INHIBITION EFFECT OF SURFACTANTS IN ALKALINE KMnO_4 OXIDATION OF DISACCHARIDES; A KINETIC STUDY

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ABSTRACT

An inactive premicellar/micellar {Surfactant- MnO_4^- } aggregate has been found to inhibit the rate of oxidation of disaccharides viz. maltose and lactose by alkaline KMnO_4 . The order of reaction in oxidant is unity while that in Substrate and alkali has been found to decrease from unity at higher [Substrate] and $[\text{OH}^-]$, respectively. The observed rate constants were in order of $k_{\text{aq}} > k_{\text{NaLS}} > k_{\text{Tx-100}} > k_{\text{CTAB}}$, which has been explained in terms of electrostatic and hydrophobic forces.

Keywords: Surfactants, Inhibition, KMnO_4 , Disaccharides, Kinetics.

INTRODUCTION

The permanganate oxidation process is eco-friendly and gained importance in green chemistry. The synthetic and mechanistic aspects of permanganate have recently been discussed by Mishra et al¹. Due to biological importance of carbohydrates to living organism

the kinetics of oxidation of sugars have also been a subject of extensive research²⁻¹⁰. Micelles have become a subject of great interest¹¹⁻¹⁷ to the organic chemists because of their unusual catalysis of organic reactions and to biochemists because of their similarity to biological membrane and globular proteins. The reaction in micellar media may follow two patterns, one in which the surfactants provides a medium for reaction but does not participate in it. The second type includes the reactions in which the surfactant does participate directly in the reaction, either as a catalyst or a substrate.

In some cases an inhibition effect of surfactants on the rate of oxidation of organic compounds has been observed¹⁸⁻²² due to formation of inactive {substrate-surfactant} aggregates. However, an inhibition effect of surfactants on the rate of oxidation of glucose and fructose (monosaccharides) by alkaline KMnO_4 was found²³, due to formation of inactive { KMnO_4 -Surfactant} aggregates. It was, therefore, thought worthwhile to extend the study in case of disaccharides in order to understand mechanistic aspects of the reaction. In the present investigation the kinetics of oxidation of two disaccharides viz maltose and lactose by alkaline KMnO_4 in presence of anionic surfactant (sodium lauryl sulphate, NaLS), cationic surfactant (cetyl tri-methyl ammonium bromide, CTAB) and non-ionic surfactant (TritonX-100, Tx-100) have been studied and the results are reported in the present communication.

EXPERIMENTAL

Permanganate (MnO_4^-) was prepared by dissolving potassium permanganate (KMnO_4) (GR grade Loba; Mumbai, India) in doubly distilled water. Freshly prepared solutions of D-maltose and D-lactose (AR Thomas Baker, Mumbai, India) in doubly distilled water were used through out the experiments.

The surfactants NaLS (AR, s.d. fine Mumbai, India) CTAB and Tx-100 (AR, Thomas Baker, Mumbai, India) were used as such. However, their critical micelle concentrations (CMC) were, determined by surface tension measurement, were obtained as $8.2 \times 10^{-3} \text{ mol dm}^{-3}$, $9.6 \times 10^{-4} \text{ mol dm}^{-3}$ and $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ for NaLS, CTAB and Tx-100, respectively at 25°C . The values of CMC were matching with reported values of CMC which are $8.0 \times 10^{-3} \text{ mol dm}^{-3}$, $9.8 \times 10^{-4} \text{ mol dm}^{-3}$ and $1.6 \times 10^{-4} \text{ mol dm}^{-3}$ in case of NaLS²⁴, CTAB²⁵ and Tx-100²⁶, respectively at 25°C . All other reagents viz. sodium hydroxide (NaOH), sodium nitrate (NaNO_3) etc. were used of AR grade. All the solutions including that of surfactants were prepared in doubly distilled water.

Method:-

To a reaction mixture containing appropriate quantities of solutions of KMnO_4 , NaOH, NaNO_3 , surfactants and required amount of doubly distilled water was added so that the total volume of mixture was 50 ml after adding substrate (maltose/lactose). The reaction mixture was then placed in a water bath maintained at desired temperature $\pm 0.1^\circ\text{C}$. The reaction mixture was allowed to attain the bath temperature. The reaction was then initiated by adding requisite

amount of maltose/lactose placed separately in the same bath. The rates were measured by monitoring the absorbance due to KMnO_4 as function of time at 520 nm (λ_{max} of KMnO_4) on a spectrophotometer (Toshniwal, TVSP-25, India).

The absorbance due to other substance i.e. surfactants, substrate etc was negligible. The concentration of KMnO_4 was kept within the limits of Beer's law.

Determination of Rate Constants:-

The reactions were studied at different initial concentrations of reactants in absence as well as in the presence of surfactants. The log (Absorbance) versus time plots (Fig.1) was found to be good straight lines, suggesting a first order dependence of rate with respect to MnO_4^- .

Fig.1: log (Absorbance) vs time i.e. pseudo-first order plots in KMnO_4 at 35°C . [Substrate] = $20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$, a, b, c and d represents the plots in aqueous medium in presence of $7.0 \times 10^{-3} \text{ mol dm}^{-3}$ [NaLS], in presence of $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ Tx-100 and in presence of $0.50 \times 10^{-4} \text{ mol dm}^{-3}$ CTAB, respectively.

Therefore, the pseudo-first order rate constants in MnO_4^- (k_{obs}) have been evaluated from the slopes of these straight lines. The reported rate constant data, represented as an average of duplicate runs, were reproducible to within $\pm 5\%$.

Stoichiometry and Product Analysis:

The stoichiometry of the reactions between maltose/lactose and alkaline KMnO_4 in absence as well as in presence of surfactants has been studied. The reaction mixtures containing a large excess of MnO_4^- over maltose/lactose in alkaline medium in presence and absence of surfactants were kept for 72 h at

40°C until the reaction was complete. Estimation of unreacted MnO_4^- showed that 1 mol of maltose or lactose consumes 12 mols of MnO_4^- .

Chromotropic acid (1, 8-dihydro-naphthalene-3, b-disulfonic acid) was added to reaction mixture. The development of a violet pink colour confirmed the presence of formic acid in the reaction mixture²⁷. The Formation of lower sugar has also been reported earlier²⁸. Thus the products of lactose and maltose under the kinetic conditions are formic acid corresponding lower sugars.

RESULTS AND DISCUSSIONS

Although the oxidation of some monosaccharide's by alkaline MnO_4^- is reported²⁹, in order to compare the kinetic results of oxidation of maltose and lactose by alkaline MnO_4^- with those in presence of surfactants we have investigated the detail kinetics of reactions in absence as well as in presence of surfactants at constant ionic strength (0.2 mol dm^{-3}) maintained by NaNO_3 .

The observed pseudo first order rate constants in absence and in the presence of each surfactant at various $[\text{MnO}_4^-]_0$ remained identical (Table 1) confirming the first order dependence of rate with respect to $[\text{MnO}_4^-]$.

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

$[\text{KMnO}_4] \times 10^4$	$(k_{\text{obs}}) \times 10^4 (\text{s}^{-1})$							
	Maltose				Lactose			
	k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$	k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$
3.0	3.10	2.75	2.15	2.45	3.15	2.85	2.40	2.75
4.0	3.18	2.80	2.15	2.40	3.15	2.80	2.45	2.75
5.0	3.10	2.75	2.20	2.40	3.10	2.85	2.45	2.75
6.0	3.10	2.80	2.15	2.45	3.15	2.85	2.40	2.80

$[\text{Maltose}] = [\text{Lactose}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{CTAB}] = 0.50 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaLS}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{Tx-100}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$.

The results of effect of [Substrate] and $[\text{OH}^-]$ on the observed rate constants were identical (Table 2). The plots of (k_{obs}) versus [Substrate] or $[\text{OH}^-]$ showed derivation from linearly at higher concentration of substrate or OH^- . However, the plots of $(1/k_{\text{obs}})$ versus $1/[\text{Substrate}]$ (Fig.2) and plots of $(1/k_{\text{obs}})$ versus $1/[\text{OH}^-]$ (Fig.3) were linear with positive intercepts. The observed results suggest that the order of reaction in substrate and alkali decreases from unity at higher [Substrate] and $[\text{OH}^-]$, respectively.

Table-2: Effect of [Substrate] and $[\text{OH}^-]$ on k_{obs} at 35°C.

$[\text{Substrate}] \times 10^3 (\text{mol dm}^{-3})$	$[\text{NaOH}] \times 10^4 (\text{mol dm}^{-3})$	$(k_{\text{obs}}) \times 10^4 (\text{s}^{-1})$							
		Maltose				Lactose			
		k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$	k_{aq}	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$
5.0	10.0	2.16	2.00	0.75	1.50	2.50	2.08	1.58	1.75
10.0	10.0	2.53	2.49	1.90	1.66	2.91	2.66	2.00	2.16
15.0	10.0	2.83	2.68	2.20	2.08	3.08	2.75	2.16	2.50
20.0	10.0	3.10	2.80	3.10	2.40	3.15	2.80	2.40	2.75
30.0	10.0	3.91	3.75	4.05	7.50	4.25	3.91	3.50	3.16
40.0	10.0	2.58	2.30	4.95	2.08	2.50	7.50	1.85	1.91
20.0	2.5	2.75	2.80	0.85	2.25	3.10	2.83	2.50	2.98
20.0	5.0	3.08	2.75	1.50	9.41	3.75	3.41	3.08	3.76
20.0	15.0	3.25	3.00	4.20	2.66	8.08	3.65	3.50	3.66
20.0	20.0	3.66	3.30	5.30	3.08	4.25	3.91	3.25	3.75

$[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaLS}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CTAB}] = 0.50 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{Tx-100}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Tx-100, respectively. It is observed from the results that (k_{obs}) decreases on increasing the [Surfactant]. The retarding effect of NaLS and CTAB on the rate of oxidation (or on k_{obs}) has been observed below CMC of the surfactants. However, the inhibition effect of [Tx-100] on the rate of oxidation (or on k_{obs}) was observed at above the CMC ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) of the surfactant. The intercepts of the plots of (k_{obs}) versus [Surfactant] (Fig. 4-6) were matching with the observed rate constants at [Surfactant] = 0.

The effect of ionic strength on the rate of oxidation was investigated by varying the concentration of NaNO_3 and keeping other reactants at a fixed concentration. The observed rate constants (k_{obs}) are reported in (Table 3). The value of k_{obs} was found increased with an increase in NaNO_3 concentration,

suggesting an involvement of similar charged ions in the rate determining step.

The activation parameters ($\Delta E_{\text{act}}^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$) in presence as well as in absence of the surfactants have been evaluated using Arrhenius and Eyring equations with second order rate constant determined at 35, 40, 45°C and are reported in (Table 4). The large values of $\Delta E_{\text{act}}^\ddagger$ and $\Delta H^\ddagger$ in presence of surfactants in comparison to those in aqueous medium are in consistent with the accepted view that the slow reaction (in the presence of surfactants) would require a higher $\Delta E_{\text{act}}^\ddagger / \Delta H^\ddagger$. The entropy of activation $\Delta S^\ddagger$ in the presence of surfactants is less negative, which suggests that the reactants become relatively more rigid in presence of surfactants. This is not surprising in view of the binding association of one of the reactants (MnO_4^-) with surfactants.

Table-3: Effect of added $[\text{NaNO}_3]$ on the observed rate constant at 35°C.

$[\text{NaNO}_3] \times 10^2$ (mol dm ⁻³)	$(k_{\text{obs}}) \times 10^4$ (s ⁻¹)							
	Maltose				Lactose			
	$k_{\text{aq.}}$	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$	$k_{\text{aq.}}$	k_{NaLS}	k_{CTAB}	$k_{\text{Tx-100}}$
5.0	2.16	2.08	1.75	1.83	3.00	7.00	1.83	1.91
10.0	3.08	3.75	2.16	2.41	3.16	2.83	4.41	2.75
20.0	3.16	2.91	-8.66	2.83	3.50	3.08	7.83	9.91

$[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Substrate}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaLS}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CTAB}] = 0.50 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{Tx-100}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$.

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

temperature	second order rate constants (mol ⁻¹ dm ³ s ⁻¹)							
	Maltose				Lactose			
	aq.	NaLS	CTAB	Tx-100	aq.	NaLS	CTAB	Tx-100
308 K	0.78	0.69	0.54	0.60	0.79	0.70	0.40	0.68
313 K	0.92	0.73	0.62	0.65	0.96	0.74	0.65	0.70
318 K	1.02	0.80	0.70	0.73	1.06	0.79	0.71	0.81
Activation Parameters								
$E_{\text{act}} \pm 0.25$ (kJ mol ⁻¹)	11.5	19.4	13.4	17.3	14.4	21.0	15.3	17.3
$\text{DH}^\# \pm 0.25$ (kJ mol ⁻¹)	8.9	16.7	10.8	14.7	11.8	18.5	12.7	14.7
$-\text{DS}^\# \pm 1.00$ (JK ⁻¹ mol ⁻¹)	247.9	224.6	244.8	232.2	238.4	218.8	238.2	231.1
$\text{DG}^\# \pm 0.50$ (kJ mol ⁻¹)	86.5	87.0	88.8	87.2	86.4	87.0	87.6	87.0

$[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Substrate}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$, $[\text{NaLS}] = 7.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CTAB}] = 0.50 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{Tx-100}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Fig.2: Plots of $(1/k_{\text{obs}})$ vs $1/[\text{Substrate}]$ at 35°C. $[\text{KMnO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$. a, b, c and d are same as in Fig.1.

The effect of each surfactant on the rate of oxidation has been studied at three different temperature viz. 35, 40 and 45°C. The results are represented graphically in form of plots of (k_{obs}) versus $[\text{Surfactant}]$ in Fig.4, Fig.5 and Fig.6 in case of NaLS, CTAB and

Mechanism:

A first order dependence of rate with respect to each alkali and substrate at lower $[\text{OH}^-]$ and $[\text{Substrate}]$, respectively in absence as well as in presence of

Fig.3: Plots of $(1/k_{\text{obs}})$ vs $1/[\text{OH}^-]$ at 35°C. $[\text{KMnO}_4] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Substrate}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$. a, b, c and d are same as in Fig.1.

the surfactants, indicate the enolization of reducing sugar.

In absence of the other reactants these anions undergo epimerization and isomerization to form mixture of aldoses and ketoses (The Lobry de Bruyn alberda Van Ekenstion Transformations Aldoses and ketoses generally yield a mixture of Z- and E- enediols, the proportion of which differ from sugar to sugar and experimental conditions viz. Strength and nature of alkali and temperature. In presence of an oxidant or a catalyst, the enediol anion has been

considered as the reactive species of the reducing sugar. There are evidences³⁰ for the formation of small complexes between surfactant molecules and substrate as oxidant at the concentration of the surfactant below CMC. In such instances the catalysis or inhibition occurs at the surfactant concentrations lower than that for CMC.

Fig.4: Plots of (k_{obs}) vs [NaLS] at 35, 40 and 45°C. [Substrate] = $20.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{NaOH}] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{NaNO}_3] = 0.2 \text{ mol dm}^{-3}$, a, maltose; b, lactose.

Fig.5: Plots of (k_{obs}) vs [CTAB] at 35, 40 and 45°C. Other conditions are same as in Fig.4

Fig.6: Plots of (k_{obs}) vs [Tx-100] at 35, 40 and 45°C. Other conditions are same as in Fig.4.

The inhibition effect of surfactants on the rate of oxidation of reducing sugars by alkaline hexacyanoferrate(III) ($\text{Fe}(\text{CN})_6^{3-}$) has been explained² on the basis of formation of [Substrate-Surfactant] aggregates and its inactivity towards $\text{Fe}(\text{CN})_6^{3-}$. However, in the present investigations, the reactions have been studied in high ionic strength. The kinetic results are also different. The premicellar inhibition has been observed in case of both the ionic surfactants viz. NaLS and CTAB; it therefore, appears that reactions follow a different mechanism. On the basis of the observed kinetic results, it appears that the surfactant molecules form an inactive aggregate with MnO_4^- i.e. $\{\text{MnO}_4^- - \text{Surfactant}\}$ aggregates.

Thus, a common mechanism for oxidation of disaccharides by alkaline KMnO_4 in presence of surfactants may be proposed as given in scheme 1.

Scheme 1

In Absence of Surfactants

Steps (i), (ii) and (iii) of Scheme 1 represents the mechanism in absence of surfactants. According to Scheme 1, the rate of disappearance of MnO_4^- in absence of surfactant may be given as,

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

where, $[I] = K_2 [E^-] [MnO_4^-]$, (from step (ii)) – (2)

and $[E^-] = K_1 [Sugar] [OH^-]$, (from step (i)) – (3)

and, therefore; $[I] = K_1 K_2 [Sugar] [OH^-] [MnO_4^-]$ – (4)

Further the total concentration of $[MnO_4^-]$ in absence of surfactant, is given as,

$$[MnO_4^-]_T = [MnO_4^-] + [I] \quad - (5)$$

On substituting the value of $[I]$ in equation (5) and solving it, the value of $[I]$ in terms of $[MnO_4^-]_T$ may be obtained as,

$$[I] = \frac{K_1 K_2 [Sugar] [OH^-] [MnO_4^-]_T}{1 + K_1 K_2 [Sugar] [OH^-]} \quad - (6)$$

On substituting the value of $[I]$ in equation (1), the rate law becomes,

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3 K_1 K_2 [Sugar] [OH^-] [MnO_4^-]_T}{1 + K_1 K_2 [Sugar] [OH^-]} \quad - (7)$$

The rate law (7) suggests, first order dependence of rate with respect to $[MnO_4^-]$ and a decrease of order of reaction from unity to zero in substrate and OH^- at higher concentration of reducing sugar and OH^- , respectively. The experimental results in absence of the surfactant are in agreement with rate law (7). A positive effect of ionic strength is also in favour of the proposed mechanism.

In Presence of Surfactants:

In presence of surfactant, the step (iv) of the proposed mechanism (Scheme 1) is also operative and, therefore, total concentration of $[MnO_4^-]_T$ may be given as

$$[MnO_4^-]_T = [MnO_4^-] + [I] + [X] \quad - (8)$$

where,

$$[X] = K_4 [Surfactant] [MnO_4^-] \text{ (from step (iv))}$$

Thus, by finding the $[I]$ in terms of $[MnO_4^-]_T$ and substituting its value in equation (1), the rate law become,

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_3 K_1 K_2 [Sugar] [OH^-] [MnO_4^-]_T}{1 + K_1 K_2 [Sugar] [OH^-] + K_4 [Surfactant]} \quad (9)$$

The rate law (9) suggests a retarding effect of surfactant on the rate of reaction, which has also been observed experimentally.

The formation of aggregate/complex between MnO_4^- and surfactant depends on electrostatic and hydrophobic forces. In case of NaLS, the electrostatic repulsion between negatively charged MnO_4^- and anionic surfactant opposes the binding between NaLS and MnO_4^- . Thus in case of NaLS hydrophobic interaction favours the binding whereas electrostatic repulsion opposes it. Consequently the binding between NaLS and MnO_4^- should be much less and therefore, the retarding effect of NaLS should be less.

In case of CTAB, the electrostatic attraction between MnO_4^- and positively charged surfactant favor the binding between MnO_4^- and CTAB in addition to hydrophobic interactions. Thus the aggregation or complex formation will dominate and in case of CTAB. Consequently retarding effect of CTAB on the rate of reaction should be very high.

There are no electrostatic interaction with polar head groups of non-ionic surfactants i.e. triton X-100. The poly (oxyethylene) head groups of non-ionic surfactants play a significant role in favoring the incorporation or solubilization of the MnO_4^- in the micelles. The binding between the MnO_4^- and triton X-100 should be between NaLS and CTAB.

CONCLUSION

A premicellar inhibition of anionic and cationic surfactants and a micellar inhibition of non-ionic surfactant has been observed in the alkaline $KMnO_4$ oxidation of disaccharides.

The observed experimental rate constants in NaLS, CTAB and Tx-100 are in order of

$$k_{aq} > k_{NaLS} > k_{TX-100} > k_{CTAB}$$

suggesting highest retardation of rate by CTAB. The experimental results

are in agreement with the proposed mechanism. Thus the inhibition effect is observed due to formation of inactive premicellar/micellar {Surfactant- MnO_4^- } aggregates.

REFERENCES

1. S. Dash, S. Patel, B. K. Mishra, Tetrahedron, **65**, 707-739, (2009).
2. R. Shukla, S. K. Upadhyay, International J. Chemical Kinetics, **39(11)**, 595-604, (2007).
3. A. K. Das, S. K. Mandal, Das. Inorg. React. Mech. **3(1)**, 63-72, (2001).
4. H. Singh, A. Gupta, A. Singh, B. Singh, Transition Metal Chemistry, **23(3)**, 277-281, (1998).
5. K. Venkata, P.R. Jaya, Transition. Metal. Chem. **20**, 344-346, (1995).
6. A. S. Ogunlaja, E. O. Odeunmi, S. O. Owolude, The pacific Journal and Technology, **10(1)**, 451-461, (2009).
7. H. K. Okaro, E. O. Odeunmi, Scientific Research and Essays, **5(17)**, 2588-2594, (2010).
8. E. O. Odeunmi, S. O. Owolude, J. Chem. Soc. Nigeria. **30(2)**, 187-191, (2005).
9. N. Kambo, S. K. Upadhyay, Transition Metal Chemistry. **25**, 461-464, (2000).
10. H.K. Okaro, E. O. Odeunmi, International Journal of Physical Sciences. **4(9)**, 471-476, (2009).
11. J. H. Fendlar, E. J. Fandler, Catalysis in Micellar and Macromolecular System, Academic Press, New York, 1975.
12. K. K. Sundram, M. Cratzel, Kinetics and Catalysis in Micro molecular System, 1975.
13. I. V. Berezin, K. Martinek, A. K. Yatsimirsky, Catalysis. Russ. Chem. Rev. **42(2-3)**, 787-802, (1973).
14. M.N. Khan, Micellar Catalysis, Taylor and Francis, London, New York, 2000.
15. A. Kithara, Advance Colloid. Interface Science. **12(2-3)**, 109-140, (1980).
16. J. H. Fendler, Membrane Mimetic Chemistry, Wiley Interscience, New York, 1982.
17. C. A. Buntan, Catal. Rev. Sci. Eng. **20(1)**, 1-56, (1979).
18. G. P. Panigrahi, R. Swain, Indian J. Chem. **40**, 1191, (2001).
19. G. P. Panigrahi, S. K. Mishra, Indian J. Chem. **32A** (11), 956-960, (1991).
20. A. K. Das, Inorg. React. Mech. **1**, 161-168, (1999).
21. A. K. Das, A. Roy, B. Saha, M. J. Das, Chem. Res(S) 334-335, (2001).
22. A. K. Das, A. Roy, B. Saha, M. J. Das, Chem. Res(S), 62-64, (2001).
23. E.O. Odeunmi, S.A. Iwarere, S. O. Owolude, International Jour. Chem, **16(3)**, 167-176, (2006).
24. F.M. Menger, C.E. Portnoy, J. Am. Chem. Soc. **89(18)**, 4698-4703, (1967).
25. G.S. Hartley, B. Collie, C.S. Samis, Trans Faraday Soc. **32**, 795-815, (1936).
26. I. T. Yeon, M. M. Gosh, C. D. Cose, Robinson, K. G. Environ Sci. Technol. **29** (12), 3015-3021, (1995).
27. A.G. Fadnis, S. K. Kulshrestha, Carbohydrate Res, **112**, 137, (1983).
28. E. O. Odeunmi, S. O. Owolude, J. Trans. Chem. Soc, **5**, 623, (2008).
29. R. Tripathi, N. Kambo, S.K. Upadhyay, J. Disp. Sci. Tech, (2012) (in press).
30. E.H. Cordes, C. Gilter, In Progress in Bio-organic Chemistry, E.T. Kaiser, F. J. Kezdy, Wiley, New York, 1973.