Inhibitory Effect of {Surfactant- MnO4−} Aggregation in KMnO4 Oxidation of Proline and Methionine: A Kinetic Study

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(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 oxiadation L-proline and L-methionine by alkaline KMnO4. 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, KMnO4, Proline, Methionine

INTRODUCTION

The surfactants may affect[1−7] 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 catalysis[8−16] or micellar inhibition[17−19] has been observed during various electron- transfer reactions.

The oxidation of proline and methionine by alkaline hexacyanofeerate(III) (one- electron transfer oxidant) has been found[20] 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 KMnO4 (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 KMnO4 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 KMnO4 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 KMnO4 in presence of anionic (sodium lauryl sulphate; NaLS) cationic (cetyl trymethyl 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] NaLS[22] and Tween-80,[23] respectively.

To a reaction mixture containing appropriate quantities of solutions of KMnO4, NaOH, surfactant and required quantity of double distilled water was added so that total volume of mixture was 50 ml after adding substrate (amino
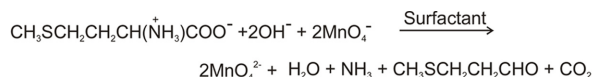
acid). The above reaction mixture was placed in a water bath maintained at desired temperature $\pm 0.1\,°C$. The reaction mixture was allowed to attain the bath temperature and the reaction was then initiated by adding requisite amount of amino acid solution placed separately in the same bath.
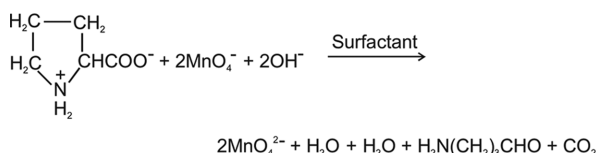
Kinetic Measurement

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:

$$CH_3SCH_2CH_2CH(\overset{+}{N}H_3)COO^- + 2OH^- + 2MnO_4^- \xrightarrow{\text{Surfactant}}$$

$$2MnO_4^{2-} + H_2O + NH_3 + CH_3SCH_2CH_2CHO + CO_2$$

and

$$\begin{array}{c} H_2C - CH_2 \\ | \quad\quad | \\ H_2C \quad CHCOO^- + 2MnO_4^- + 2OH^- \xrightarrow{\text{Surfactant}} \\ \overset{+}{N} \\ | \\ H_2 \end{array}$$

$$2MnO_4^{2-} + H_2O + H_2O + H_2N(CH_2)_3CHO + CO_2$$

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 aminoacid by alkaline $KMnO_4$.[25]

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 ($=k_{obs}/2.303$) of these linear plots.

The rate constants were found to be reproducible within $\pm5\%$ 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 ($\mu=0.05$ mol dm^{-3}) maintained by sodium perchlorate. The results of effect of substrate and alkali on the rate constant were identical (*Table* 2).
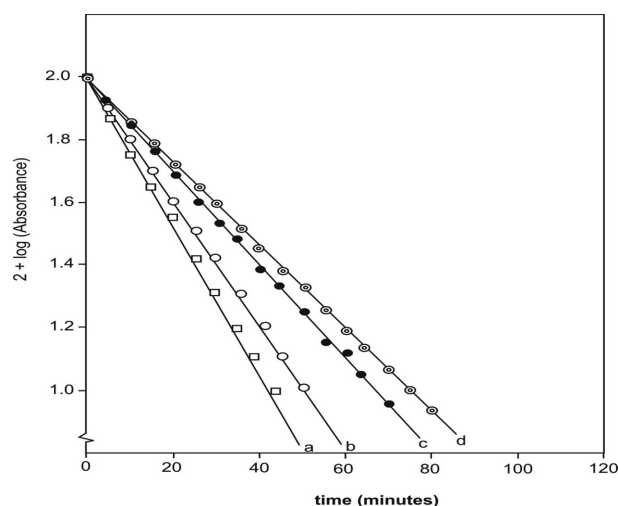

***Figure* 1.** log (Absorbance) versus time plots i.e. pseudo first-order plots in $KMnO_4$ at 35 $°C$. [Substrate] = 2.0×10^{-3} mol dm^{-3}, [$KMnO_4$] = 4.0×10^{-4} mol dm^{-3}, [NaOH] = 10.0×10^{-3} mol dm^{-3}, a, b, c and d represents the plots in presence of aqueous medium, 6.90×10^{-3} mol dm^{-3}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

***Table* 1.** Effect of [$KMnO_4$] on the observed rate constant (k_{obs}) at 35 $°C$

[$KMnO_4$] $\times 10^4$	(k_{obs}) $\times 10^4$ (s^{-1})							
	Proline				Methionine			
	$k_{aq.}$	k_{NaLS}	k_{CTAB}	$k_{Tween-80}$	$k_{aq.}$	k_{NaLS}	k_{CTAB}	$k_{Tween-80}$
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

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

Table 2. Effect of [Substrate] and [OH$^-$] on kobs at 35 $^\circ$C

[Substrate] $\times 10^3$ (mol dm^{-3})	[NaOH] $\times 10^4$ (mol dm^{-3})	(kobs) $\times 10^4$ (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

[KMnO$_4$] = 4.0 $\times$ 10^{-4} mol dm^{-3}, [NaLS] = 6.90 $\times$ 10^{-3} mol dm^{-3}, [CTAB] = 0.55$\times$ 10^{-4} mol dm^{-3} and [Tween-80] = 10.5 $\times$ 10^{-3} mol dm^{-3}.
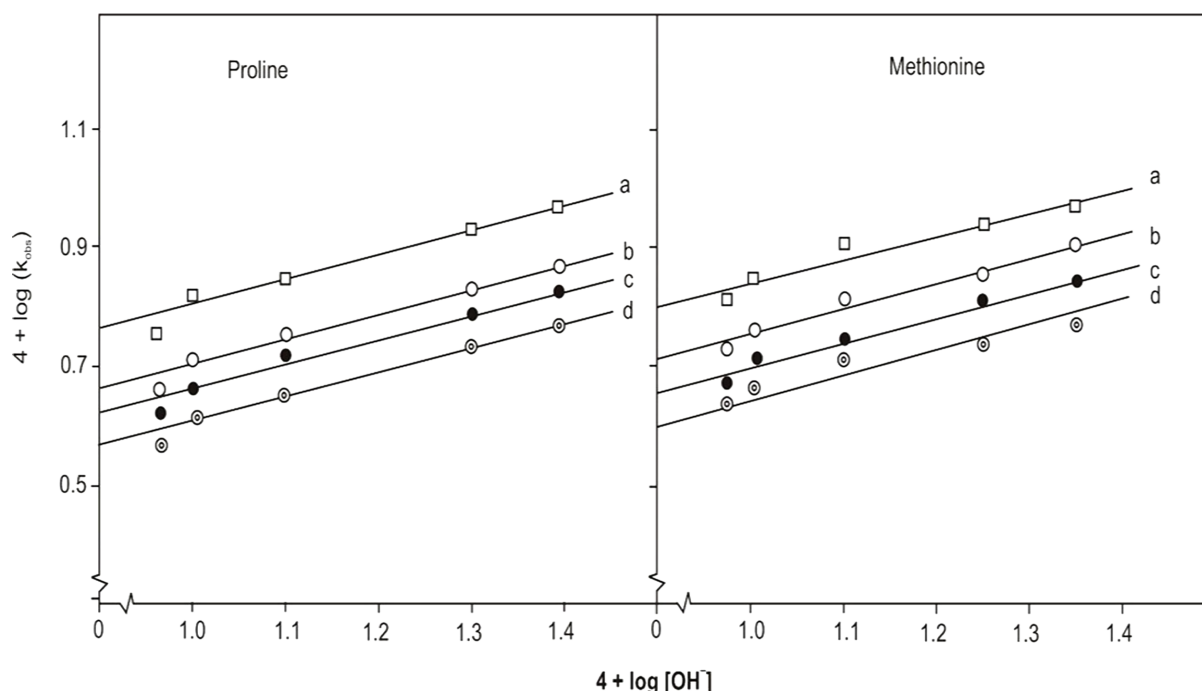
Figure 2. Plots of log k$_{obs}$ versus log [OH$^-$] at 35 $^\circ$C. [Substrate] = 2.0 $\times$ 10^{-3} mol dm^{-3}, [KMnO$_4$] = 4.0 $\times$ 10^{-4} mol dm^{-3}. a, b, c and d are same as in *Fig. 1*.

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 $^\circ$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 NaClO$_4$ in the reaction mixture (*Table* 3). The values of second-order rate constants {k$_{obs}$/[MnO$_4^-$]} 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 $\Delta G^{\#}$ for both the substrate (amino acid) suggests a common mechanism for the oxidation
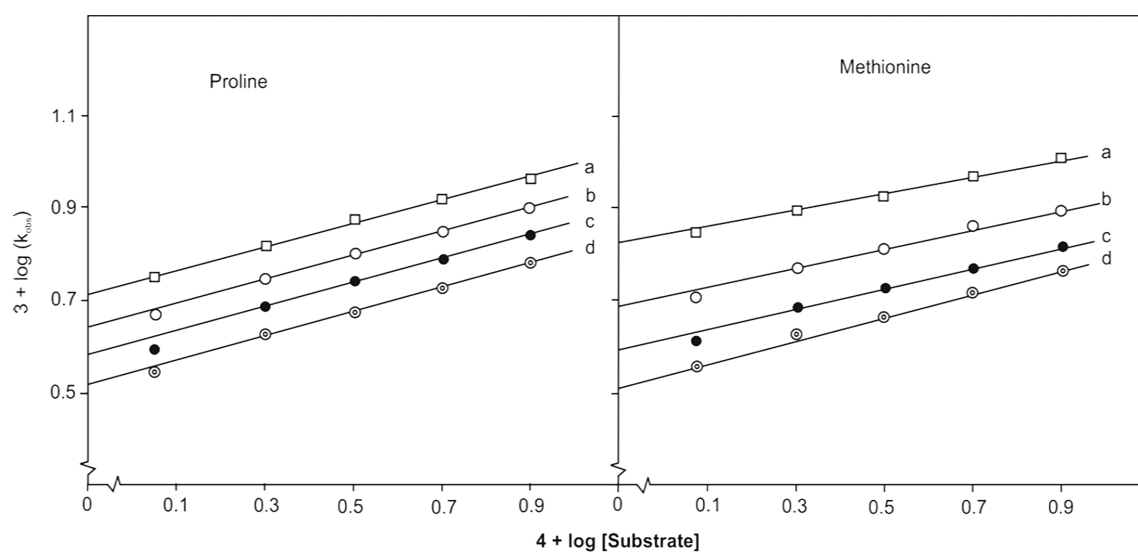
Figure 3. Plots of log k_{obs} versus log [Substrate] at 35 °C. [KMnO$_4$] = 4.0 × 10^{-4} mol dm^{-3}, [NaOH] = 10.0 × 10^{-3} mol dm^{-3}. a, b, c and d are same as in *Fig*. 1.
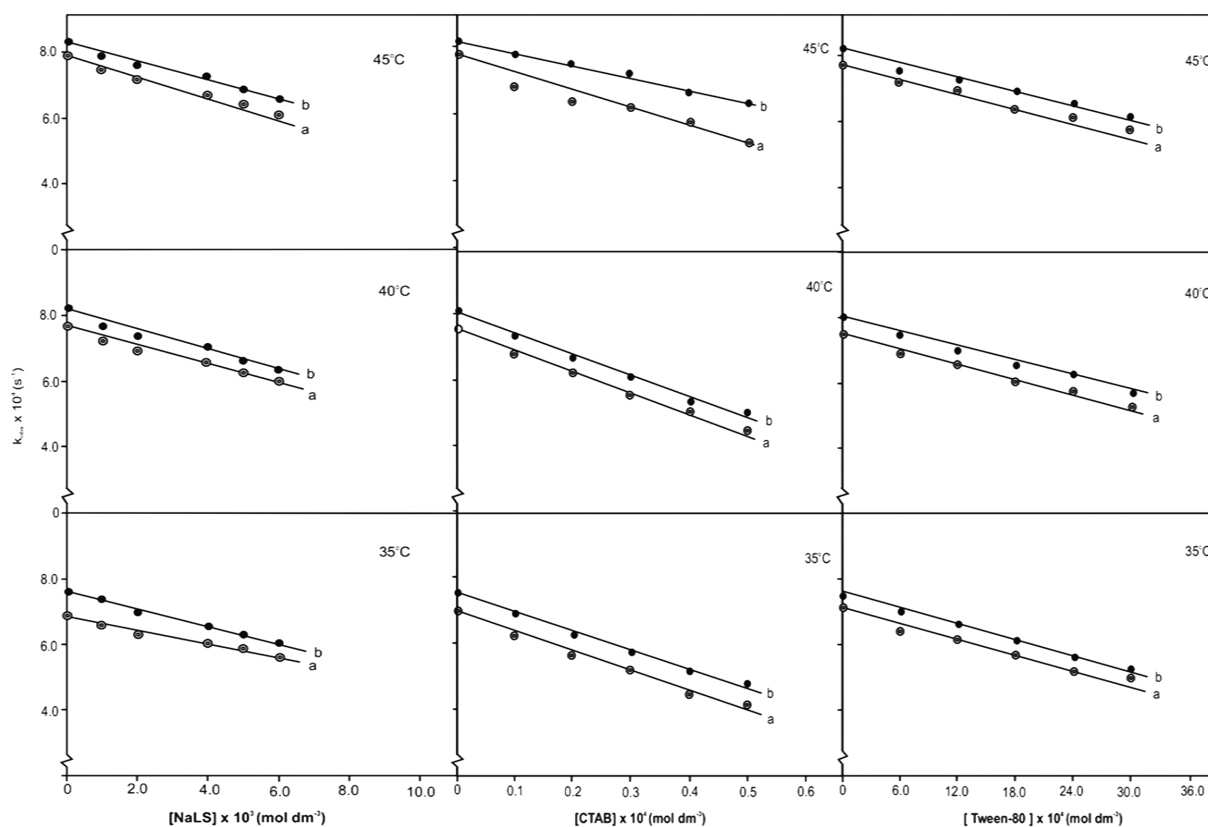
Figure 4. Plots of (k_{obs}) versus [Surfactant] at 35, 40 and 45 °C. [Substrate] = 2.0 × 10^{-3} mol dm^{-3}, [KMnO$_4$] = 4.0 × 10^{-4} mol dm^{-3}, [NaOH] = 10.0 × 10^{-4} mol dm^{-3}. a: methionine, b: proline.

process. The negative value of ΔS$^#$ indicates the compactness of transition state.

Free Radical Testing

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

***Table* 3.** Effect of [NaClO$_4$] on the observed rate constant at 35 °C

[NaClO$_4$] × 10^2 (mol dm^{-3})	(kobs) × 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

[KMnO$_4$] = 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

[KMnO$_4$] = 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.
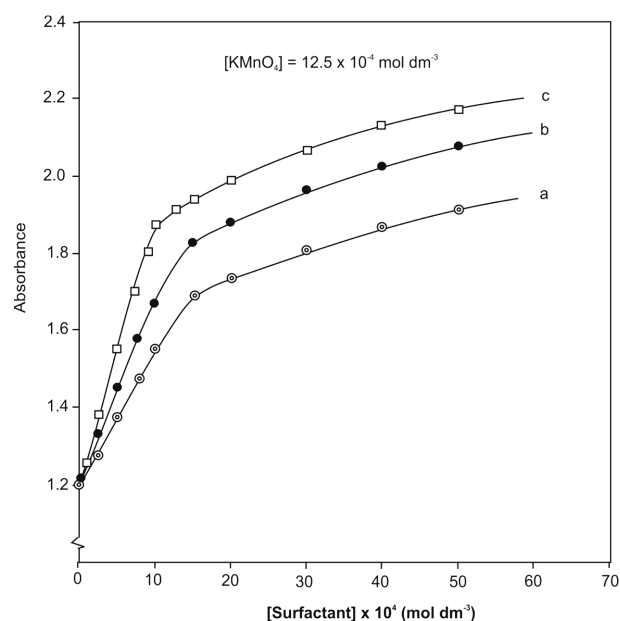
***Figure* 5.** Plots of (Absorbance) versus Surfactant at room tempertature = 30 °C. a: NaLS; b: Tween-80; c: CTAB.

Evidence for Complex Formation Between KMnO$_4$ and Surfactant

In order to confirm any association or binding between the surfactant and KMnO$_4$, the absorbance of a series of solutions containing a fixed amount of KMnO$_4$ (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 KMnO$_4$ (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]:[KMnO$_4$] ratio becomes nearby unity and then it tends to become constant. The results clearly indicate a 1:1 association between KMnO$_4$ 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
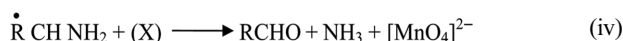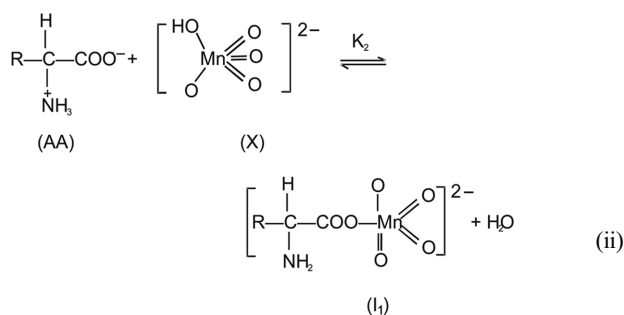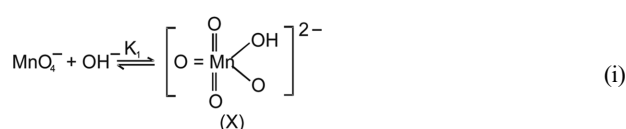
of water insoluble colloidal MnO_2.

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 evidences[27] 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-permanaganate species $[MnO_4.OH]^{2-}$, 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,

(i)

(ii)

$(I_1) \xrightarrow{k_3} \dot{R}\,CH\,NH_2 + CO_2 + [MnO_4]^{2-}$ (iii)

$\dot{R}\,CH\,NH_2 + (X) \longrightarrow RCHO + NH_3 + [MnO_4]^{2-}$ (iv)

Scheme 1.

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

$$-\frac{d[MnO_4^-]}{dt} = k_3[I] \tag{1}$$

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

$$[X] = K_1\,[MnO_4^-]\,[OH^-] \tag{2}$$

and

$$[I_1] = K_2\,[AA]\,[X] = K_1K_2\,[AA][MnO_4^-][OH^-] \tag{3}$$

Now, the total concentration of $[MnO_4^-]$ at any time may be given as,

$$[MnO_4^-]_T = [MnO_4^-] + [X] + [I_1] \tag{4}$$

From equations (2), (3) and (4), the $[MnO_4^-]$ at any time in terms of $[MnO_4^-]_T$ may be given as,

$$[MnO_4^-] = \frac{[MnO_4^-]_T}{\{1 + K_1[OH^-] + K_1K_2[AA][OH^-]\}} \tag{5}$$

and, therefore, $[I_1]$ is give as,

$$[I_1] = \frac{K_1K_2[AA][OH^-][MnO_4^-]_T}{\{1 + K_1[OH^-] + K_1K_2[AA][OH^-]\}} \tag{6}$$

On substituting the value of $[I_1]$ from equation (6), the rate law (1), becomes as,

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3K_1K_2[AA][OH^-][MnO_4^-]_T}{\{1 + K_1[OH^-] + K_1K_2[AA][OH^-]\}} \tag{7}$$

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

$$[MnO_4^-] + \text{Surfactant} \underset{(I_2)}{\overset{K_4}{\rightleftharpoons}} \text{Aggregate} \tag{v}$$
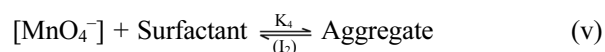
In presence of the surfactant, the total concentration of MnO_4^- at any time will be as,

$$[MnO_4^-]_T = [MnO_4^-]\,[X] + [I_1] + [I_2] \tag{8}$$

and thus, $[MnO_4^-]$ in terms of $[MnO_4^-]_T$ may be given as,

$$[MnO_4^-]_T = \frac{[MnO_4^-]_T}{\{1 + K_1[OH^-] + K_1K_2[AA] + K_4[\text{Surfactant}]\}} \tag{9}$$

and the rate of disappearance is given as,

$$-\frac{d[MnO_4^-]}{dt}$$

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

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 KMnO$_4$ and surfactants and electrostatic interactions. The hydrophobic interactions were responsible for association/binding between KMnO$_4$ 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 MnO$_4^-$ species, there was repulsion between them and this opposed the association. A less observed inhibition effect of NaLS on the rate of disappearance of KMnO$_4$ 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 MnO$_4^-$ dominated. This resulted in a greatest inhibition effect of CTAB on the k$_{obs}$. This is also supported by the complex formation/association between KMnO$_4$ and surfactant (*Fig.* 5) where the absorbance of the complex between CTAB and KMnO$_4$ is maximum while that between NaLS and KMnO$_4$ is minimum.

CONCLUSION

The inhibitory effect of surfactants on the rate of oxidation of proline and methionine by alkaline KMnO$_4$ has been observed. The inhibitory effect was observed due to the formation/association of an inactive aggregate between MnO$_4^-$ (oxidant) and surfactant. Electrostatic forces of attraction/repulsion and hydrophobic forces play the important role in the inhibition effect of the surfactants.

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