

Inhibitory Effect of {Surfactant- MnO_4^- } Aggregation in KMnO_4 Oxidation of Proline and Methionine: A Kinetic Study

Ritu Tripathi and Santosh K. Upadhyay*

Department of Chemistry, H.B. Technological Institute, Kanpur-208 002, India

*E-mail: upadhyay_s_k@rediffmail.com

(Received March 4, 2014; Accepted May 5, 2014)

ABSTRACT. Anionic (sodium lauryl sulphate, NaLS) cationic (cetyl ammonium bromide, CTAB) and non-ionic (Tween-80) surfactants have been found to inhibit the rate of oxidation of L-proline and L-methionine by alkaline KMnO_4 . A first order dependence of rate of oxidation was observed with respect to MnO_4^- . The order of reaction in substrate and alkali was found to be fractional nearby 0.65 and 0.55 in Aminoacid and OH^- , respectively. An aggregation/association between MnO_4^- and surfactant has been confirmed spectrophotometrically. A mechanism, involving kinetically inactive [MnO_4^- surfactant] aggregate and consistent with kinetic data, has been proposed. The effect of surfactants has been discussed in terms of hydrophobic and electrostatic interactions.

Key words: Inhibition, Surfactants, KMnO_4 , Proline, Methionine

INTRODUCTION

The surfactants may affect¹⁻⁷ the rate of reactions either by providing a medium for the reaction or by participating directly in the reaction as a catalyst/substrate. The formation of self-aggregates of the surfactant and mix-aggregates between the surfactant and substrate/oxidant and consequently premicellar/micellar catalysis⁸⁻¹⁶ or micellar inhibition¹⁷⁻¹⁹ has been observed during various electron-transfer reactions.

The oxidation of proline and methionine by alkaline hexacyanoferrate(III) (one-electron transfer oxidant) has been found²⁰ to be catalysed by the non-ionic surfactant, viz Tween-80. The reaction was found to proceed via formation of an intermediate, between surfactant and aminoacid, which reacts with hexacyanoferrate(III) to give the products. However, there was no effect of the anionic or cationic surfactant on the rate of oxidation under these conditions. It has been observed that the kinetic results of proline and methionine by alkaline KMnO_4 (one electron transfer oxidant) in presence of anionic, cationic and non-ionic surfactants were different with those observed during the oxidation of proline and methionine by alkaline hexacyanoferrate(III).²⁰ The rate of oxidation of the above amino acids by KMnO_4 was found to retard by each i.e. anionic, cationic and non-ionic surfactant. A strong evidence has also been observed for the aggregation/association between KMnO_4 and each of the surfactant.

It is, therefore, thought worthwhile to investigate the

detail kinetics of the reaction from the mechanistic point of view. In the present communication, the results of the oxidation of proline and methionine by alkaline KMnO_4 in presence of anionic (sodium lauryl sulphate; NaLS) cationic (cetyl trimethyl ammonium bromide; CTAB) and non-ionic (Tween-80) surfactants are reported and a suitable mechanism consistent with kinetic data is proposed.

EXPERIMENTAL

Material and Methods

The reagents viz. methionine (s.d fine, Mumbai, India), proline (Thomas Baker, Mumbai, India), potassium permanganate (Loba Chemie, Mumbai, India), sodium lauryl sulphate (Thomas Baker, Mumbai, India), cetyl trimethyl ammonium bromide (Thomas Baker, Mumbai, India), Tween-80 (Thomas Baker, Mumbai, India) and sodium hydroxide (Thomas Baker, Mumbai, India) were used of analytical grade.

The critical micelle concentration (CMC) of the surfactants which were used such, were determined by surface tension measurement and were found to be 9.5×10^{-4} , 8.2×10^{-3} and 1.2×10^{-5} mol dm^{-3} at 25 °C in case of CTAB, NaLS and tween-80, respectively. The reported values of CMC are 9.8×10^{-4} , 8.0×10^{-3} and 1.0×10^{-5} mol dm^{-3} at 25 °C in case of CTAB,²¹ NaLS²² and Tween-80,²³ respectively.

To a reaction mixture containing appropriate quantities of solutions of KMnO_4 , NaOH, surfactant and required quantity of double distilled water was added so that total volume of mixture was 50 ml after adding substrate (amino

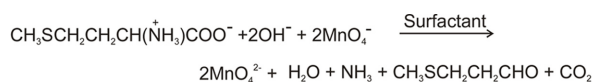
acid). The above reaction mixture was placed in a water bath maintained at desired temperature ± 0.1 °C. The reaction mixture was allowed to attain the bath temperature and the reaction was then initiated by adding requisite amount of amino acid solution placed separately in the same bath.

Kinetic Measurement

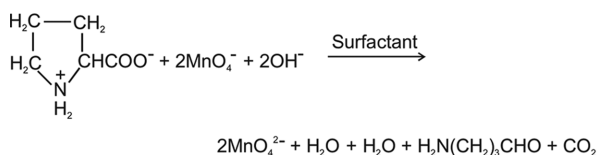
The kinetics of the reactions was followed by monitoring the absorbance, due to potassium permanganate as a function of time at 520 nm (λ_{max} of KMnO_4) on a spectrophotometer (Toshniwal, TVSP-25, India). The concentration of permanganate was kept within the limits of Beer's law. The absorbance due to other reactants was negligible at 520 nm.

Stoichiometry and Product Analysis

The stoichiometry of the reactions between KMnO_4 and proline/methionine in absence as well as in presence of surfactants has been studied by keeping the reaction mixtures containing a known excess of KMnO_4 over amino acid in alkaline medium for 2 h at 35 °C and by analyzing unreacted amount of KMnO_4 spectrophotometrically. It was observed that one mole of amino acid (proline or methionine) consumed 2 mole of KMnO_4 . The reactions may be represented as follows:



and



The presence of corresponding aldehyde as the oxidation product was confirmed by spot test.²⁴ The results are also in agreement with the earlier reported work on the oxidation of amino acid by alkaline KMnO_4 .²⁵

Table 1. Effect of $[\text{KMnO}_4]$ on the observed rate constant (k_{obs}) at 35 °C

$[\text{KMnO}_4] \times 10^4$	$(k_{\text{obs}}) \times 10^4 (\text{s}^{-1})$							
	Proline				Methionine			
	k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tween-80}}$	k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tween-80}}$
3.0	7.67	6.10	4.95	5.50	7.15	5.90	4.40	5.15
4.0	7.60	6.15	4.90	5.52	7.10	5.95	4.45	5.10
5.0	7.60	6.10	4.95	5.52	7.15	5.90	4.45	5.15
6.0	7.67	6.10	4.90	5.50	7.10	5.95	4.40	5.10

$[\text{Proline}] = [\text{Methionine}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CTAB}] = 0.55 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaLS}] = 6.90 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Tween-80}] = 10.5 \times 10^{-3} \text{ mol dm}^{-3}$.

RESULTS

Kinetic Results

The reactions were studied at different initial concentrations of the reactants. The log (Absorbance) versus time plots at various initial concentrations of the reactants were linear upto 85–90% of the reactions (Fig. 1). Therefore, pseudo first-order rate constants in KMnO_4 (k_{obs}) were determined from the slopes ($=k_{\text{obs}}/2.303$) of these linear plots.

The rate constants were found to be reproducible within $\pm 5\%$ in replicate kinetic runs. KMnO_4 had no effect on the k_{obs} values (Table 1) confirming first order dependence of rate in permanganate. The effect of OH^- on the rate was studied at a fixed ionic strength ($\mu=0.05 \text{ mol dm}^{-3}$) maintained by sodium perchlorate. The results of effect of substrate and alkali on the rate constant were identical (Table 2).

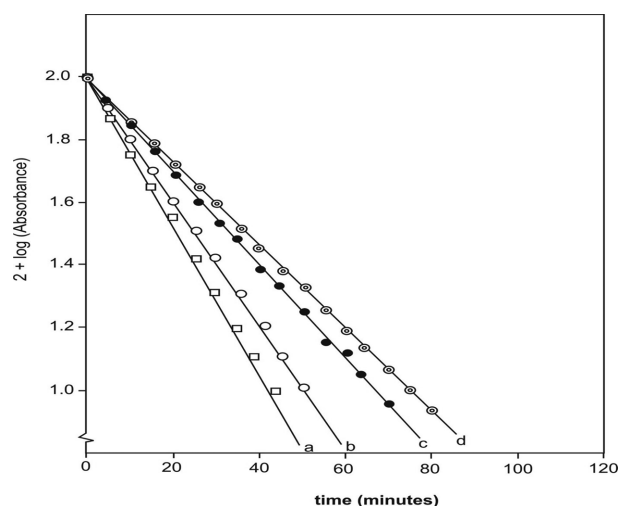


Figure 1. log (Absorbance) versus time plots i.e. pseudo first-order plots in KMnO_4 at 35 °C. $[\text{Substrate}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$, a, b, c and d represents the plots in presence of aqueous medium, $6.90 \times 10^{-3} \text{ mol dm}^{-3}$ NaLS, $10.5 \times 10^{-3} \text{ mol dm}^{-3}$ Tween-80 and $0.55 \times 10^{-4} \text{ mol dm}^{-3}$ CTAB, respectively.

Table 2. Effect of [Substrate] and [OH⁻] on k_{obs} at 35 °C

[Substrate] × 10 ³ (mol dm ⁻³)	[NaOH] × 10 ⁴ (mol dm ⁻³)	(k _{obs}) × 10 ⁴ (s ⁻¹)							
		Proline				Methionine			
		k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}	k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}
1.0	10.0	5.75	4.95	3.80	4.60	5.35	4.80	3.65	4.05
2.0	10.0	7.65	6.15	4.95	5.55	7.10	5.94	4.45	5.15
3.0	10.0	8.25	6.52	5.55	5.95	7.45	6.70	4.80	5.75
4.0	10.0	8.63	7.65	6.15	6.90	7.85	6.90	5.55	6.20
5.0	10.0	9.25	8.25	7.30	7.65	8.40	7.45	6.15	6.50
2.0	5.0	6.51	5.35	4.20	5.20	5.95	4.95	3.85	4.40
2.0	15.0	8.05	6.70	5.75	6.15	7.65	6.35	4.95	5.75
2.0	20.0	8.45	7.30	6.15	6.90	8.25	6.70	5.95	6.50
2.0	25.0	9.40	8.25	6.90	7.65	8.80	7.30	6.15	6.90

[KMnO₄] = 4.0 × 10⁻⁴ mol dm⁻³, [NaLS] = 6.90 × 10⁻³ mol dm⁻³, [CTAB] = 0.55 × 10⁻⁴ mol dm⁻³ and [Tween-80] = 10.5 × 10⁻³ mol dm⁻³.

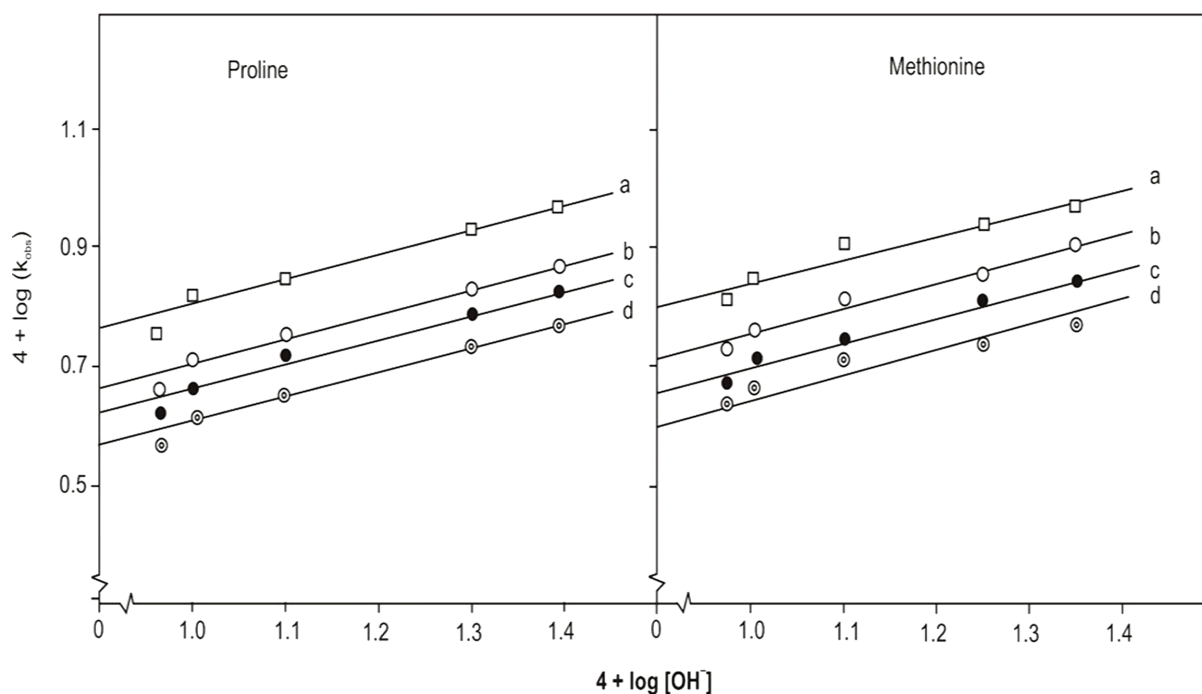


Figure 2. Plots of log k_{obs} versus log [OH⁻] at 35 °C. [Substrate] = 2.0 × 10⁻³ mol dm⁻³, [KMnO₄] = 4.0 × 10⁻⁴ mol dm⁻³. a, b, c and d are same as in Fig. 1.

The plots of log(k_{obs}) versus log [substrate] or log [OH⁻] were found to be linear with the positive intercepts. The slopes of these plots were ~0.5 to 0.6 in case of alkali (Fig. 2) and ~0.6 to 0.7 in case of amino acid (Fig. 3).

In order to investigate the effect of surfactant, the reactions have been studied in absence as well as presence of surfactants at three different temperatures viz. 35, 40 and 45 °C. A retarding effect of each surfactant on the rate has been observed. The results are represented graphically in the form of the plots (k_{obs}) versus [Surfactant] in Fig. 4. The value of k_{obs} in absence of each surfactant has also

been included in the plot of k_{obs} versus [Surfactant].

The effect of salt on the rate of reaction was studied by the successive addition of sodium perchlorate in the reaction mixture, k_{obs} were found to increase with an increase in NaClO₄ in the reaction mixture (Table 3). The values of second-order rate constants {k_{obs}/[MnO₄⁻]} at various temperatures are reported in Table 4. The activation parameters, evaluated with the help of Arrhenius and Eyring plots using second order rate constants, are also given in (Table 4). The same value of ΔG[‡] for both the substrate (amino acid) suggests a common mechanism for the oxidation

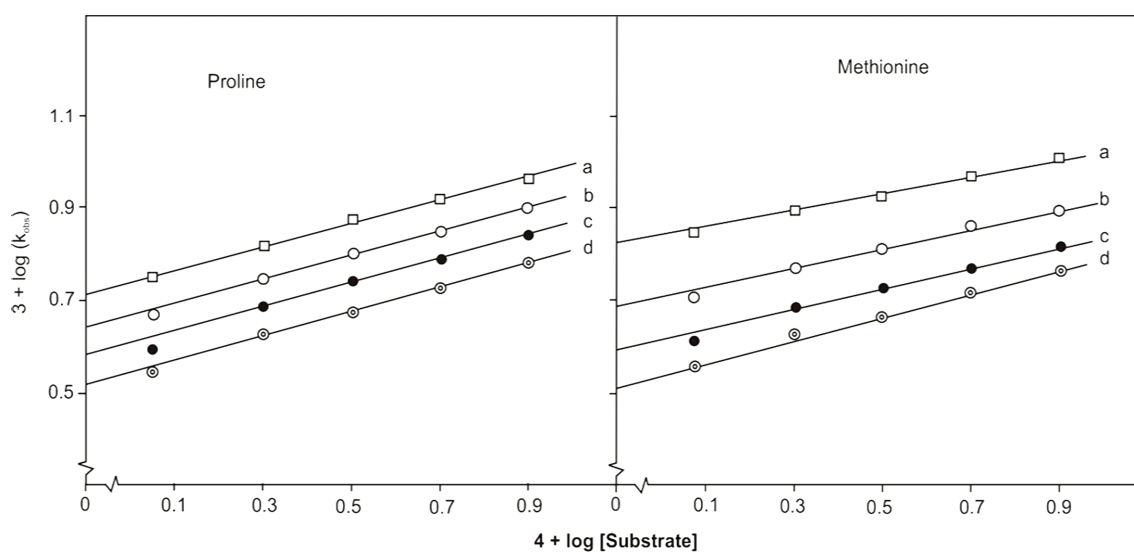


Figure 3. Plots of $\log k_{\text{obs}}$ versus $\log [\text{Substrate}]$ at $35\text{ }^{\circ}\text{C}$. $[\text{KMnO}_4] = 4.0 \times 10^{-4}\text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-3}\text{ mol dm}^{-3}$. a, b, c and d are same as in Fig. 1.

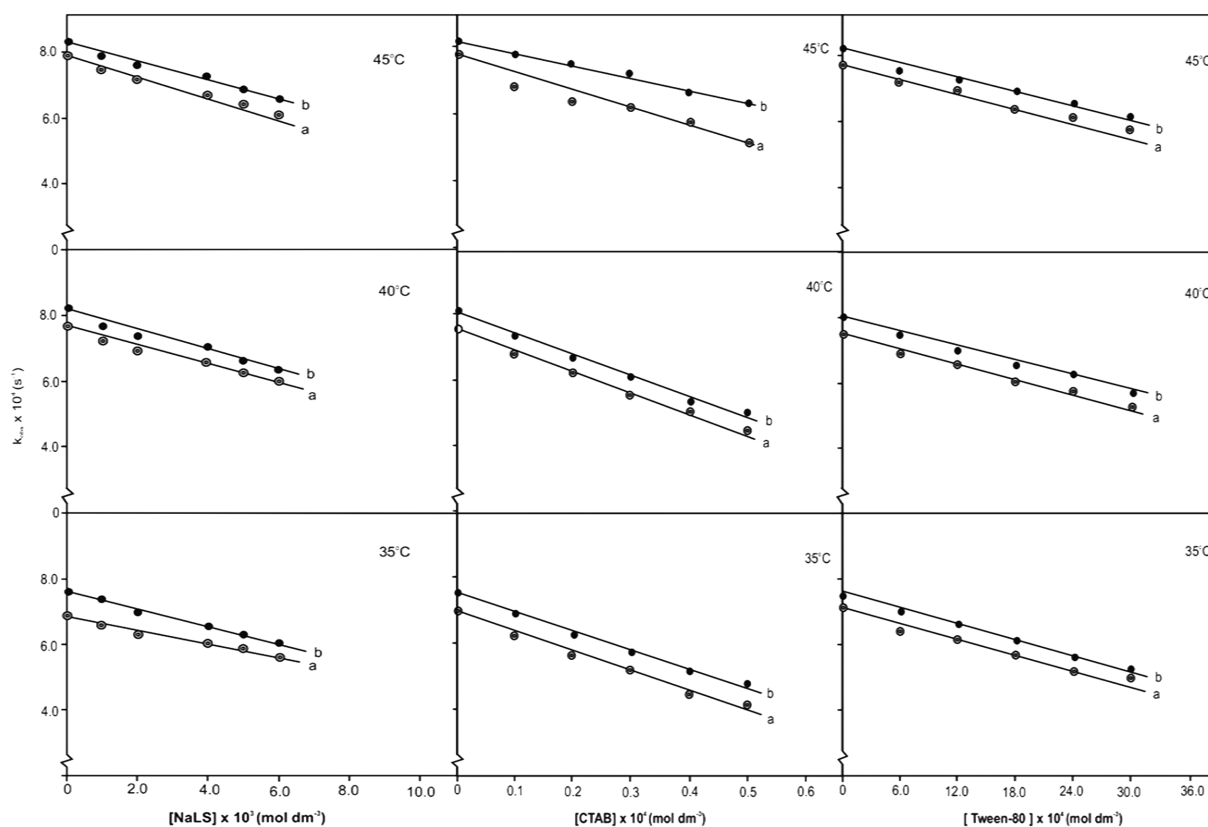


Figure 4. Plots of (k_{obs}) versus $[\text{Surfactant}]$ at 35 , 40 and $45\text{ }^{\circ}\text{C}$. $[\text{Substrate}] = 2.0 \times 10^{-3}\text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 4.0 \times 10^{-4}\text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-4}\text{ mol dm}^{-3}$. a: methionine, b: proline.

process. The negative value of ΔS^{\ddagger} indicates the compactness of transition state.

Free Radical Testing

To test for the involvement of free radical, acrylonitrile was added to the reaction mixture which was kept for 24 h

Table 3. Effect of [NaClO₄] on the observed rate constant at 35 °C

[NaClO ₄] × 10 ² (mol dm ⁻³)	(k _{obs}) × 10 ⁴ (s ⁻¹)							
	Proline				Methionine			
	k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}	k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}
Nil	7.65	6.15	4.95	5.55	7.10	5.95	4.45	5.15
1.0	8.05	6.90	5.75	6.15	7.65	6.50	4.98	5.55
2.0	8.65	7.30	6.35	6.90	8.45	6.90	5.75	6.15
3.0	9.60	7.85	6.90	7.30	8.80	7.65	6.55	7.10

[KMnO₄] = 4.0 × 10⁻⁴ mol dm⁻³, [Substrate] = 2.0 × 10⁻³ mol dm⁻³, [NaOH] = 10.0 × 10⁻⁴ mol dm⁻³, [NaLS] = 6.90 × 10⁻³ mol dm⁻³, [CTAB] = 0.55 × 10⁻⁴ mol dm⁻³ and [Tween-80] = 10.5 × 10⁻³ mol dm⁻³.

Table 4. Second order rate constants at different temperatures and activation parameters

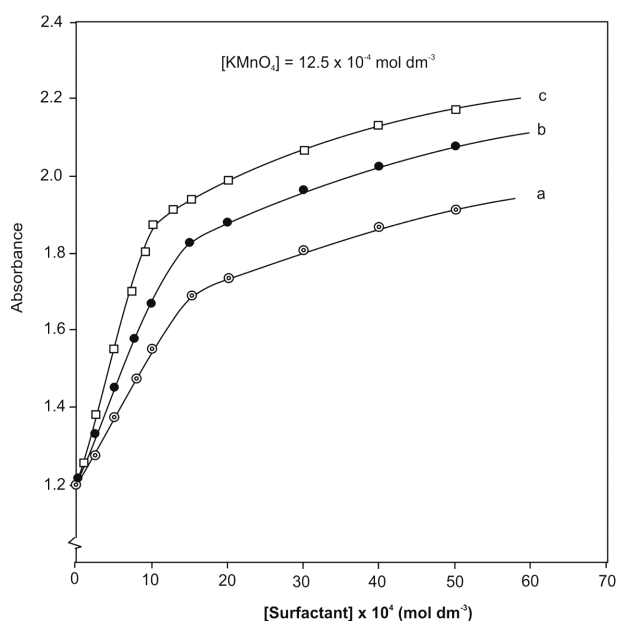
Temperature (K)	Second order rate constants (mol ⁻¹ dm ³ s ⁻¹)							
	Proline				Methionine			
	k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}	k _{aq.}	k _{NaLS}	k _{CTAB}	k _{Tween-80}
308	1.91	1.53	1.23	1.38	1.77	1.48	1.11	1.28
313	2.01	1.58	1.28	1.43	1.92	1.53	1.15	1.34
318	2.08	1.63	1.33	1.53	2.01	1.63	1.29	1.48

ACTIVATION PARAMETERS

E _{act} ± 0.25 (kJ mol ⁻¹)	11.48	9.57	6.70	7.65	15.31	13.40	8.61	10.53
ΔH [#] ± 0.25 (kJ mol ⁻¹)	8.88	6.98	4.08	5.04	12.70	10.79	6.09	7.92
-ΔS [#] ± 1.00 (JK ⁻¹ mol ⁻¹)	279.48	287.49	298.53	294.44	267.65	275.37	291.77	286.79
ΔG [#] ± 0.50 (kJ mol ⁻¹)	96.35	96.95	97.51	97.21	96.44	96.99	97.32	97.69

[KMnO₄] = 4.0 × 10⁻⁴ mol dm⁻³, [Substrate] = 2.0 × 10⁻³ mol dm⁻³, [NaOH] = 10.0 × 10⁻⁴ mol dm⁻³, [NaLS] = 6.90 × 10⁻³ mol dm⁻³, [CTAB] = 0.55 × 10⁻⁴ mol dm⁻³ and [Tween-80] = 10.5 × 10⁻³ mol dm⁻³.

under nitrogen atmosphere. Addition of methanol resulted in the precipitation of a polymer, suggesting the involvement of the free radical in the reaction. The addition of acrylamide also decreased the rate of reaction.

**Figure 5.** Plots of (Absorbance) versus Surfactant at room temperature = 30 °C. a: NaLS; b: Tween-80; c: CTAB.**Evidence for Complex Formation Between KMnO₄ and Surfactant**

In order to confirm any association or binding between the surfactant and KMnO₄, the absorbance of a series of solutions containing a fixed amount of KMnO₄ (12.5 × 10⁻⁴ mol dm⁻³) and NaOH (10 × 10⁻⁴ mol dm⁻³) and a varying amount of the surfactant (NaLS, CTAB, or Tween-80) were measured at λ_{max} of KMnO₄ (i.e 520 nm) at room temperature (~30 °C).

The results are represented in the form of Absorbance versus [Surfactant] in Fig. 5. It is observed from the Fig. 5 that the absorbance of solution increases linearly until [Surfactant]:[KMnO₄] ratio becomes nearby unity and then it tends to become constant. The results clearly indicate a 1:1 association between KMnO₄ and surfactant in presence of alkali. However, no evidence was observed for association of amino acid and surfactant.

DISCUSSION

At high [CTAB], the turbidity in reaction mixture was observed, therefore the rate constant in presence of CTAB at above CMC of CTAB could not be determined. At higher concentration of CTAB the turbidity may be due to formation

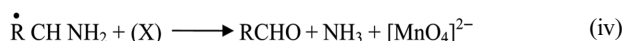
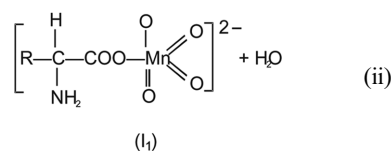
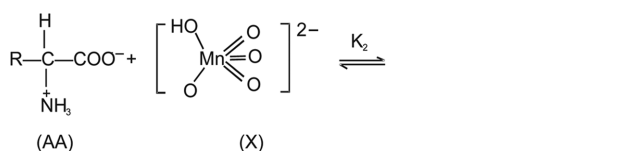
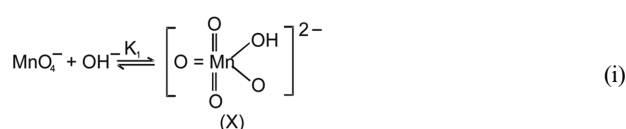
of water insoluble colloidal MnO_2 .

However, the retarding effect of the surfactant on the rate of oxidation was observed even below CMC of CTAB and NaLS. It was also observed that a small inhibition of Tween-80 (non-ionic surfactant) was started below of CMC, but it was more pronounced at above CMC. There was no turbidity in case of NaLS or Tween-80.

The inhibition effect by ionic surfactant below CMC may be caused by the interaction between the substrate/oxidant and submicellar aggregate of the surfactant that stabilizes the initial state or the substrate/oxidant might promote micellization of the surfactant by the formation molecular complex between substrate/oxidant and surfactant.²⁶ There are also evidences²⁷ for the formation of small complexes between surfactant molecules and reactants (substrate/oxidant) at the concentration of the surfactants below CMC. In such cases, catalysis/inhibition occurs at the surfactant concentration lower than that for CMC.

According to the results reported on oxidation by permanganate,²⁵ it is proposed that the alkali combines with permanganate to form an alkali-permanganate species $[\text{MnO}_4\text{OH}]^{2-}$, in a pre equilibrium step, which reacts with L-arginine or reacting species of the substrate in a slow step to form a free radical. The free radical further reacts with another permanganate species in a fast step to yield the products.

On the basis of above facts and experimental results, a common mechanism for the oxidation of methionine/proline by potassium permanganate may be represented as follows,



Scheme 1.

According to *Scheme 1*, in absence of the surfactants the rate of disappearance of MnO_4^- may be given as

$$-\frac{d[\text{MnO}_4^-]}{dt} = k_3[\text{I}] \quad (1)$$

Again, from steps (i) and (ii), we have

$$[\text{X}] = K_1 [\text{MnO}_4^-] [\text{OH}^-] \quad (2)$$

and

$$[\text{I}_1] = K_2 [\text{AA}] [\text{X}] = K_1 K_2 [\text{AA}] [\text{MnO}_4^-] [\text{OH}^-] \quad (3)$$

Now, the total concentration of $[\text{MnO}_4^-]$ at any time may be given as,

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-] + [\text{X}] + [\text{I}_1] \quad (4)$$

From equations (2), (3) and (4), the $[\text{MnO}_4^-]$ at any time in terms of $[\text{MnO}_4^-]_{\text{T}}$ may be given as,

$$[\text{MnO}_4^-] = \frac{[\text{MnO}_4^-]_{\text{T}}}{\{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{AA}][\text{OH}^-]\}} \quad (5)$$

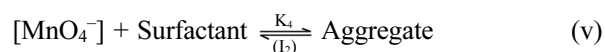
and, therefore, $[\text{I}_1]$ is give as,

$$[\text{I}_1] = \frac{K_1 K_2 [\text{AA}][\text{OH}^-][\text{MnO}_4^-]_{\text{T}}}{\{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{AA}][\text{OH}^-]\}} \quad (6)$$

On substituting the value of $[\text{I}_1]$ from equation (6), the rate law (1), becomes as,

$$-\frac{d[\text{MnO}_4^-]}{dt} = \frac{k_3 K_1 K_2 [\text{AA}][\text{OH}^-][\text{MnO}_4^-]_{\text{T}}}{\{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{AA}][\text{OH}^-]\}} \quad (7)$$

In presence of surfactant, spectrophotometric evidence has been observed for an aggregate formation between KMnO_4 and the surfactant. The following equilibrium (step v) may be considered for the aggregation



In presence of the surfactant, the total concentration of MnO_4^- at any time will be as,

$$[\text{MnO}_4^-]_{\text{T}} = [\text{MnO}_4^-] + [\text{X}] + [\text{I}_1] + [\text{I}_2] \quad (8)$$

and thus, $[\text{MnO}_4^-]$ in terms of $[\text{MnO}_4^-]_{\text{T}}$ may be given as,

$$[\text{MnO}_4^-]_{\text{T}} = \frac{[\text{MnO}_4^-]_{\text{T}}}{\{1 + K_1[\text{OH}^-] + K_1 K_2 [\text{AA}] + K_4[\text{Surfactant}]\}} \quad (9)$$

and the rate of disappearance is given as,

$$-\frac{d[\text{MnO}_4^-]}{dt}$$

$$= \frac{k_3 K_1 K_2 [AA][OH^-][MnO_4^-]_T}{\{1 + K_1 [OH^-] + K_1 K_2 [AA] + K_4 [Surfactant]\}} \quad (10)$$

The rate law (10) explains all the experimental results i.e. first order dependence of rate with respect to oxidant, a fractional order of reaction in OH⁻ and substrate and a retarding effect of the surfactant on the rate of oxidation. An observed positive salt effect is also in agreement with the proposed mechanism (Scheme 1, step ii).

The inhibition effect of the surfactant on the rate of oxidation can be explained on the basis of the association or complex formation between the reacting species of KMnO₄ and surfactants and electrostatic interactions. The hydrophobic interactions were responsible for association/binding between KMnO₄ and the non-ionic surfactant. In case of ionic surfactant, electrostatic interactions also becomes dominating. In case of NaLS, because of the similar changes on the surfactant and MnO₄⁻ species, there was repulsion between them and this opposed the association. A less observed inhibition effect of NaLS on the rate of disappearance of KMnO₄ or on k_{obs} was in agreement. However, in case of CTAB, which is a cationic surfactant, association involved interactions between oppositely charged species and because of attractive forces, the association between the cationic surfactant and MnO₄⁻ dominated. This resulted in a greatest inhibition effect of CTAB on the k_{obs}. This is also supported by the complex formation/association between KMnO₄ and surfactant (Fig. 5) where the absorbance of the complex between CTAB and KMnO₄ is maximum while that between NaLS and KMnO₄ is minimum.

CONCLUSION

The inhibitory effect of surfactants on the rate of oxidation of proline and methionine by alkaline KMnO₄ has been observed. The inhibitory effect was observed due to the formation/association of an inactive aggregate between MnO₄⁻ (oxidant) and surfactant. Electrostatic forces of attraction/repulsion and hydrophobic forces play the important role in the inhibition effect of the surfactants.

Acknowledgments. Publication cost of this paper was supported by the Korean Chemical Society.

REFERENCES

1. Fendler, J. H.; Fendler, E. H. *Catalysis in Micellar and Micromolecular Systems*; Academic Press: New York, 1975.
2. Romsted, L. S. In *Micellization, Solubilization and Micro-*

- emulsion*; K. L. Mittal, Ed.; Plenum: New York, 1977; Vol. 2.
3. Das, A. K. Micellar Effect on the Kinetics and Mechanism of Chromium(VI) Oxidation of organic Substrates. *Coordination Chem. Review* **2004**, *248*, 81.
4. Buntan, C. A. The Dependence of Micellar Rate Effects upon Reaction Mechanism. *Advances in Colloids and Interface Science* **2006**, *123*, 333.
5. Khan, M. N. *Micellar Catalysis; Surfactant Science Series*; Taylor and Frances: London, New York, 2006.
6. Upadhyay, S. K.; Kambo, N.; Shukla, R. Micellar Effect in Redox Reactions. *Current Focus on Colloids and Surfaces* **2009**, 345–389.
7. Panigrahi, G. P.; Swain, R. Kinetics and Mechanism of Oxidation Hydroxyl Amine Hydrochloride by Vanadium(V) in the Presence of Sodium Lauryl Sulphate. *Indian J. Chem. Sect. A* **2001**, *40*, 1191.
8. Din, K. U.; Hartani, K.; Khan, Z. Micellar Catalysis on the Redox-Reactions of Glycolic acid with Chromium (VI). *Int. J. Chem. Kinetics* **2001**, *33*, 377.
9. Din, K. U.; Morshed, A.; Mohammad, A.; Khan, Z. Micellar Effects of on the Chromium(VI) Oxidation of D(+)-Xylose. *Inorg. React. Mech. (USA)* **2002**, *3*, 255–266.
10. Pandey, S.; Upadhyay, S. K. Effect of Cationic Micellar Aggregates on the Kinetics of Oxidation of Aminoalcohols by N-Bromosuccinimide in Alkaline Medium. *J. Colloid. Inter. Sci.* **2005**, *285*, 789.
11. Pandey, E.; Upadhyay, S. K. Effect of Micellar Aggregates on the Kinetics of Oxidation alpha Amino Acid by Chloramine-T in Perchloric Acid Medium. *Colloids Surfaces A* **2005**, *269*, 7.
12. Panda, J.; Panigrahi, G. P. Kinetics of Cationic Micelle Catalyzed Oxidation of Cyclohexane by Vanadium(V). *J. Ind. Chem. Soc.* **2002**, *79*, 58.
13. Malik, M. A.; Alo-thabaiti, S. A.; Khan, Z. Kinetics of Oxidation D-Glucose by Permannaganate in Aqueous Solution of Cetyl Trimethyl Ammonium Bromide. *J. Colloid. Inter. Sci.* **2009**, *337*, 9–14.
14. Khan, Z.; Din, K. U. Kinetics and Mechanism of Oxidation D-Glucose by Chromium(VI) in Perchloric Acid. *Ind. J. Chem.* **2000**, *39A*, 522–527.
15. Shukla, R.; Upadhyay, S. K. Inhibition Effect of {Surfactant-Substrate} Aggregation on the Rate of Oxidation of Reducing Sugars by Alkaline Hexacyanoferrate(III); A Kinetic Study. *Int. J. Chem. Kinet.* **2007**, *39*, 595.
16. Shukla, R.; Upadhyay, S. K. Non-ionic Micellar Inhibition on the Rate of Oxidation of L-Histidine by Alkaline Hexacyanoferrate(III). *Ind. J. Chem.* **2008**, *47A*, 551.
17. Gautam, A.; Kambo, N.; Upadhyay, S. K.; Singh, R. P. Anionic Gemini Surfactant viz. Sodium Salt of bis(1-Dodecyl succinamic acid); Synthesis, Surface Properties And micellar Effect of Oxidation of Reducing Sugars by Hexacyanoferrate(III). *Colloids Surf., A* **2007**, *296*, 117.
18. Kambo, N.; Upadhyay, S. K. Antagonism in (Conventional Anionic-Gemini Anionic) Mixed Catalysed Oxida-

- tion of D-Fructose by Alkaline Chloramine-T; A Kinetic study. *Int. J. Chem Kinet.* **2009**, *41*, 123.
19. Rosen, M. J.; Dahanayake, M. Industrial Utilization of Surfactants: Principle and Practice; AOCS: 2000.
 20. Shukla, R.; Upadhyay, S. K. Tween-80 Micellar Catalysed Oxidation of Methionine and Proline by Alkaline Hexacyanoferrate(III). *Colloid Surf. A* **2008**, *331*, 245.
 21. Harley, C. S.; Collie, B.; Samis, C. S. Transport Numbers of Paraffine-Chain Salts in Aqueous Solution Part-1 Measurement of Transport Numbers of Cetyl Pyridinium and cetyl Trimethylammonium Bromide and Their Interpretation in Terms of Micelle Formation, with Some Data Also for Cetane Sulphuric Acid. *Trans Faraday Soc.* **1936**, *32*, 795.
 22. Menger, F. M.; Portnoy, C. E. Chemistry of Reactions Proceeding Inside Molecular Aggregate. *J. Am. Chem. Soc.* **1967**, *89*, 4698.
 23. Hølemberg, K.; Jonson, B.; Kromberg, B.; Lindman, B. *Surfactants and Polymer in Aqueous Solution*: Sweden, Stockholm, 1997.
 24. Feigl, F. *Spot Test in Organic Analysis*; Elsevier Publishing Co: New York, 1956; pp 208–236.
 25. Dash, S.; Patel, S.; Mishra, B. K. Oxidation by Permanganate: Synthetic and Mechanistic Aspects *Tetrahedron.* **2009**, *65*, 707–739.
 26. Menger, F. M.; Bender, M. L. The Effect of Charge Transfer Complexation on the Hydrolysis of Some Carboxylic Acid Derivatives. *J. Am. Chem. Soc.* **1966**, *88*, 131.
 27. Cordes, E. H.; Gilter, C. *Reaction Kinetics in Presence of Micelle-Forming Surfactant in Progress in Bio. Organic Chemistry*; Kaiser, E. T., Kezdy, F. J. Wiley: New York, 1973; Vol. 2.
-