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Kinetic of oxidation of methyl orange by vanadium(V) under conditions VO_2^+ and decavanadates coexist: Catalysis by Triton X-100 micellar medium

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ABSTRACT

The kinetics of oxidation of methyl orange by vanadium(V) $\{V(V)\}$ has been investigated in the pH range 2.3-3.79. In this pH range $V(V)$ exists both in the form of decavanadates and VO_2^+ . The kinetic results are distinctly different from the results obtained for the same reaction in highly acidic solution ($\text{pH} < 1$) where $V(V)$ exists only in the form of VO_2^+ . The reaction obeys first order kinetics with respect to methyl orange but the rate has very little dependence on total vanadium concentration. The reaction is accelerated by H^+ ion but the dependence of rate on $[\text{H}^+]$ is less than that corresponding to first order dependence. The equilibrium between decavanadates and VO_2^+ explains the different kinetic pattern observed in this pH range. The reaction is markedly accelerated by Triton X-100 micelles. The rate-[surfactant] profile shows a limiting behavior indicative of a unimolecular pathway in the micellar pseudophase.

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Capsule Summary: The kinetics of oxidation of methyl orange by vanadium(V) in the pH range 2.3-3.79 where $V(V)$ exists in the form of VO_2^+ and decavanadates has been investigated. The results are distinctly different from that obtained under highly acidic conditions.

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INTRODUCTION

In strongly acidic solutions vanadium (V) exists only in the form of VO_2^+ , whereas in the pH range 2.0-4.3 it exists as VO_2^+ and decavanadates i.e. $\text{V}_{10}\text{O}_{28}^{6-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$, $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$, $\text{H}_4\text{V}_{10}\text{O}_{28}^{2-}$ (Pope and Dale, 1968; Rossotti and Rossotti, 1956; Newmann and Quinlan, 1959; Clare et al., 1973). In acid media when $\text{pH} \leq 1.0$, where $V(V)$ exists in the form of VO_2^+ , a large number of kinetic investigations have been reported (Bengtsson, 1971; Saha, 2008; Tandel 2015, 2016; Swain

2001; Ghosh 2009, 2012; Sar 2015 and Padhiyar 2015). But in the pH range 2.0-4.3 where decavanadates and VO_2^+ coexist, not much work has been reported. The only kinetic study in the presence of decavanadates is the oxidation of 2-mercapto succinic acid, investigated by Pickering and Mc Auley (Pickering and Mc Auley, 1968). They stated that the interconversion of decavanadates and VO_2^+ takes place within the time of mixing. The kinetic investigations were carried out isolating $V(V)$ by taking a relatively high concentration of 2-mercapto succinic acid. From these studies, not much information is obtained about the reactivity of

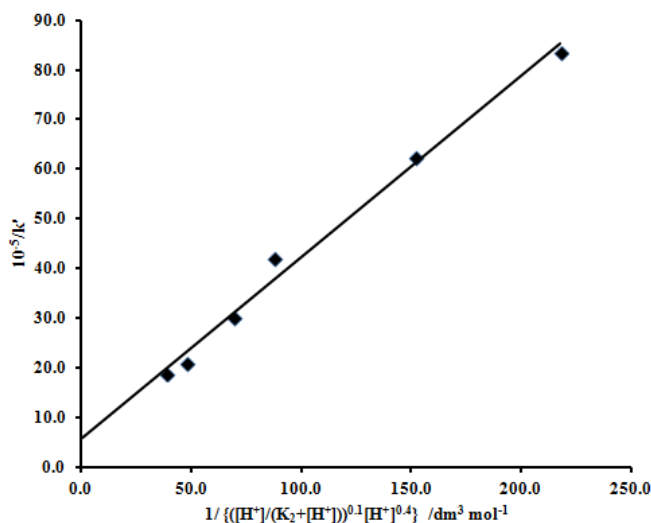


Fig. 1: Plot of $1/k'$ versus $1/\{([H^+]/(K_2+[H^+]))^{0.1}[H^+]^{0.4}\}$ ($k_1 = 13.3 \times 10^{-4} \text{ s}^{-1}$, $K_a K_3 K_1^{0.1}$ were found to be 421×10^{-4}).

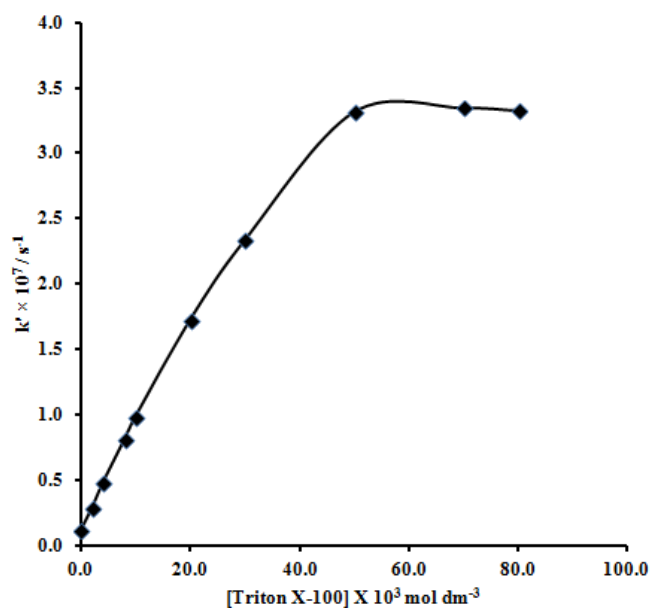


Fig. 2: Plot of k' versus $[\text{Triton X-100}]$; $[\text{MO}] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{V(V)}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} = 2.79$, $\mu = 0.5 \text{ mol dm}^{-3}$, $T = 303 \text{ K}$

decavanadates. To obtain detailed information about the kinetic patterns and to assess the reactivities of decavanadate species it is necessary to carry out the kinetic study keeping total $[\text{V(V)}]$ much higher than the substrate. The oxidation of iron (II) by V(V) under these conditions has been reported earlier from this laboratory (Rama Babu et al., 2000). We have carried out such a study taking methyl orange as the reductant. The reaction was also studied in micellar medium. Our preliminary studies on the effect of

micelles on the rate of the reaction showed that the reaction is catalysed by Triton X-100 micelles. Hence, a detailed study of the reaction has been carried out in the presence of Triton X-100 micellar media. The results are reported.

MATERIAL AND METHODS

Chemical and reagents

All solutions were prepared in double distilled water and chemicals used were of analytical reagent grade. A 0.1 mol dm^{-3} solution of sodium vanadate and 0.1% of methyl orange (MO) were prepared and standardised using standard methods reported in literature (Vogel, 1971). Triton X-100 was received from Merck, India and used without further purification.

Stoichiometry

The stoichiometry for the reaction was determined by spectrophotometry using mole ratio method, keeping the concentration of the methyl orange (MO) constant at $2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 3.4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.5 \text{ mol dm}^{-3}$ and Triton X-100 = 0.05 mol dm^{-3} and varying the concentrations of V(V) from $(5.0 \times 10^{-4} \text{ to } 5.0 \times 10^{-2})$. The absorbance of the reaction mixture (the absorbance corresponding to unreacted methyl orange) was measured at $\lambda_{\text{max}} = 510 \text{ nm}$ after a fixed time interval of 24 hours. The mole ratio corresponding to the intersection point from the plot of absorbance versus mole ratio $([\text{V(V)}]/[\text{MO}])$ indicates that one mole of methyl orange reacts with four moles of V(V).

Product analysis

100 mg of methyl orange was mixed with 10.0 ml of 0.1 mol dm^{-3} V(V) and 25.0 ml of 5.0 mol dm^{-3} HCl. The reaction mixture was allowed to stand until the reaction was complete. The products were extracted into ether. The extract was dried with anhydrous calcium carbonate and evaporated in a china dish and dissolved in ether. It was found that the products formed are the corresponding nitroso compounds which were detected using spot test prescribed by Feigl (Feigl, 1966).

Method of the course of the reaction

The reaction was followed by measuring the absorbance of the unreacted methyl orange at 510 nm using Shimadzu UV-1800 spectrophotometer. The experiments were carried out in a temperature controlled thermostat at 303 K. The reaction was initiated by adding V(V) ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) to a solution of methyl orange ($2.0 \times 10^{-5} \text{ mol dm}^{-3}$), hydrochloric acid ($3.4 \times 10^{-4} \text{ mol dm}^{-3}$) and Triton X-100 (0.05 mol dm^{-3}). Ionic strength was maintained constant at 0.5 mol dm^{-3} with NaCl. Plots of $\log(A_t)$ (where A_t is the absorbance at time t) were perfectly linear for at least 90% of the reaction. The kinetic data are the averages from triplicate runs with reproducibility $\pm 3\%$.

Determination of critical micellar concentration (CMC) of Triton X-100

Table 1: Effect of methyl orange, vanadium (V) and $[H^+]$ on rate (Triton X-100 = 0.05 mol dm^{-3} , $\mu = 0.5 \text{ mol dm}^{-3}$, $T = 303 \text{ K}$)

$[MO] \times 10^5 \text{ mol dm}^{-3}$	$[V(V)] \times 10^3 \text{ mol dm}^{-3}$	$[VO_2^+] \times 10^4 \text{ mol dm}^{-3}$ (from iterative method)	$[HCl] \times 10^4 \text{ mol dm}^{-3}$	pH	$k' \times 10^7 \text{ s}^{-1}$
0.5	5.0	2.69	16.2	2.79	3.23
1.0					3.29
2.0					3.32
2.0	0.5	0.24	3.4	3.47	1.19
	1.0	0.25			1.22
	5.0	0.29			1.26
	10.0	0.32			1.49
	50.0	0.38			1.61
	5.0	0.09	1.62	3.79	1.20
		0.29	3.4	3.47	1.26
		1.36	10.0	3.00	2.37
		2.69	16.2	2.79	3.32
		8.81	38.0	2.42	4.77
		12.8	50.0	2.30	5.31

CMC of Triton X-100 under the present experimental conditions was determined by surface tension measurements using a stalagmometer in the presence of $[MO]$ ($= 2.0 \times 10^{-5} \text{ mol dm}^{-3}$), $[HCl]$ ($= 3.4 \times 10^{-4} \text{ mol dm}^{-3}$) and ionic strength, μ ($= 0.5 \text{ mol dm}^{-3}$) maintained with NaCl. CMC of Triton X-100 under the present experimental conditions was found to be $1.81 \times 10^{-4} \text{ mol dm}^{-3}$.

RESULTS AND DISCUSSION

This reaction has been investigated earlier in strong acid media where only VO_2^+ species is present (Subba Rao et al., 1977). Under these conditions the reaction obeys first order kinetics with respect to both the reactants. A linear plot of k' against $[H^+]^2$ was obtained with a positive intercept. But the kinetic results in the pH range 2.3-3.79 are completely different. The results show very little change in the pseudo

first order rate constant, k' , with change in total vanadium(V) concentration under the conditions $[V(V)] \gg [MO]$; k' remains constant with change in $[MO]$ showing first order kinetics with respect to methyl orange. k' increases with increase in $[H^+]$ but dependence is less than that found in a first order behavior with respect to $[H^+]$ (Table 1).

In the pH range 2.3 - 3.79, vanadium(V) is present in the form of VO_2^+ , $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$. The total stoichiometric vanadium concentration, $[V(V)]_t$ is equal to the sum of the concentrations of VO_2^+ , $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$.

$$[V(V)]_t = [VO_2^+] + [HV_{10}O_{28}^{5-}] + [H_2V_{10}O_{28}^{4-}]$$

The three species are related by the equilibria as shown in Eqs. 1-2.

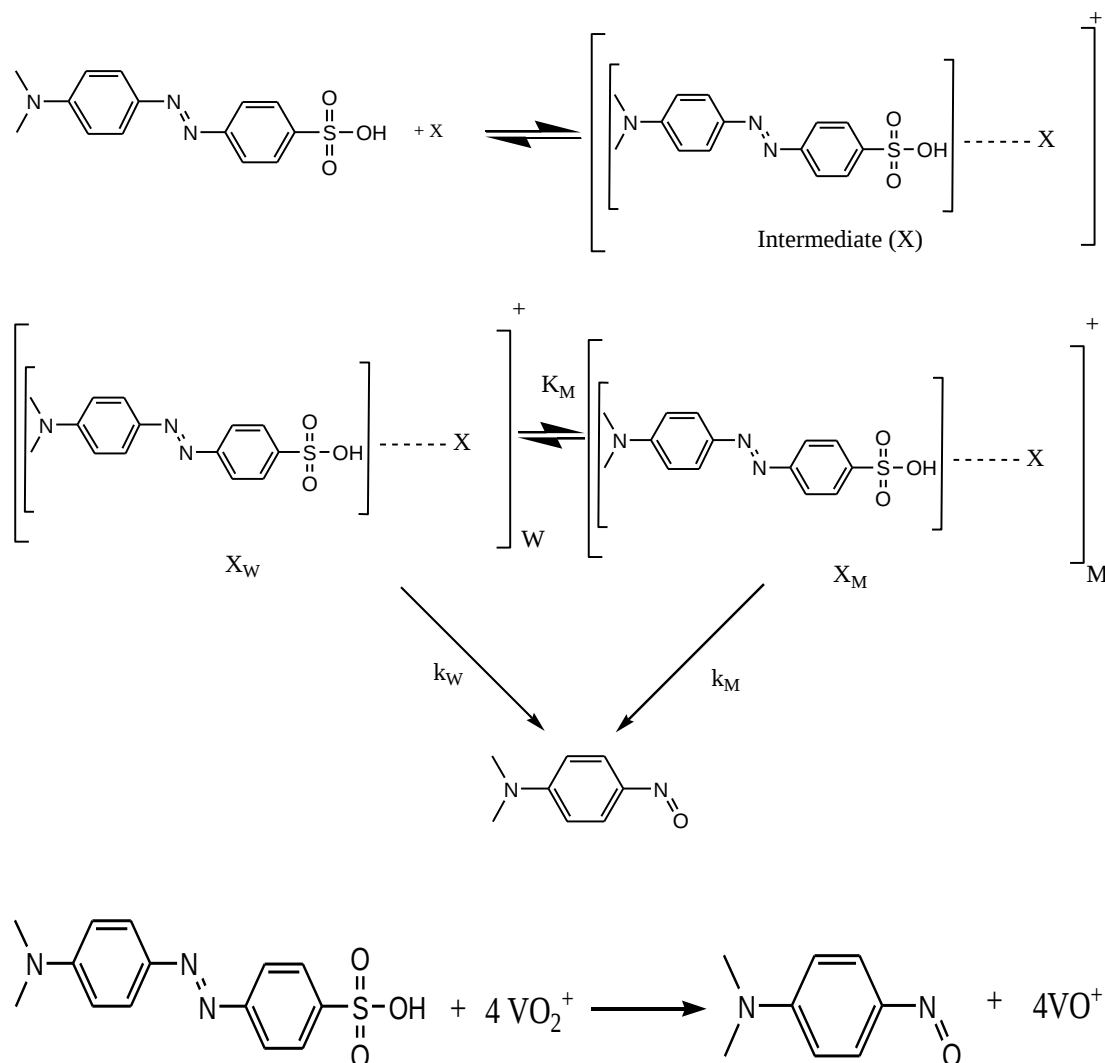
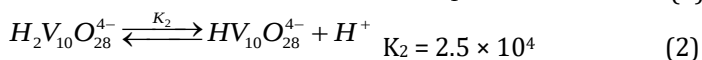
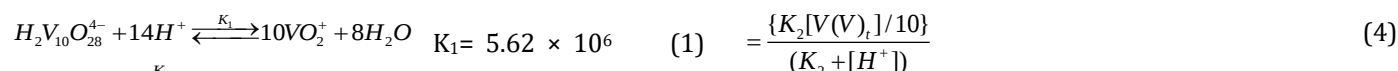


Fig. 3: Mechanism for the observed kinetics in the presence of Triton X-100 micelles where X is VO_2^+ or $HV_{10}O_{28}^{5-}$ or $H_2V_{10}O_{28}^{4-}$



From the above equations, the concentrations of VO_2^+ , $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ are given as

$$[H_2V_{10}O_{28}^{4-}] = \frac{[Decavanadate]_t [H^+]}{(K_2 + [H^+])} \quad (3)$$

$$= \frac{[H^+] \{ [V(V)] - [VO_2^+] / 10 \}}{(K_2 + [H^+])}$$

Where

$$[Decavanadate]_t = [HV_{10}O_{28}^{5-}] + [H_2V_{10}O_{28}^{4-}] = \frac{[V(V)]_t - [VO_2^+]}{10}$$

$$[HV_{10}O_{28}^{5-}] = [Decavanadate]_t - [H_2V_{10}O_{28}^{4-}]$$

$$= \frac{\{K_2[V(V)]_t / 10\}}{(K_2 + [H^+])} \quad (4)$$

and VO_2^+ in equation (1) is given by

$$[VO_2^+] = \{K_1[H_2V_{10}O_{28}^{4-}]\}^{0.1} [H^+]^{1.4} \quad (5)$$

Substituting the value of $H_2V_{10}O_{28}^{4-}$ in equation (5)

$$[VO_2^+] = \left\{ \frac{K_1 \left(\frac{[V(V)]}{10} \right) [H^+]}{(K_2 + [H^+])} \right\}^{0.1} [H^+]^{1.4} \quad (6)$$

Applying the Newton-Raphson iteration method to equation (6) (a program written in FORTRAN by the authors), the concentration of VO_2^+ was calculated in this pH range.

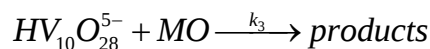
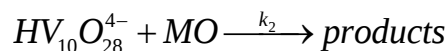
The unprotonated species of methyl orange is the active reducing species because electrons can be more easily abstracted from the unprotonated form.



Since $[H^+] \gg K_a$; $[HMO^+] = [HMO^+]_t$ where $[HMO^+]_t$ is the total concentration of methyl orange. The concentration of the unprotonated methyl orange is

$$[MO] = \frac{K_a [HMO^+]_t}{[H^+]} \quad (8)$$

A general scheme involving VO_2^+ , $HV_{10}O_{28}^{5-}$ or $H_2V_{10}O_{28}^{4-}$ can now be given as



The scheme gives the rate – law,

$$-\frac{d[HMO^+]_t}{dt} = k_1[VO_2MO^+] + k_2[H_2V_{10}O_{28}^{5-}][MO] + k_3[HV_{10}O_{28}^{5-}][MO] \quad (9)$$

By applying the equilibrium method, $[VO_2MO^+]$ is given by the Eqs. (10 and 11).

$$[VO_2MO^+] = \frac{K_3 K_a [VO_2^+][HMO^+]_t}{(K_a + [H^+] + K_3 K_a [VO_2^+])} \quad (10)$$

The rate – law assumes the form (11),

$$-\frac{d[HMO^+]_t}{dt} = \frac{k_1 K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4} [HMO^+]_t}{1 + K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4}} + \frac{K_2 K_a \left[\frac{[V(V)]}{10} \right] [H^+][MO]_t}{K_2 + [H^+]} + \frac{k_3 K_2 K_a \left[\frac{[V(V)]}{10} \right] [MO]}{K_2 + [H^+]}$$

Since, the rate has very little dependence of $[V(V)]$, the second and third terms in equation (11) do not contribute significantly and can be neglected. Therefore the pseudo first order rate constant, k' is derived and the relations are shown in Eqs. 12-13.

$$-\frac{d[HMO^+]_t}{dt} = \frac{k_1 K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4} [HMO^+]_t}{1 + K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4}} \quad (12)$$

$$k' = \frac{k_1 K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4}}{1 + K_3 K_a \left\{ \frac{K_1 \left[\frac{[V(V)]}{10} \right] [H^+]}{K_2 + [H^+]} \right\}^{0.1} [H^+]^{0.4}} \quad (13)$$

The above equation explains all the kinetic features observed. The order with respect to methyl orange is one in accordance to the above equation. As $[V(V)]$ varies from $(0.5 - 50.0) \times 10^{-3} \text{ mol dm}^{-3}$ ($([v(v)] \cdot [vo_2^+])/10$)^{0.1} varies from 0.35 to 0.59. The term $([v(v)] \cdot [vo_2^+])/10$ ^{0.1} is present in both numerator and denominator, further reducing the dependence of the k' on $[V(V)]$. This explains the very small dependence of rate on $[V(V)]$. As required by the rate law, a plot of $1/k'$ versus $1/\{([H^+]/(K_2 + [H^+]))^{0.1} [H^+]^{0.4}\}$ is a straight-line with positive slope and intercept and from the values of slopes

Table 2: Effect of Triton X-100 concentration on rate ($[MO] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[V(V)] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, pH = 2.79, $\mu = 0.5 \text{ mol dm}^{-3}$, T = 303 K)

[Triton X-100] $\times 10^3 \text{ mol dm}^{-3}$	$k' \times 10^7 \text{ s}^{-1}$
0.0	0.12
2.0	0.29
4.0	0.48
8.0	0.82
10.0	0.99
20.0	1.73
30.0	2.34
50.0	3.32
70.0	3.35
80.0	3.33

and intercepts, k_1 and $K_a K_3$ have been calculated (Fig. 1). Effect of Triton X-100 micellar medium on rate: The effect of Triton X-100 on this reaction has been investigated by varying the Triton X-100 concentration from 2.0 to 80.0 ($\times 10^{-3} \text{ mol dm}^{-3}$). The rate of the reaction increases with increase in concentration of Triton X-100 up to 0.05 mol

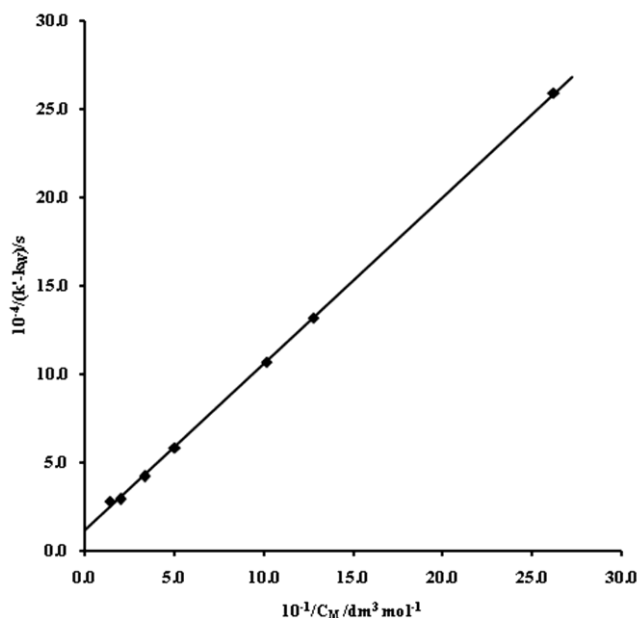


Fig. 4: Plot of $1/(k'-k_w)$ versus $1/C_M$

dm^{-3} and thereafter shows a limiting behavior with increase in micellar concentration (Fig. 2 and Table 2).

The catalysis is explained in terms of binding of the reaction intermediate on the micellar surface; greater stabilization of transition state in the micellar pseudophase than in aqueous medium. The observed rate-[surfactant] profile indicates a unimolecular pathway and the mechanism is shown in Fig. 3.

On the other hand, bimolecular reactions taking place in the micellar pseudo phases give rate-surfactant profiles with well-defined maxima. The rate law for a unimolecular micellar catalysed reaction is represented by equation (14).

$$\frac{1}{k' - k_w} = \frac{1}{k_M - k_w} + \frac{1}{(k' - k_w)K_M C_M} \quad (14)$$

k' is the observed rate constant, k_w is the rate constant in aqueous medium, k_M is the rate constant in micellar medium, K_M is the binding constant. $C_M = C - \text{CMC}$ where C is the concentration of Triton X-100 and CMC is the critical micellar concentration of Triton X-100.

According to equation (14), a plot of $1/(k'-k_w)$ versus $1/C_M$ should be linear with a positive slope and intercept. Such a plot has been obtained and the value of K_M calculated from the slope and intercept was found to be $11.89 \text{ mol}^{-1} \text{ dm}^3$ (Fig. 4).

This value is of the same order as the value expected for hydrophobic interaction with a micelle according to the expression $K_M = p\bar{V}$, where p is partition coefficient $p = e^{-Z\psi/25.7}$ and $\bar{V}$ is molar volume. The value of p lies between 75 – 280 (Berezin et al., 1973) and the value of

$\bar{V}$ is 0.57 for Triton X-100 (Mandal et al., 1980). Therefore the value of K_M is $42.75 \text{ mol}^{-1} \text{ dm}^3$.

CONCLUSIONS

The present study shows that the kinetic results obtained for the oxidations of methyl orange by V(V) in the pH range 2.3 - 3.79 where decavanadates coexist along with VO_2^+ are different from the results reported in highly acidic media ($\text{pH} < 1.0$). The order with respect to methyl orange was found to be one whereas the order with respect to V(V) was found to be much less than one. The rate of the reaction increases with H^+ ion but dependence on rate is less than that corresponding to first order. Based on the observed kinetics a reaction mechanism involving equilibrium between the different forms of V(V) was proposed. The reaction has also been carried out in the presence of Triton X-100 micelles and it was found that the rate of the reaction is around thirty times greater in the presence of Triton X-100 micelles compared to aqueous medium. The rate-surfactant profile shows a limiting value indicating a unimolecular pathway.

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