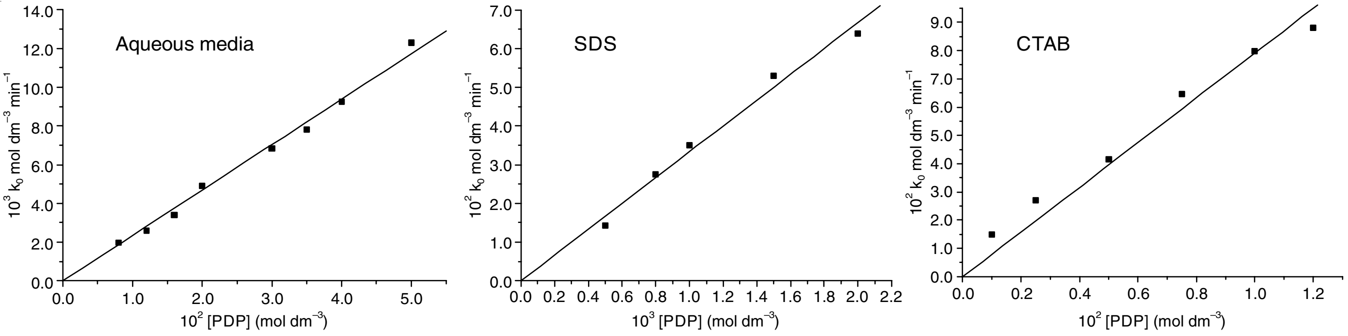


Fig. 2. Effect of [PDP] on oxidation of Indigo carmine

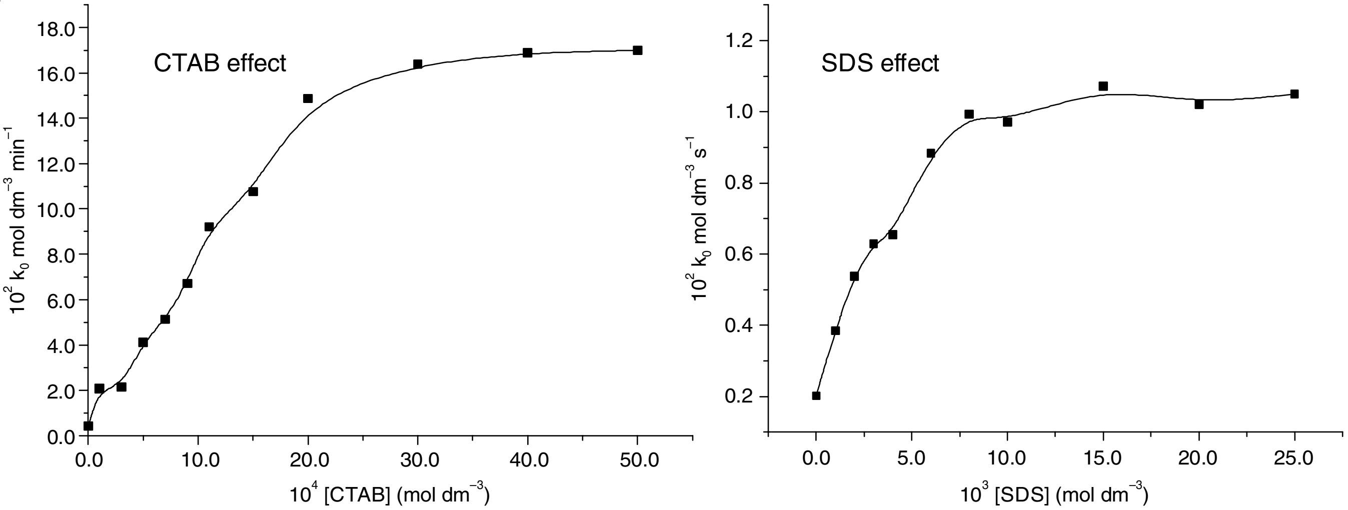


Fig. 3. Effect of [surfactant] on reaction kinetics

It has been reported in the literature [21,24-26] that the values of K_1, K_2, K_3, K_4 were as follows: $K_1 > 40$, $K_2 = 40$, $K_3 = 6.6 \times 10^{-6}$ M, $K_4 = 2.1 \times 10^{-8}$ M at room temperature.

Since the kinetic investigations have been carried out in the range of $[H^+] = 0.3$ to 1.0 mol dm^{-3}, the third and fourth dissociation equilibria need not be considered. Assuming K_1 is considerably higher than 40 M, one can conclude that PDP in aqueous acid solution is mainly in the form of $H_2P_2O_8^{2-}$ and hence the acid catalysis can be analyzed using the equilibrium: $1/K_2$

$$H_2P_2O_8^{2-} + H^+ \xrightleftharpoons{1/K_2} H_3P_2O_8^- \qquad (5)$$

Using the mass balance equation:

$$[PDP]_t = [H_3P_2O_8^-] + [H_2P_2O_8^{2-}] \qquad (6)$$

$$K_2' = \frac{[H_3P_2O_8^-]}{[H_2P_2O_8^{2-}][H^+]} \qquad (7)$$

where $K_2' = 1/K_2$.

$$[H_2P_2O_8^{2-}] = \frac{[H_3P_2O_8^-]}{K_2'[H^+]} \qquad (8)$$

$$[PDP]_t = [H_3P_2O_8^-] + \frac{[H_3P_2O_8^-]}{K_2'[H^+]} \qquad (9)$$

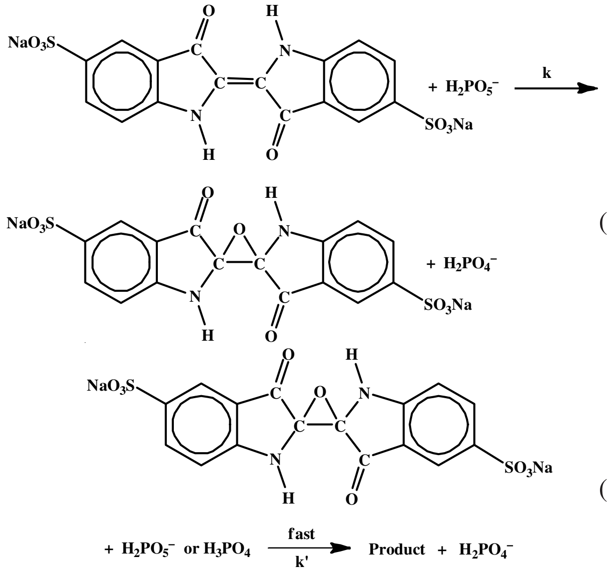
$$[PDP]_t = \frac{[H_3P_2O_8^-](K_2'[H^+]+1)}{K_2'[H^+]} \qquad (10)$$

$$[H_3P_2O_8^-] = \frac{K_2'[H^+][PDP]_t}{1+K_2'[H^+]} \qquad (11)$$

Between $[H_2P_2O_8^{2-}]$ and $[H_3P_2O_8^-]$, the former being more highly protonated can be considered to be the more active oxidizing species.

$$H_2P_2O_5^{2-} + H^+ \xrightleftharpoons[k]{K_2^1} H_3P_2O_8^- \qquad (12)$$

$$H_3P_2O_8^- + H_2O \longrightarrow H_2PO_5^- + H_3PO_4 \qquad (13)$$



(14)

(15)

Since, zero order kinetics has been observed with respect to Indigo carmine, the magnitude of k_2 must be far higher than k_1 and the oxidation step involving Indigo carmine must be fast and not rate determining.

Therefore, decomposition of $H_3P_2O_8^-$ to peroxymonophosphate ion ($H_2PO_5^-$) and H_3PO_4 should be slow and rate determining. The rate law for the proposed mechanism can be written as:

$$-d[IC]/dt = k_1 [H_3P_2O_8^-] \qquad (16)$$

$$= \frac{k_1 K_2'[PDP]_t[H^+]}{1+K_2'[H^+]} \qquad (17)$$

and

$$k_0 = \frac{k_1 K_2'[H^+]}{1+K_2'[H^+]} \qquad (18)$$

Zero-order kinetics observed for Indigo carmine conforms to this expression. The value of $K_2 = 40$ M or $K_2' = 1/40$ M^{-1}. The reaction is also first order in $[H^+]$. In the range of $[H^+]$ employed, K_2' is far less than 1and hence can be neglected. Then the rate law assumes the form:

$$-\frac{d[IC]}{dt} = k_1 K_2'[PDP]_t[H^+] \qquad (19)$$

If the rate determining step involves $H_3P_2O_8^{2-}$, the plot of k_0 *versus* $[H^+]$ would be not have passed through origin. The assumption that k_1 is very much more significant than k_2 and assumed mechanism involving the decomposition of $H_3P_2O_8^-$ to permonophosphate ion ($H_3PO_5^-$) as the sole rate determining process will be valid, if the rate constants of the reaction are in the same order as that of rate of aqueous decomposition of PDP in aqueous acidic solution.

The dependence of H^+ is same in both these reactions [28], substantiated by the reported kinetic study of latter reaction carried out by Santappa *et al.* [27-29]. The aqueous decomposition of PDP also obeys the first order kinetics in $[H^+]$. The specific rate constant of the reaction calculated from their data is 0.3×10^{-4} M^{-1} S^{-1}, which is in the same order as that observed in the present reaction (0.5×10^{-4} M^{-1} S^{-1}).

Effect of micelles: The reaction kinetics has been investigated in the presence of sodium dodecyl sulphate and cetyltrimethylammonium bromide at different concentrations of these surfactants to understand the nature and kinetic features of micellar effects. Under the experimental conditions, PDP does not oxidize either of these surfactants with detectable rate. The reaction obeys first order kinetics in PDP and H^+ ion and zero order kinetics in Indigo carmine in the presence of either of the surfactants.

Effect of CTAB: CTAB being a positive micelle can be expected to bind PDP more strongly. So in Indigo carmine, due to ionization of the sulphonic acid group is also bound CTAB micelles. The significant acceleration of the reaction in CTAB medium compared to that in the presence of SDS, which gives a negatively charged micellar pseudo phase. The binding of Indigo carmine by CTAB is not reflected in the kinetics because of the zero order behaviour with respect to Indigo carmine (*i.e.* independence of rate on bound or unbound Indigo carmine).

The rate law of the reaction is:

$$k_0 = \text{Rate} = k\,[H^+][PDP] \qquad (20)$$

Since zero order kinetics has been found with respect to Indigo carmine but first order behaviour with respect to H^+ ion and PDP, the reaction rate is equal to sum of rates of reactions in the aqueous and micellar pseudo phases.

Therefore,

$$k = \frac{k_0}{[H^+][PDP]} \qquad (21)$$

$$= \frac{k_2(1 - C\bar{V}) + k_m P_{PDP} P_{H^+} C\bar{V}}{(1 + K_{PDP}C)(1 + K_{H^+}C)} \qquad (22)$$

But $K_{PDP} = P_{PDP}\,\bar{V}$, $K_{H^+} = P_{H^+}\,\bar{V}$

Therefore

$$k = \frac{k_2(1 - C\bar{V}) + \overline{k_m} K_{PDP} K_{H^+} C}{(1 + K_{PDP}C)(1 + K_{H^+}C)} \qquad (23)$$

where

$$\bar{k}_M = \frac{k_M}{\bar{V}} \qquad (24)$$

But monopositive and most highly hydrophilic H^+ ion can be expected to be associated with low values of K_{H^+} and hence it is assumed that $(1 + K_{H^+}C) \cong 1$ in the range of values of C employed.

Therefore,

$$k = \frac{k_2(1 - C\bar{V}) + \overline{k_m} \cdot K_{PDP} K_{H^+} C}{1 + K_{PDP}C} \qquad (25)$$

The plot of k *versus* C is approaching limiting values of k at higher concentration leading to a plateau as required by eqn. 25:

If eqn. 25 involves, then these assumptions holds:

$$\frac{1}{k} = \frac{1}{\overline{k_m} K_{PDP} K_{H^+} C} + \frac{K_{PDP}C}{\overline{k_m} \cdot K_{PDP} K_{H^+} C} \qquad (26)$$

$$\frac{1}{k} = \frac{1}{\overline{k_m} K_{PDP} K_{H^+} C} + \frac{1}{\overline{k_m} \cdot K_{H^+}} \qquad (27)$$

Then a plot of 1/k *versus* 1/C should be linear with intercept = 1/ $\bar{k}_M K_{H^+}$ and slope = 1/ $\bar{k}_M K_{H^+} K_{PDP}$.

Therefore,

$$\frac{\text{Intercept}}{\text{Slope}} = K_{PDP}\,(\text{Binding constant of PDP with CTAB})$$

Such a linear behaviour (Fig. 4) was observed from the experimental results (Berezin kinetic model), which yield K_{PDP} = 2194.0 ± 109.7 $dm^3\ mol^{-1}$ and $\bar{k}_M K_{H^+} = 0.197\ mol\ dm^{-3}\ min^{-1}$. The K_{PDP} obtained from this plot was in good agreement with the value of 2441.7 ± 122.08 $dm^3\ mol^{-1}$ determined separately.

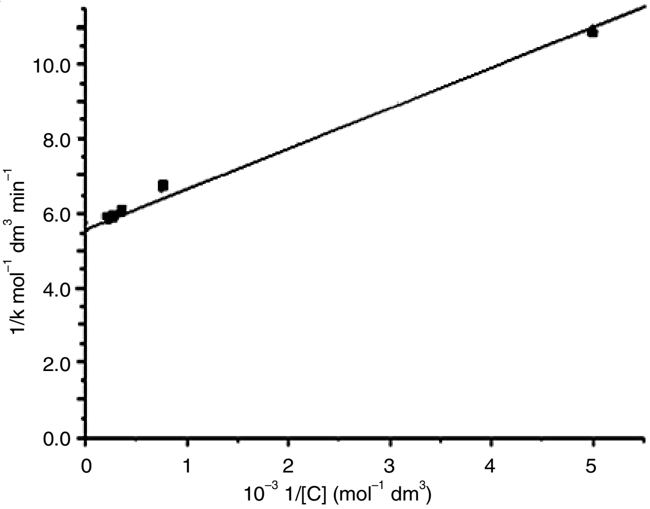


Fig. 4. CTAB effect (plot between 1/k and 1/[C])

Effect of SDS: Since the positive CTAB micelles have catalytic effect on the reaction, it is interesting to study the micellar effect in the presence of negative micelles. Contrary to the usual behaviour of the reaction involving anion in the presence of negative micelles, which is the inhibitory effect, acceleration of the reaction has been observed though the acceleration observed is less than that in the CTAB effect. The accelerating effect of SDS has also been observed on the reactions involving anionic reactants like chromium(VI) [30], potassium hexacyanoferrate (III) [31], Ag(I) catalyzed persulphate oxidation of phenylazodiphenylamine [32].

Ion-pairs are assumed to be formed between head groups of SDS, Ag^+ and these ion-pairs will, in turn, react more predominantly with oxidant ion, leading to the increase in overall rate. In the case of chromic acid oxidation of maleic acid [33], the acceleration has been attributed to binding of the neutral chromic acid followed by interaction between H^+ and $HCrO_4^-$. The oxidation of aniline by hexacyanoferrate(III) is also catalyzed by negative SDS micelles [31]. The author proposed that ion-pair formation between Na^+ and $[Fe(CN)_6]^{3-}$ appears to be a factor in determining the rate, which increase with [SDS]. The free $[Na^+]$ increases attracting $[Fe(CN)_6]^{3-}$ ions towards stern layer increasing its effective concentration, which then reacts with aniline present in the stern layer [31].

The binding constant of PDP with SDS was determined as procedure similar to CTAB using eqn. 28:

$$\frac{1}{k} = \frac{1}{\overline{k_m} \cdot K_{PDP} K_{H^+} C} + \frac{1}{\overline{k_m} \cdot K_{H^+}} \qquad (28)$$

Then a plot of 1/k *versus* 1/C should be linear with intercept = 1/ $\bar{k}_M K_{H^+}$ and slope = 1/ $\bar{k}_M K_{H^+} K_{PDP}$

Therefore,

$$\frac{\text{Intercept}}{\text{Slope}} = K_{PDP}\,(\text{Binding constant of PDP with SDS})$$

Such a linear behaviour (Fig. 5) was observed from the experimental results, which yield K_{PDP} = 944.05 ± 47.2 $dm^3\ mol^{-1}$ and $\bar{k}_M K_{H^+} = 0.0104\ min^{-1}$. The value of K_{PDP} obtained from this plot was in good agreement with the value of 1176.0 ± 58.3 $dm^3\ mol^{-1}$ determined separately.

It is considered that repulsion between $H_2P_2O_8^{2-}$ and the negative charge on the micelle must be overcome if its decomposition to permonophosphoric acid is to take place in

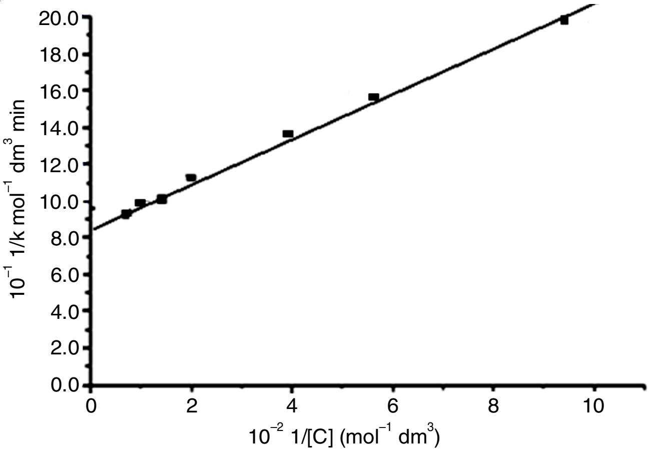


Fig. 5. SDS effect (plot between 1/k and 1/[C])

the micellar pseudo phase. It is accomplished by the H$^+$ ions, which can be expected to be present at higher concentration at the micellar interface and forming ion-pairs with $H_3P_2O_8^{2-}$ in that region which can thus decompose to form permonophosphoric acid ion. The latter oxidizes the Indigo carmine in a fast step. This proposed ion-pair formation can be justified by the different micro-dielectric properties of the water present in the micelles using NMR and charge transfer studies [34] definitely point to the lower dielectric constant of water in the micellar region. It can undoubtedly promote the ion-pair formation between H$^+$ and $H_2P_2O_8^{2-}$, which subsequently decomposes to permonophosphate ion. Hydrogen ion concentration at the interface increases with increase in the micellar concentration as [SDS] increased.

Determination of binding constant of PDP with SDS and CTAB: For determining binding constant values of PDP with SDS and CTAB micelles at [H$^+$] = 0.7 mol dm^{-3} and μ = 3.0 mol dm^{-3} adjusted with Na_2SO_4. The spectra of these substances have been scanned at different concentrations of SDS and CTAB above critical micellar concentration and under the condition [SDS, CTAB] < [PDP]. The A_M and A_w^0 are the absorbance in presence and absence of micelles, respectively, have been determined for various SDS and CTAB concentrations. The spectrophotometric data is reported in Tables 5 and 6, respectively. The binding constant of PDP (K_{Ox}) was determined by the following equation:

$$\frac{1}{\left(A_M - A_W^0\right)} = \frac{1}{\left(A_M^0 - A_W^0\right)} + \frac{1}{\left(A_M^0 - A_W^0\right)K_{Ox}C}$$

where, A_M and A_W^0 are the absorbance in the presence and absence of micelles respectively, A_M^0 is limiting absorbance in the presence of micelles. The binding constant was determined from the value of slope and intercept obtained from the plot of $1/(A_M - A_W^0)$ *versus* 1/C {C = ([SDS, CTAB] – CMC of SDS, CTAB)}. The binding constant of PDP with SDS and CTAB from spectrophotometric method was found to be 1176.0 ± 58.3 dm^3 mol^{-1} and 2441.7 ± 122.08 dm^3 mol^{-1}.

TABLE-5
DETERMINATION OF BINDING CONSTANT OF PDP IN PRESENCE OF SDS (SPECTROPHOTOMETRIC METHOD)
[PDP] = 1.0 × 10^{-2} mol dm^{-3}, [H$^+$] = 7.0 × 10^{-1} mol dm^{-3}, μ = 3.0 mol dm^{-3}, λ_{max} = 220 nm

10^3 [SDS] (mol dm^{-3})	Absorbance	10^3 [SDS] (mol dm^{-3})	Absorbance
0.0	0.039	5.0	0.097
2.0	0.077	6.0	0.102
3.0	0.089	8.0	0.109

TABLE-6
DETERMINATION OF BINDING CONSTANTS OF PDP IN PRESENCE OF CTAB (SPECTROPHOTOMETRIC METHOD)
[PDP] = 1.0 × 10^{-2} mol dm^{-3}, [H$^+$] = 7.0 × 10^{-1} mol dm^{-3}, μ = 3.0 mol dm^{-3}

10^3 [CTAB] (mol dm^{-3})	Absorbance	10^3 [CTAB] (mol dm^{-3})	Absorbance
0.0	0.039	5.0	0.107
1.0	0.058	7.0	0.118
2.0	0.078	9.0	0.130
3.0	0.098	–	–

Conclusion

The oxidation of Indigo carmine (IC) was investigated using potassium peroxydiphosphate (PDP) in aqueous and micellar media. The kinetics of the reaction was followed by varying [IC], [H$^+$] and [PDP]. The rate constant of the reaction was determined and found to be

$$-\frac{d[IC]}{dt} = k_1 K_2'[PDP]_t[H^+]$$

The reaction was accelerated with varying [SDS] and [CTAB] and reached a limiting value. The binding constant of PDP with CTAB and SDS was determined by following Berezin kinetic model and reported as 2194.0 ± 109.7 dm^3 mol^{-1} and 944.05 ± 47.2 dm^3 mol^{-1}.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S. Chakraborty, S. Chowdhury and P. Das Saha, *Carbohydr. Polym.*, **86**, 1533 (2011); https://doi.org/10.1016/j.carbpol.2011.06.058
2. S. Ibrahim, I. Fatimah, H.M. Ang and S. Wang, *Water Sci. Technol.*, **62**, 1177 (2010); https://doi.org/10.2166/wst.2010.388
3. M.C.D. Ngaha, L.G. Djemmoe, F. Njanja and I.T. Kenfack, *J. Encapsulation Adsorption Sci.*, **8**, 156 (2018); https://doi.org/10.4236/jeas.2018.83008
4. A.A. Jalil, S. Triwahyono, S.M. Adam, N.D. Rahim, M.A.A. Aziz, N.H.H. Hairom, N.A.M. Razali, M.A.Z. Abidin and M.K.A. Mohamadiah, *J. Hazard. Mater.*, **181**, 755 (2010); https://doi.org/10.1016/j.jhazmat.2010.05.078
5. H.A. Hamad, W.A. Sadik, M.M. Abd El-latif, A.B. Kashyout and M.Y. Feteha, *J. Environ. Sci. (China)*, **43**, 26 (2016); https://doi.org/10.1016/j.jes.2015.05.033

6. V.S. Mane and P.V. Vijay Babu, *J. Taiwan Inst. Chem. Eng.*, **44**, 81 (2013); https://doi.org/10.1016/j.jtice.2012.09.013
7. U.A. Guler, M. Ersan, E. Tuncel and F. Dügenci, *Process Saf. Environ. Prot.*, **99**, 194 (2016); https://doi.org/10.1016/j.psep.2015.11.006
8. M. Greluk and Z. Hubicki, *Chem. Eng. J.*, **170**, 184 (2011); https://doi.org/10.1016/j.cej.2011.03.052
9. A. Andreotti, I. Bonaduce, M.P. Colombini and E. Ribechini, *Rapid Commun. Mass Spectrom.*, **18**, 1213 (2004); https://doi.org/10.1002/rcm.1464
10. E.M. Saggioro, A.S. Oliveira, T. Pavesi, M. Jiménez-Tototzintle, M.I. Maldonado, F.V. Correia and J. Costa-Moreira1, *Int. J. Photoenergy*, **2015**, 656153 (2015); https://doi.org/10.1155/2015/656153
11. M.A. El Hamd, S.M. Derayea, O.H. Abdelmageed and H.F. Askal, *Int. J. Spectrosc.*, **2013**, 243059 (2013); https://doi.org/10.1155/2013/243059
12. M.A. Sanromán, M. Pazos, M.T. Ricart and C. Cameselle, *Chemosphere*, **57**, 233 (2004); https://doi.org/10.1016/j.chemosphere.2004.06.019
13. M.T. Yagub, T.K. Sen, S. Afroze and H.M. Ang, *Adv. Colloid Interface Sci.*, **209**, 172 (2014); https://doi.org/10.1016/j.cis.2014.04.002
14. H. Benaïssa and M.A. Elouchdi, *J. Hazard. Mater.*, **194**, 69 (2011); https://doi.org/10.1016/j.jhazmat.2011.07.063
15. P.S.N. Murty, K.V. Subbaiah and P.V. Subba Rao, *React. Kinet. Catal. Lett.*, **11**, 79 (1979); https://doi.org/10.1007/BF02098338
16. J.N. Edokpayi, J.F. Iyun and S.O. Idris, *Arch. Appl. Sci. Res.*, **2**, 126 (2011).
17. S.B. Jonnalagadda, R.H. Simoyi and G.K. Muthakia, *J. Chem. Soc. Perkin. Trans. II*, 1111 (1988); https://doi.org/10.1039/P29880001111
18. M.K. Chakravarthy and K. Ramakrishna, *J. Appl. Chem.*, **8**, 403 (2019).
19. G.G. Rao and N.V. Rao, *Talanta*, **8**, 539 (1961); https://doi.org/10.1016/0039-9140(61)80132-X
20. J. Mendham, R.C. Denney, J.D. Barnes and M.J.K. Thomas, Vogel's, A Text Book of Vogels Quantitative Chemical Analysis, Prentice Hall, Ed.: 6 (1988).
21. A.A. Green Sr., J.O. Edwards and P. Jones, *Inorg. Chem.*, **5**, 1858 (1966); https://doi.org/10.1021/ic50045a005
22. Hong-Yan, *Bull. Korean Chem. Soc.*, **24**, 1444 (2003); https://doi.org/10.5012/bkcs.2003.24.10.1444
23. F. Feigl, Spot tests in Organic Analysis, Elsevier Publishing Company: London, p. 540 (1966).
24. M. Andersen, S.J.O. Edwards, S.A.A. Green and S.M.D. Wiswell, *Inorg. Chim. Acta*, **3**, 655 (1969); https://doi.org/10.1016/S0020-1693(00)92571-4
25. E. Chaffee, I.I. Creaser and J.O. Edwards, *Inorg. Nucl. Chem. Lett.*, **7**, 1 (1971); https://doi.org/10.1016/0020-1650(71)80111-3
26. J.O. Edwards, R.J. Lussier and W.M. Risen Jr., *J. Phys. Chem.*, **74**, 4039 (1970); https://doi.org/10.1021/j100717a006
27. P. Maruthamuthu, K.V. Seshadri and M. Santappa, *Indian J. Chem.*, **10**, 762 (1972).
28. P. Maruthamuthu and M. Santappa, *J. Inorg. Nucl. Chem.*, **37**, 1305 (1975); https://doi.org/10.1016/0022-1902(75)80491-X
29. P. Maruthamuthui and M. Santappa, *Indian J. Chem.*, **14A**, 35 (1975).
30. S.K. Mandal, M. Das, D. Kar and A.K. Das, *Indian J. Chem.*, **40A**, 352 (2001).
31. A. Rodríguez, M.D.M. Graciani, R. Balahura and M.L. Moyá, *J. Phys. Chem.*, **100**, 16978 (1996); https://doi.org/10.1021/jp961175r
32. M. Al-Sayed Salem, A. Zaki and A.A. Ismail, *Z. Phys. Chem.*, **192S**, 87 (1995); https://doi.org/10.1524/zpch.1995.192.Part_1.087
33. M. Islam, B. Saha and A.K. Das, *J. Mol. Catal. Chem.*, **266**, 21 (2007); https://doi.org/10.1016/j.molcata.2006.10.042
34. W.V. Walter and R.G. Hayes, *Biochim. Biophys. Acta*, **249**, 528 (1971); https://doi.org/10.1016/0005-2736(71)90128-3