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EFFECTS OF NON-IONIC SURFACTANTS ON THE OXIDATION OF METHYL ORANGE

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ABSTRACT

The kinetics of oxidation of aromatic azo dyes viz., methyl orange (MO) has been studied in aqueous sulphuric acid medium by V (V). The spectrophotometric study of the reaction in aqueous sulphuric acid medium is first order in vanadium (V) and methyl orange (MO). Plots of k_{obs} *versus* $[H^+]$ *are linear with positive intercepts on* k_{obs} *axes, which suggest the formation of a complex of dye and vanadium. The investigation of oxidation of methyl orange (MO) by V (V) in aqueous sulphuric acid media in the presence of non-ionic surfactants at different temperatures has been observed. The activation and thermodynamic parameters have been calculated.*

Keywords: Activation energy, Kinetics, Micellar systems, Oxidation, Thermodynamic parameters

I. INTRODUCTION

Though kinetic study of oxidation of various organic compounds by vanadium (V) has been reported, kinetic study of oxidation of aromatic compounds by V (V) has not been made. A kinetic study of oxidation of methyl orange (MO) by vanadium (V) in aqueous sulphuric acid medium has been investigated. The effect of the added non-ionic surfactants on the reaction has also been carried out. 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 process [1-3]. It is reported that micelles have effect on the rate of reactions [4-9].

II. MATERIAL AND METHODS

The chemicals used were of AR grade. The solutions (i.e., ammonium metavanadate (prepared in 2M H_2SO_4) and methyl orange (MO)) were prepared and standardized according to the method of Gopala Rao et. al. [10, 11]. Surfactants solutions were prepared in double distilled water. Before the use purities of the chemicals were checked.

III. 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 468 λ_{max} for methyl red. 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 Piszkiewiczl [13].

IV. STOICHIOMETRY

The stoichiometry of the reaction was determined by mixing methyl orange in micellar environment with non-ionic surfactant, in 0.5 M H_2SO_4 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.

V. 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_∞) versus time, which was linear under the condition [V(V)] >> [Dye] indicating the order in the methyl orange (MO) to be unity [Fig. 1]. The figures show 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 [Fig. 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_∞) versus time, t (min) is linear under the fixed concentration of MO, 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 [Fig. 3].

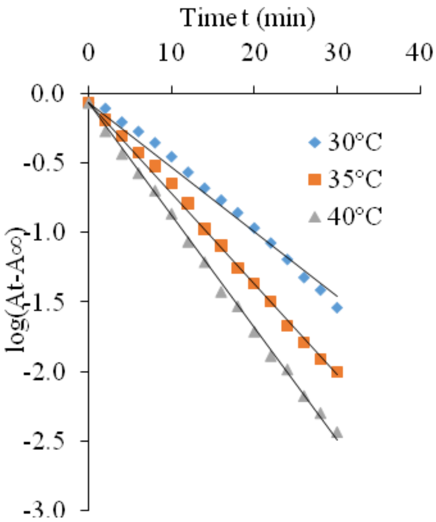


Fig.1: Plot of $\log(A_t - A_\infty)$ versus time t (min) for the oxidation of Methyl orange in absence of surfactant at different temperatures. [Methyl orange] =4.0×10^{-5} M, [V (V)] = 5×10^{-4} M, [H^+] = 0.5 M

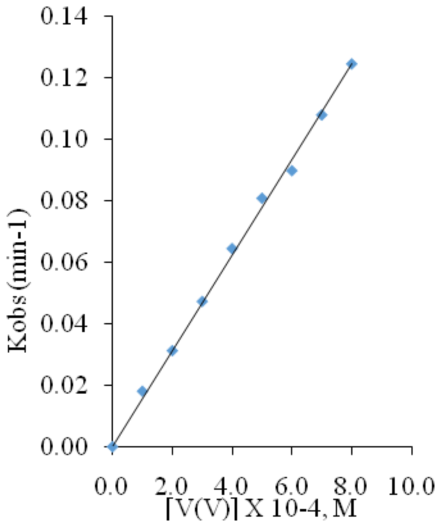


Fig. 2: Pseudo first-order rate constants for the oxidation of Methyl orange in aqueous phase at different concentration of V (V) at 30°C temperature. [Methyl orange] = 4.0×10^{-5} M, [H^+] = 0.5 M

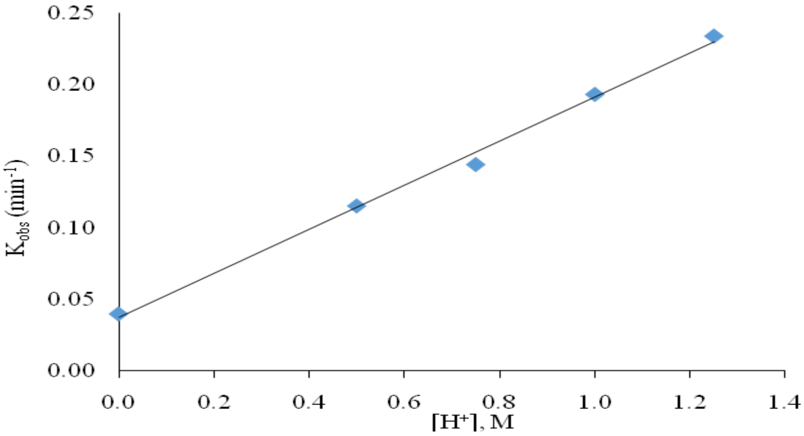
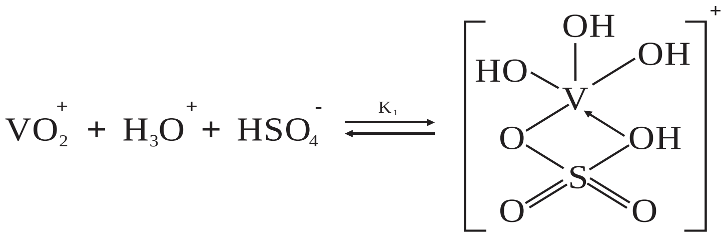


Fig. 3: Pseudo first-order rate constants for the oxidation of Methyl red in aqueous phase at different concentration of [H$^+$] M at 30°C temperature. [Methyl red] = 4.0×10^{-5} M, [V (V)] = 1×10^{-3} M

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)$_3$]$^{+2}$ species which depends on the acid types and their concentration range. It has been established by research workers [14-16] that in aqueous sulphuric media (≤ 4.5 mol.dm^{-3}), the kinetically active species of V (V) is [V (OH)$_3$ HSO$_4$]$^+$ and the equilibrium leading to the active species is given by [14-18],

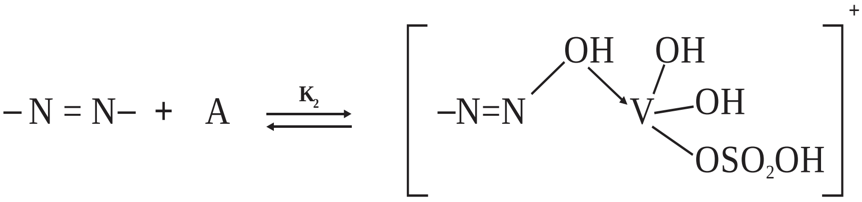
$$VO_2^+ + H_3O^+ + HSO_4^- \rightleftharpoons [V(OH)_3\ HSO_4]^+ \qquad (1)$$

The result can be explained by considering the proposed mechanism (Scheme)



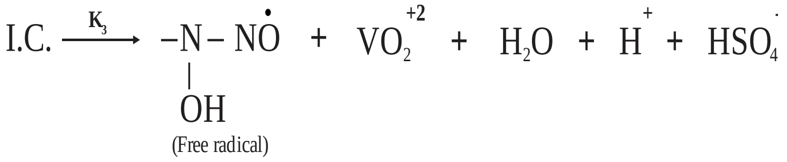
A

(2)



(Intermediate Complex)

(3)



$$\text{I.C.} \xrightarrow{K_3} \underset{\substack{|\\ \text{OH}\\ \text{(Free radical)}}}{-\text{N}-\dot{\text{NO}}} + VO_2^{+2} + H_2O + H^+ + HSO_4^{\cdot} \qquad (4)$$

$$\text{Free radical} + \text{V(V)} \xrightarrow{\text{Fast}} 2\ \underset{\text{(Nitroso Compound)}}{-\text{NO}} + \text{V(IV)} + H^+ \qquad (5)$$

The rate of oxidation of MO by V (V) depends on the first power of the concentrations of two reactants. Therefore, the rate law for the oxidation of dye can be given by the expression,

$$-d\,[\text{dye}]/dt = k'\,[V\,(V)]\,[\text{dye}]\,[H^+]\,[HSO_4^-] \qquad (6)$$

Where, k' is the second order rate constant. At constant $[H^+]$ the rate laws equation (1) reduces to

$$-d\,[\text{dye}]/dt = k'\,[V\,(V)]\,[\text{dye}] \qquad (7)$$

Non-ionic surfactants (Triton X-100, Triton X-102, Tween-80) inhibited the rate of oxidation of methyl orange by V (V) (Fig-4). 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.

Tween-80 < Triton X-102 < Triton X-100

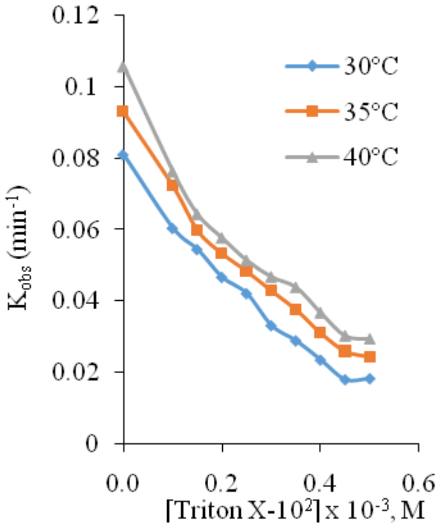


Fig. 4: Influence of Triton X-102 on oxidation of Methyl orange by V (V) at different temperatures.

[Methyl orange] = 4.0×10^{-5} M, [V (V)] = 5×10^{-4} M, [H$^+$] = 0.5 M

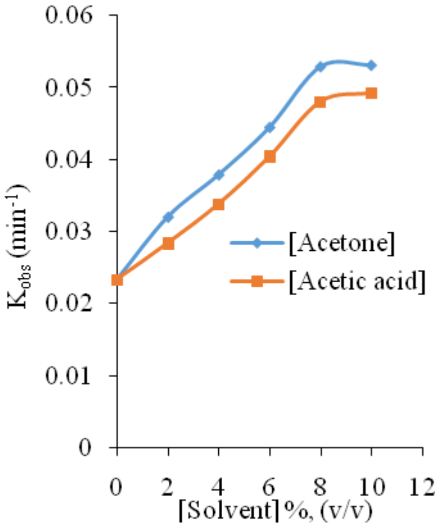


Fig. 5: Influence of solvents on oxidation of Methyl orange by V (V) at 30°C

[Methyl orange]=4.0 × 10^{-5} M, [V (V)]=5×10^{-4} M, [H$^+$]=0.5 M, [Triton X-102]=0.4 × 10^{-3} M

The kinetics of the reaction of varying concentration of solvent water mixture in presence of fixed concentration of non-ionic surfactants (Triton X-100, Triton X-102, Tween-80) and the substrate has been studied at 30°C (Fig-5). 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:

Acetone > Acetic acid

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 $[V(OH)_3HSO_4]^+$ at reaction sites.

The effect of temperature on the oxidation reaction of MO 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_{obs} versus 1/T in absence and presence of surfactants is linear (Fig-6). The values of activation parameters viz., $Ea^{\#}$, frequency factor Z, $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ are given in Table:1

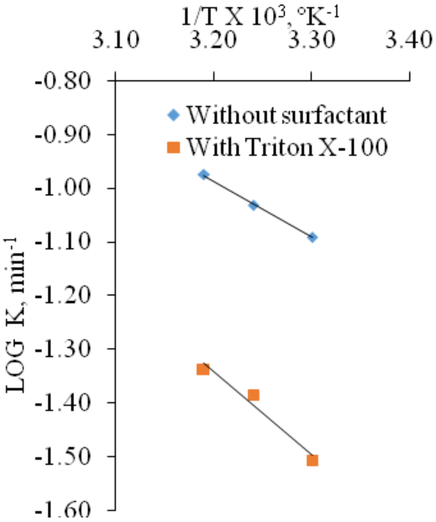


Fig 6: Arrhenius plots for the oxidation of Methyl orange by V (V) in absence and presence of Triton X-100

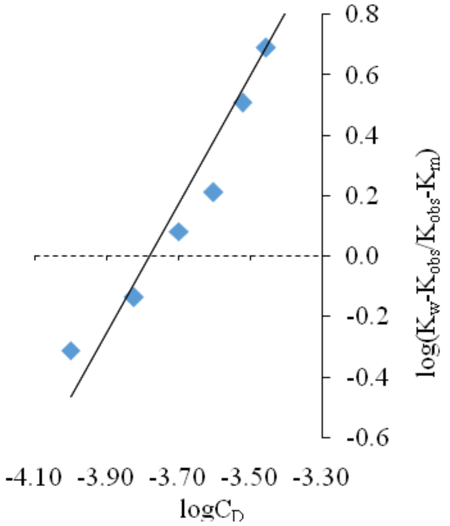


Fig.7: Index of co-operativity (n) for the oxidation of Methyl orange by V (V) in presence of Triton X-102

Table 1 Activation parameters for the oxidation of Methyl orange 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	20.27	2.52×10^2	15.24	-215.74	80.60
Triton X-100	29.91	4.4×10^3	24.88	-191.86	83.01
Triton X-102	34.12	1.78×10^4	29.08	-180.35	83.74
Tween -80	36.56	5.77×10^4	31.52	-170.58	83.21

Table 2 Values of n, log $[D]_{50}$, $1/K_D$ and K_D in oxidation of Methyl orange by V (V) in presence of anionic and non-ionic surfactants at 30°C.

Surfactants	n	$\log[D]_{50}$	k_D	$1/k_D$
Triton X-100	3.82	-3.66	9.12×10^{-15}	1.08×10^{14}
Triton X-102	3.14	-3.70	2.57×10^{-12}	3.88×10^{11}
Tween-80	3.56	-5.22	2.75×10^{-19}	3.62×10^{18}

The kinetic results of retardation of the rate constant by non-ionic surfactants (viz., Triton X-100, Triton X-102, Tween-80) surfactants have been rationalized on the basis of a model proposed by Bruice et. al. and applied by Piszkiewicz. 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 (Fig-7). Values of log $[D]_{50}$ represent the concentration of detergent required for half maximal catalysis or inhibition of reaction.The value of n >1 indicates positive cooperativity. K_b is the binding constant which is reciprocal of $K_{D.}$ (Table: 2).

VI. CONCLUSION

The decrease in activation energy in presence of non-ionic 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 $\Delta G^{\#}$ in absence and presence of surfactants shows that similar mechanism for oxidation is operative in aqueous and micellar media. The values of $\Delta S^{\#}$ 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 affect the reaction rate. The value of frequency factor in presence and in absence of non ionic surfactants shows that the large number of collisions are required to produce the forward reaction in the presence of non ionic surfactants Values of log $[D]_{50}$ represent the existence of function sub-micellar aggregates involving detergent and substrate molecules of varying stoichiometries. The value of n >1 indicates the stimulation of additional molecule by interaction of the first molecule with the micelle. The values of binding constants (K_b) non ionic surfactants are higher. However, the inhibition in case of non-ionic 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.

REFERENCE

[1] Bruice T C, Katzhendler J and Fedor L R, J Am Chem Soc., 1968, 90(5), 1333-1348; DOI:10.1021/ja01007a040.

[2] Piszkiewicz D, J Am Chem Soc., 1977, 99(5), 1550-1557; DOI:10.1021/ja00447a044; 1977, 99(23), 7695-7697; DOI:10.1021/ja00465a046; 1976, 98(10), 3053-3055; DOI:10.1021/ja00426a083.

[3] Dwars T, Pactzold B and Oehme G, Angew Chem Int Edn., 2005, 44(44), 7174-7199; DOI:10.1002/anie.200501365.

[4] Seo S H, Chang J Y and Tew G N, Angew Chem Int Edn., 2006, 45(45), 7526-7530; DOI:10.1002/anie.200600688.

[5] Islam M, Saha B and Das A K, J Mol Catal: A Chem., 2005, 236(1-2), 260-266; DOI:10.1016/j.molcata.2005.04.019.

[6] Bayer R, Islam M, Saha B and Das A K, Carbohyd Res., 2005, 340(13), 2163-2170; DOI:10.1016/j.carres.2005.07.002.

[7] Islam M, Saha B and Das A K, J Mol Catal: A Chem., 2007, 266(1-2), 21-30; DOI:10.1016/j.molcata.2006.10.042.

[8] Saha B, Sarkar S and Choudhury K M, Int J Chem Kinet., 2008, 40(5), 282-286; DOI:10.1002/kin.20314.

[9] Saha B, Choudhury K M and Mandal J, J Sol Chem., 2008, 37(10), 1321-1328; DOI:10.1007/s10953-008-9304-0.

[10] Choudhury K M, Mandal J and Saha B, J Coord Chem., 2009, 62(11), 1871-1875; DOI:10.1080/00958970802687547.

[11] Gopala Rao G. Rao V P & Murty B V S R, Z analyt chem., 147 (1955) 161. DOI:10.1007/BF00457729.

[12] Gopala Rao G and Venkateswara Rao N, Talanta, 1961, 8(7), 539-546; DOI:10.1016/0039-9140(61)80132-X.

[13] Waters W A and Littler J S, J Chem Soc., 1959, 3014-3019; DOI:10.1039/JR9590003014.

[14] Jones J R and Waters W A, J Chem Soc., 1963, 352-356; DOI:10.1039/JR9630000352.

[15] Shankar J and Joshi S N, Indian J Chem., 1963, 1, 289.

[16] Saccubai S and Santappa M, Indian J Chem., 1970, 8, 533.

[17] Sengupta K K, Chakladar J K, Pal B P and Mukherjee D C, J Chem Soc Perkin 11, 1973, 7, 926.