



Kinetics of Oxidation of Indigo Carmine by Vanadium (V) in Presence of Surfactants

Amita V. Tandel and Nilesh B. Padhiyar

Mahatma Gandhi Institute of Technical Education and Research Centre, Navsari, Eru-Aat road, Gujarat, INDIA

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Abstract

The kinetics of oxidation of Indigo carmine by V (V) has been investigated in aqueous sulphuric acid media. The reaction studied spectrophotometrically in aqueous sulphuric acid medium is first order in vanadium (V) and indigo carmine. Plots of k_{obs} versus $[H^+]$ are linear with positive intercepts on k_{obs} axes, suggesting the formation of a complex between vanadium (V) and dye. The oxidation of indigo carmine by V (V) in aqueous sulphuric acid media in the presence of cationic, anionic and non-ionic surfactants at different temperatures has been investigated. The activation and thermodynamic parameters have been calculated.

Keywords: Oxidation, indigo carmine, vanadium (V), kinetics.

Introduction

Though kinetics of oxidation of a number of organic compounds by vanadium (V) have been reported, kinetic study of oxidation of aromatic compounds by V (V) has not been made so far. A detailed kinetic study of oxidation of indigo carmine in aqueous sulphuric acid media in presence of vanadium (V) has been carried out. The influence of the added anionic and non-ionic surfactants on the reaction has also been investigated. The results enable us to understand the nature of the species involved in the reaction and their relative reactivities. Micellar systems well suited for various separation and catalytic process¹⁻³. It is reported that micelles have effects on the rate of reactions⁴⁻⁹.

Material and Methods

The entire chemicals used were of AR grade. Ammonium metavanadate (prepared in 2M H₂SO₄) and indigo carmine solutions were prepared and standardized according to the method of Gopala Rao et. al.^{10,11}. The dye solution was always prepared fresh. Surfactants solutions were prepared in double distilled water. Purities of all the chemicals were checked before the use.

Rate measurement: The course of the reaction was followed by measuring the optical density of the unreacted dye with a Shimadzu (UV-2450) UV-Visible double beam spectrophotometer at 617 λ_{max} . Under these conditions Beer's law was obeyed by the dye which has absorption maxima in this range. Kinetic model use in this study to describe the dependence of rate constant on the reaction mechanism proposed by Bruice et. al.¹² and applied by Piszkiwicz¹³.

Stoichiometry: The stoichiometry of the reaction was

determined by mixing indigo carmine in micellar environment with anionic and non-ionic surfactant, in 0.5 M H₂SO₄ with known excess of V (V), after the completion of the reaction which is indicated by the discharge of the blue colour of the dye was found to consume four moles of V (V). The formation of free radicals during the reaction was confirmed by the induced polymerization of acrylonitrile, whereas neither V (V) nor dye solution alone induced polymerization.

Results and Discussion

The reaction is found to be pseudo first order in the absence of surfactant at different temperatures as evidenced by the plot of $\log (A_t - A_\infty)$ versus time, which was linear under the condition $[V(V)] \gg [\text{Indigo carmine}]$ indicating the order in the indigo carmine to be unity (figure-1). The figure shows the effect of temperature in the absence of surfactants, an increase in temperature tended to pronouncedly increase in the oxidation of the dye. The observed pseudo first order rate constants (k_{obs}) were calculated from these plots which increase with increase in the temperature. The plot of pseudo first order rate constants (k_{obs}) versus V (V) concentrations is found to be linear and passing through the origin indicating the reaction is first order figure-2. The rate constants determined at different V (V) concentration is found to increase the rate of reaction. The plot of logarithms of $-\log (A_t - A_\infty)$ versus time, t (min) is linear under the fixed concentration of indigo carmine, fixed concentration of V (V) ion and varying the concentration of $[H^+]$ at 30°C. The plot of rate constants (k_{obs}) versus $[H^+]$ concentrations are found to be linear and passing through the origin indicating the reaction is first-order figure-3.

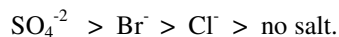
The acceleration of the reaction with increase in $[H^+]$ in the case of many V (V) oxidations has been explained by Waters et al.¹⁴ as due to the formulation of the active species $[V(OH)_3]^{+2}$

The effect of varying concentration of [V (V)] has been studied in presence of fixed [SDS] = 0.9×10^{-2} M at fixed [IC] = 6.0×10^{-5} M, at fixed [H⁺] = 0.5 M concentration at 30°C. The result shows that overall catalysis factor slowly increases with an increase in concentration of [V(V)].

A resemblance between micellar enzymatic reactions may be shown by considering the factor of overall for SDS and SDES micelle catalysed reaction.

The plot of logarithms of $-\log (A_t - A_\infty)$ versus time, t (min) is linear under the fixed concentration of V (V) ion, and varying the concentration of IC at 30°C (figure-5). Such plots at different initial concentrations of IC were found to be parallel which indicated the reaction of dye with V (V) in the micellar environment of SDS and SDES follows pseudo first order.

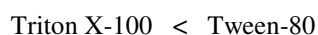
The rate constant of the SDS and SDES catalysed reaction in presence of added salts viz., KCl, NaCl, KBr and Na₂SO₄ has also been studied. Various salts strongly retarded the oxidation of anionic catalysed dyes. It is found that initially rate decreases and become almost constant with increase in the concentration of salts (figure-6). The order of retardation with respect to anion is as follows:



Hence the observed retardation in the presence of electrolytes may be due to the interaction between anion of the salt with the positively charged species [V (OH)₃HSO₄]⁺ and a less reactive species may be formed.

It may be seen that the addition of acetone and acetic acid with IC to the reaction system reduces the overall catalysis by SDS and SDES (figure-7). It may be noted that acetone is more effective than acetic acid in reducing the overall catalysis by SDS and SDES.

Non-ionic surfactants (Triton X-100, Tween-80) inhibited the rate of oxidation of indigo carmine by V (V) (figure-8). The rate decreases rapidly and then becomes almost constant with the increase in the non-ionic surfactant concentration. It has been found that non-ionic surfactants have good affinity for the dye, 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 is in the following order.



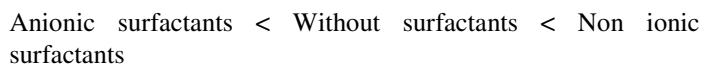
The kinetics of the reaction of varying concentration of solvent-

water mixture in presence of fixed concentration of non-ionic surfactants (Triton X-100, Tween-80) and the substrate has been studied at 30°C (figure-9). It is observed from these kinetic data that the addition of solvents to micelle-affected reaction markedly diminishes the overall inhibition caused due to presence of non-ionic surfactants. The effectiveness of solvents reduced the extent of overall inhibition is found to increase in the following order:



The participation of solvent molecules in reorganizing the structure of micellar aggregates seems to be responsible for the observed effect, which result in the reorganization of [V (OH)₃HSO₄]⁺ at reaction sites.

The effect of temperature on the oxidation reaction of IC with V (V) ion has been studied at fixed concentrations of surfactant, substrate and V (V). The reaction is found to obey Arrhenius equation. The plot of $\log k_{\text{obs}}$ versus 1/T in absence and presence of surfactants is linear (figure-10). The values of activation parameters viz., E_a[#], frequency factor Z, ΔS[#], ΔH[#], ΔG[#] are given in table: 1. The values of activation energies obtained from the slopes of Arrhenius plots for SDS and SDES catalysed reaction and for Triton X-100 and Tween-80 inhibited reactions in aqueous solutions suggest that a decrease in activation energy in presence of anionic surfactants (SDS and SDES) relative to aqueous medium is one of the factors responsible for the catalysis and a higher activation energy in presence of non-ionic (viz., Triton X-100, Tween-80) surfactants as compared to those in absence are consistent with the fact that the reaction is inhibited in presence of non-ionic surfactants. Nearly same values of ΔG[#] in absence and presence of surfactants shows that similar mechanism for oxidation is operative in aqueous and micellar media. The values of ΔS[#] in all systems are negative indicating that the reaction is occurring between ionic species. Micelles do not alter the mechanism of the reaction but only effect the reaction rate. The values of ΔS[#] and E_a[#] follow the order.



The value of frequency factor in presence and in absence of ionic and non ionic surfactants shows that the large number of collisions are required to produce the forward reaction in the presence of non ionic surfactants (viz., Triton X-100, Tween-80) where as lesser number of collision result in forward reaction in the presence of anionic surfactants (viz., SDS and SDES).

The kinetic results of enhancement of the rate constant by anionic surfactant (SDS, SDES) and retardation of the rate constant by non-ionic surfactants (viz., Triton X-100, Tween-

80) surfactants have been rationalized on the basis of a model proposed by Bruice et. al. and applied by Piskiewicz. A plot of $\log(k_w - k_{obs}) / (k_{obs} - k_m)$ versus $\log [C_D]$ is found linear with a slope (n) called the index of co-operativity (figure-11). Values of $\log [D]_{50}$ represent the concentration of detergent required for half maximal catalysis or inhibition of reaction. This demonstrates the existence of function sub-micellar aggregates involving detergent and substrate molecules of varying stoichiometries. The value of $n > 1$ indicates positive co-operativity, which implies the stimulation of additional molecule by interaction of the first molecule with the micelle. The values of binding constants (K_b which is reciprocal of K_D) for non ionic surfactants are higher than anionic surfactants. In presence of SDS and SDES catalysed effect is observed due to approachability $[V(OH)_3(HSO)_4]^+$ to the strongly bound substrate in the catalytic aggregate of opposite charge and due to the stabilization of ground state of dyes.

However, the inhibition in case of Triton X-100, Tween-80 may be due to strongly bound substrate in the catalytic aggregates of substrate and surfactant aggregate as there is no electrostatic attraction between aggregate and positive oxidant species. (table-2)

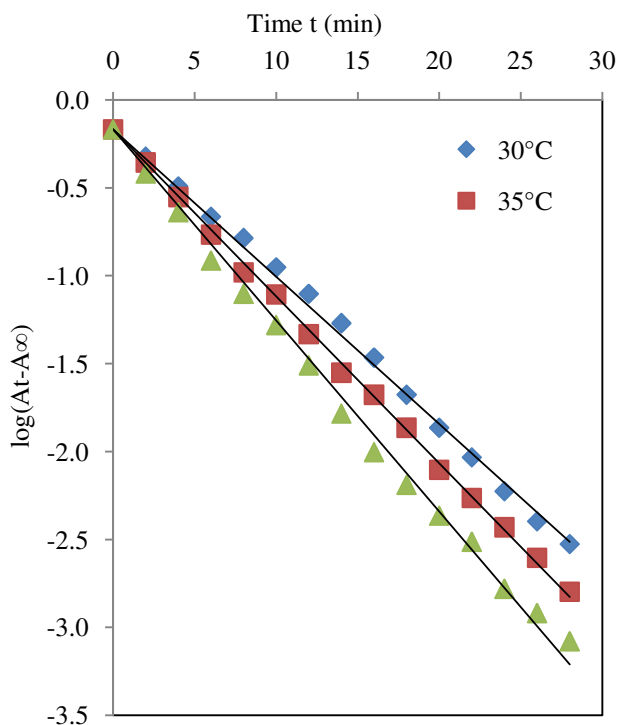


Figure-1

Plot of $\log(A_t - A_\infty)$ versus Time, t (min) for the oxidation of Indigo carmine in absence of surfactant at different temperatures. $[Indigo\ carmine] = 6.0 \times 10^{-5} M$, $[V(V)] = 2 \times 10^{-3} M$, $[H^+] = 0.5 M$

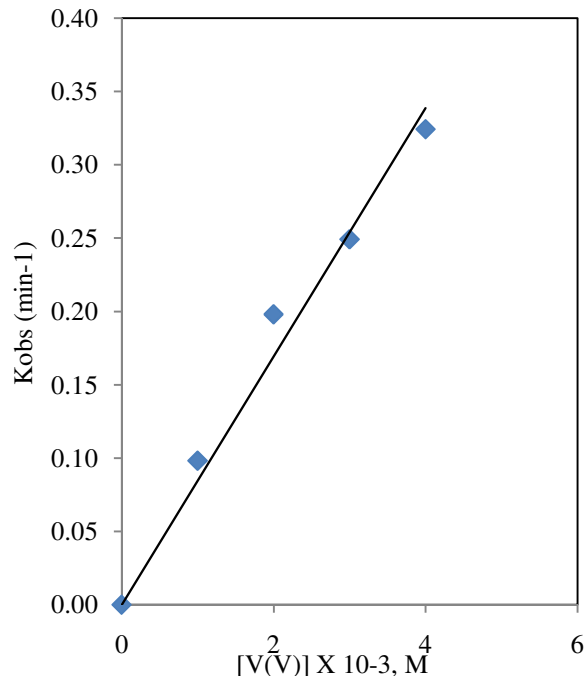


Figure-2

Pseudo first-order rate constants for the oxidation of Indigo carmine in aqueous phase at different concentration of V (V) at 30°C temperature $[Indigo\ carmine] = 6.0 \times 10^{-5} M$, $[H^+] = 0.5 M$

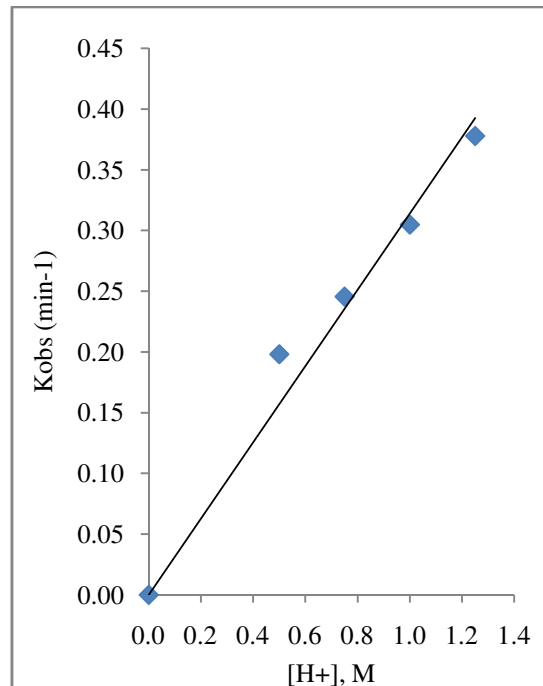


Figure-3

Pseudo first-order rate constants for the oxidation of Indigo carmine in aqueous phase at different concentration of $[H^+]$ M at 30°C temperature $[Indigo\ carmine] = 6.0 \times 10^{-5} M$, $[V(V)] = 2 \times 10^{-3} M$

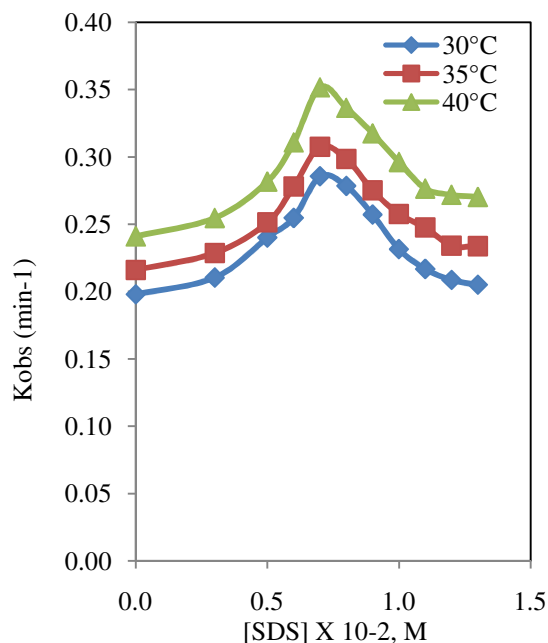


Figure-4

Influence of SDS on oxidation of Indigo carmine by V(V) at different temperatures. [Indigo carmine] = 6.0×10^{-5} M, [V(V)] = 2×10^{-3} M [H⁺] = 0.5 M

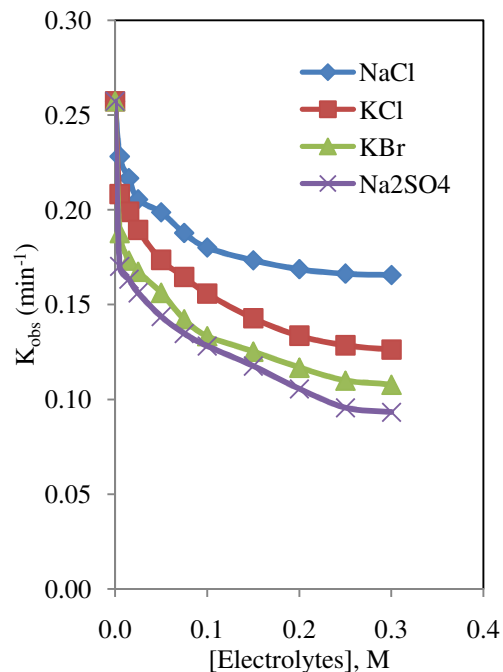


Figure-6

Effect of electrolytes on SDS catalysed oxidation of Indigo carmine by V(V) at 30°C [Indigo carmine] = 6.0×10^{-5} M, [V(V)] = 2×10^{-3} M, [H⁺] = 0.5 M [SDS] = 0.9×10^{-2} M

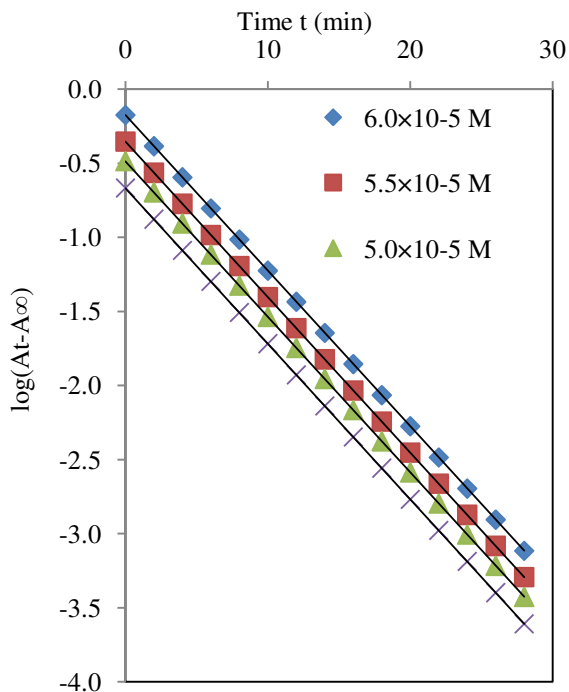


Figure-5

Plot of versus Time, t (min) for the oxidation of Indigo carmine under the condition of fixed concentration of V(V) at 30°C in presence of SDES [V(V)] = 1×10^{-3} M [H⁺] = 0.5 M [SDES] = 0.4×10^{-3} M

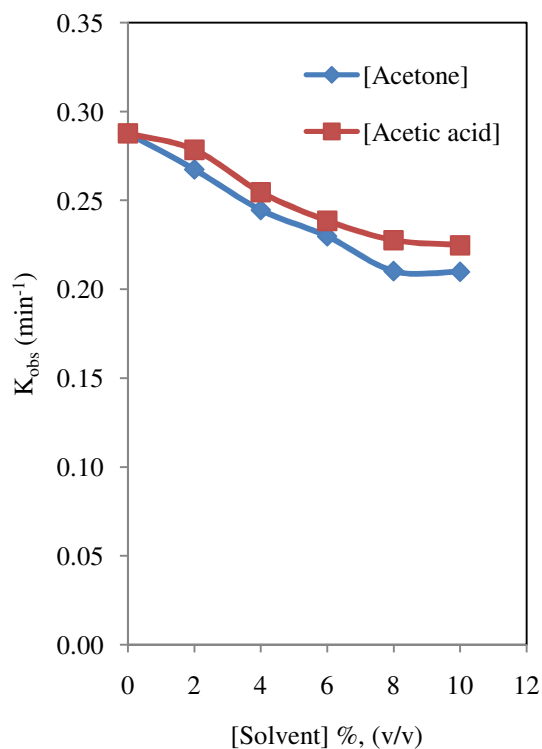


Figure-7

Influence of solvents on oxidation of Indigo carmine by V(V) at 30°C temperatures [Indigo carmine] = 6.0×10^{-5} M, [V(V)] = 2×10^{-3} M, [H⁺] = 0.5 M, [SDES] = 0.37×10^{-3} M

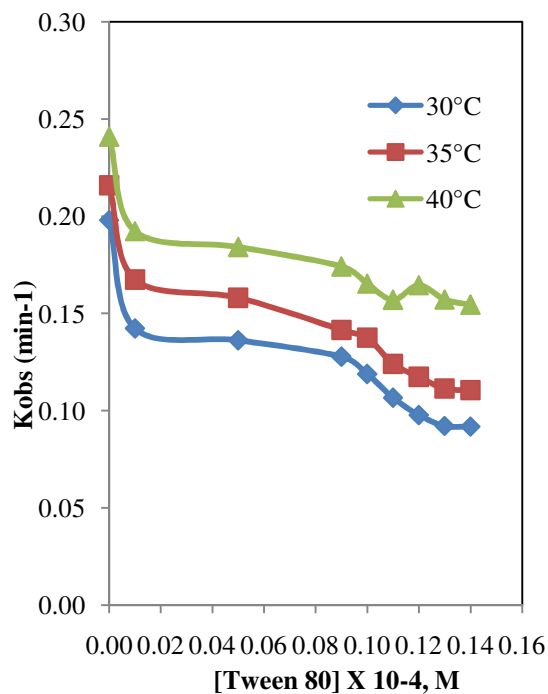


Figure-8

Influence of Tween-80 on oxidation of Indigo carmine by V (V) at different temperatures. [Indigo carmine] = 6.0×10^{-5} M [V (V)] = 2×10^{-3} M [H⁺] = 0.5 M

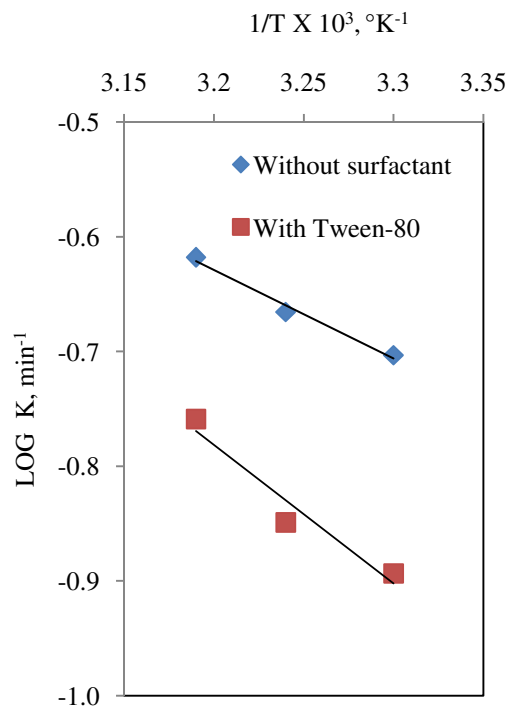


Figure-10

Arrhenius plots for the oxidation of Indigo carmine by V (V) in absence and presence of Tween-80

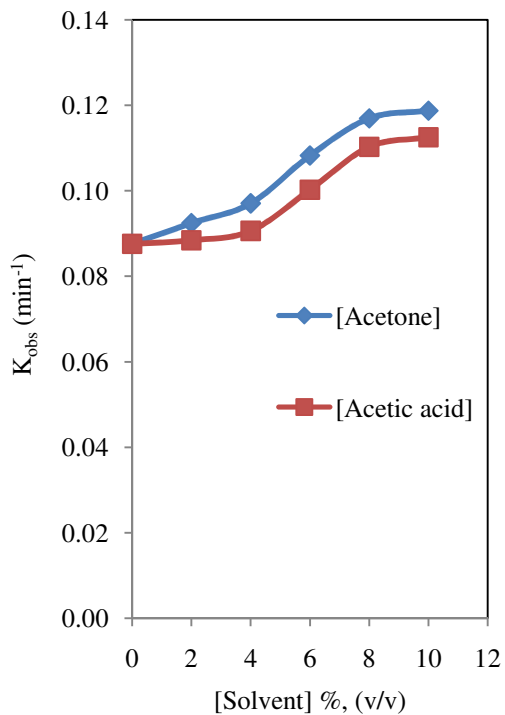


Figure-9

Influence of solvents on oxidation of Indigo carmine by V (V) at 30°C [Indigo carmine] = 6.0×10^{-5} M, [V (V)] = 2×10^{-3} M, [H⁺] = 0.5 M [Triton X-100] = 0.35×10^{-3} M

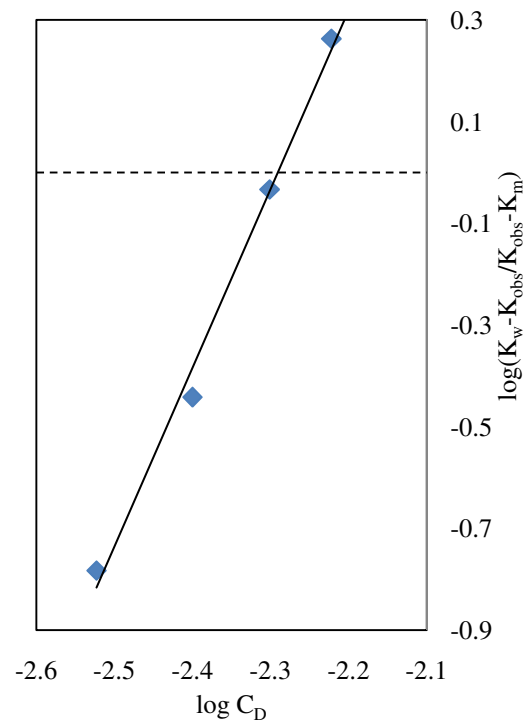


Figure-11

Index of co-operativity (n) for the oxidation of Indigo carmine by V (V) in presence of (a) SDS

Table-1
Activation parameters for the oxidation of Indigo carmine with V (V) in absence and presence of surfactants

Parameters	E_a (kJ.mol ⁻¹)	Z (l. mol ⁻¹ .s ⁻¹)	ΔH (kJ.mol ⁻¹)	ΔS (JK ⁻¹ . mol ⁻¹)	ΔG (kJ.mol ⁻¹)
In aqueous solution	14.74	68.78	9.70×10^3	-226.56	78.35
SDS	11.87	26.70	6.82	-234.40	77.86
SDES	12.17	32.52	7.14	-232.7	77.67
Triton X-100	25.91	4.04×10^3	20.87	-192.6	79.25
Tween -80	23.12	1.24×10^3	18.08	-202.54	79.45

Table-2

Values of n, log [D]₅₀, 1/K_D and K_D in oxidation of Indigo carmine by V (V) in presence of anionic and non-ionic surfactants at 30°C

Surfactants	n	Log[D] ₅₀	k _D	1/k _D
SDS	5.05	-1.88	3.04×10^{-10}	3.2×10^9
SDES	2.75	-3.36	5.24×10^{-10}	1.91×10^9
Triton X-100	3.88	-3.76	2.57×10^{-10}	3.89×10^{14}
Tween-80	2.27	-5.29	9.33×10^{-13}	1.07×10^{12}

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