Alkaline KMnO₄ Oxidation of Reducing Sugars in Microemulsions: Inhibition Effect of Surfactants¹

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Abstract—The kinetics of oxidation of reducing sugars viz. D-glucose and D-fructose by alkaline KMnO₄ in microemulsion media was investigated. The aqueous, cationic microemulsion was prepared from cetyl trimethyl ammonium bromide, *n*-butanol, *n*-hexane and water, whereas *n*-decane, aerosol-OT and water were used to prepare the anionic microemulsion. The order of reaction in oxidant was always found to be unity, while that in substrate and alkali was decreased from unity to zero at higher concentrations substrate and alkalirespectively. On decreasing [H₂O]/[Surfactant] ratio (increasing surfactant content) in microemulsion, the observed rates constants of oxidation (k_{obs}) were decreased. The inhibition effect on the rate of oxidation was greater in cationic microemulsion. A mechanism consistent with kinetic data is proposed.

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In last two decades, the microemulsion was used as a novel reaction media for the organic reactions due to their large solubilisation capacities [1, 2]. The organic reactions in microemulsion media [3–12] were widely investigated and it was observed that the rate of chemical reaction can be drastically modified by introduction of colloidal particles changing the local microenvironment. It was also found [13] that the enhancement of the rate of reaction in microemulsion is usually larger than that in micellar media.

Recently it was reported [14–16] that an addition of a surfactant (anionic, cationic, non-ionic) in the reaction mixture resulted in the retardation of the rate of oxidation of reducing sugars/amino acids by alkaline KMnO₄. The formation of an inactive complex between surfactant and KMnO4 was found to be responsible for the inhibition effect of the surfactant on the rate of oxidation in the reaction. Spectrophotometric evidence also supported complexation/association between the surfactant and KMnO₄. Since the presence of the droplets can multiply enhance or retard chemical reaction rates, the application of microemulsions as molecular scale reactors in the above reactions may be interesting. In this context we chose to study the kinetics of the oxidation of some reducing sugars viz. glucose and fructose by alkaline KMnO⁴ in microemulsion media. The goal of the study was motivated by the following conditions:

(1) the kinetics behavior of the above reactions in aqueous and micellar media is well known [14–16];

(2) a pH of the microemulsion was the same as that of the aqueous solutions indicating that the presence of microemulsion in reaction mixture does not affect its pH;

(3) the reagents are the ionic species of same sign as well as of opposite sign.

In the present communication, the kinetics results of oxidation of reducing sugars vis. glucose and fructose by alkaline $KMnO_4$ in cationic microemulsion (prepared from cetyl trimethyl ammonium bromide, **CTAB**) and anionic microemulsion (prepared from aerosol-OT, AOT) are reported and discussed.

EXPERIMENTAL

Materials

Permanganate solution was prepared by dissolving potassium permanganate (GR, Loba, India) in doubly distilled water. Freshly prepared solutions of D-glucose and D-fructose (AR, Thomas Baker, India) were used in the experiments. The surfactants viz. cetyl trimethyl ammonium bromide and aerosol-OT (Thomas Baker) were used as received. However, their critical micelles concentrations (CMC) were determined by surface tension measurements and were in agreement with their reported values. All other reagents and solvents used were of analytical grade. Doubly distilled water, prepared from alkaline KMnO₄, was used throughout the experiments for the preparation of solutions.

Two types of microemulsion were used and were prepared as follows.

¹ The article is published in the original.

The cationic microemulsion was prepared from combination (in weight percent) of cationic surfactant CTAB (30%), co-surfactant *n*-butanol (4.5%), oil phase *n*-hexane (1.5%) and water (64%). By mixing the components in the appropriate proportion the microemulsion was prepared and the solution was stirred vigorously until a clear transparent solution was obtained [17].

The anionic microemulsion was prepared [18] by mixing decane : aerosol-OT : water in weight percent composition 80:10:10. The solution was stirred vigorously to obtain a perfectly microemulsion. The values of pH of microemulsions were determined by directly immersing a glass electrode into microemulsion solutions. The pH of microemulsion was same as that of the aqueous solutions.

Method

To a reaction mixture, containing appropriate quantities of KMnO₄, NaOH, NaNO₃, microemulsion was added so that the total volume of mixture was 50 ml after adding substrate. The reaction mixture was stirred well and then placed in a water bath maintained at a desired temperature ($\pm 0.1^{\circ}$ C). The reaction mixture was allowed to attain the bath temperature. The reaction then was initiated by adding requisite amount of substrate placed separately in the same bath.

Determination of Rate Constant

The rates were measured spectrophotometrically, by monitoring the absorbance due to KMnO₄ as a function of time at 520 nm (λ_{max} of KMnO₄) on a spectrophotometer Toshniwal TVSP-25 (India). The absorbance due to other reagents was negligible at 520 nm. The concentration of KMnO₄ was kept within the limits of Beer's law.

The reactions were studied at different initial concentrations of the reactants. When the natural log of absorbance vs. time plots was plotted, each reaction showed a linear relationship with a negative slope up to 85–90%, suggesting a first-order dependence of reaction rate with respect to MnO_4^- . Therefore, pseudo first-order rate constants in MnO_4^- (k_{obs}) were evaluated from the slopes (slope = $k_{obs}/2.303$) of the straight lines (r > 0.99) plotted as log of absorbance vs. time. The reported rate constant data, represent as an average of duplicate runs, were reproducible to within $\pm 5\%$.

Stoichometry and Product Analysis

The reaction mixture containing an excess amount of KMnO₄ over the substrate in the presence of alkali in aqueous as well as in microemulsion media were kept for 72 h at 40°C.

The stoichiometric results showed that a mole of substrate (glucose or fructose) consumes 2 moles of

 MnO_4^- . The results may be represented by the following stoichiometric equations:

RCHOHCHO +
$$2OH^- + 2MnO_4^-$$

 $\rightarrow 2MnO_4^{2-} + H_2O + RCHOHCOOH,$
RCOCH₂OH + $2OH^- + 2MnO_4^-$
 $\rightarrow 2MnO_4^{2-} + H_2O + HCHO + RCOOH.$

The presence of corresponding aldonic acid and formaldehyde (in the case of fructose) as the oxidation products was identified by the spot tests. The results are also in agreement with the earlier reported data [14–16] on the oxidation of reducing sugars by KMnO₄ in aqueous and micellar media. The reaction mixture, when stored for a long time, did not contain formaldehyde in case of fructose and stoichiometric results showed that a mole of fructose consumed more

than 3 moles of MnO_4^- , indicating that formaldehyde is further oxidized in the presence of excess of oxidant.

RESULTS AND DISCUSSION

In all kinetics measurements, the substrate (glucose or fructose) was used in excess relative to KMnO₄ to ensure pseudo-first-order conditions. Although the oxidation of glucose and fructose by alkaline $KMnO_4$ in aqueous and micellar media are reported [14], in order to compare the results with those in microemulsions media, the kinetic results obtained in aqueous media are included in the present communication. The reaction has been studied at various initial concentrations of the reactants and pseudo first-order rate constants (k_{obs}) were evaluated from the slopes of straight lines plotted as log of absorbance vs. time.

The observed rate constants (k_{obs}) at various initial concentrations of KMnO₄ are shown in Table 1. The identical values of k_{obs} at various [KMnO₄] confirmed the first-order dependence of the reaction rate with respect to $[MnO_4^-]$.

The results of effect the [Substrate] and [OH⁻] on the observed rate constant were identical. The plots of $k_{\rm obs}$ vs. [Substrate] or [OH⁻] showed a deviation from linearity at higher concentrations of substrate or OH⁻. However, the plots of $1/k_{obs}$ vs. 1/[Substrate] (Fig. 1) and plots of $1/k_{obs}$ vs. $1/[OH^-]$ (Fig. 2) were linear with positive intercepts. It can be therefore inferred that the order of reaction in substrate and alkali decreases from unity at higher [Substrate] and [OH⁻], respectively.

Varying the concentration of NaNO₃ and keeping other reactants at a fixed concentration the effect of ionic strength on the rate of oxidation was stadied. The observed rate constants are reported in Table 2. An increase in of k_{obs} was observed with an increasó in [NaNO₃].

	$k_{\rm obs} imes 10^4$, s ⁻¹						
$[KMnO4] \times 10^4, mol/dm^3$		glucose		fructose			
	aqueous medium	anionic microemulsion	cationic microemulsion	aqueous medium	anionic microemulsion	cationic microemulsion	
3.0	6.15	4.45	4.05	6.50	5.50	4.40	
4.0	6.15	4.40	3.85	6.35	5.40	4.60	
5.0	5.90	4.60	3.85	6.35	5.50	4.60	
6.0	6.15	4.40	4.05	6.50	5.40	4.40	

Table 1. Effect of [KMnO₄] on the observed rate constants at 35°C

 $[Substrate] = 20.0 \times 10^{-3} \text{ mol/dm}^3, [NaNO_3] = 0.2 \text{ mol/dm}^3, [NaOH] = 10.0 \times 10^{-4} \text{ mol/dm}^3.$

Table 2. Effect of added [NaNO₃] on the observed rate constants at 35°C

	$k_{\rm obs} imes 10^4, { m s}^{-1}$						
$[NaMnO_4] \times 10^4, mol/dm^3$		glucose		fructose			
	aqueous medium	anionic microemulsion	cationic microemulsion	aqueous medium	anionic microemulsion	cationic microemulsion	
0.05	2.95	2.60	2.45	3.50	3.00	2.75	
0.10	4.40	3.65	2.80	5.00	4.00	3.20	
0.20	6.15	4.40	3.85	6.35	5.50	4.60	
0.30	4.90	4.90	4.20	6.50	5.65	5.20	

 $[Substrate] = 20.0 \times 10^{-3} \text{ mol/dm}^3, [KMnO_4] = 4.0 \times 10^{-4} \text{ mol/dm}^3, [NaOH] = 10.0 \times 10^{-4} \text{ mol/dm}^3.$

The effect of microemulsion on the rate of oxidation was studied at three different temperatures (35, 40 and 45°C) and at different $[H_2O]/[Surfactant]$ ratio in microemulsions. The k_{obs} at different $[H_2O]/[Surfac$ tant] ratio in case of cationic and anionic microemulsions are given in Tables 3 and 4, respectively. It can be seen that k_{obs} decrease on decreasing $[H_2O]/[Surfac$ tant] ratio. Thus, it is evident from the result that on increasing the surfactant content or on decreasing the water content in the microemulsion, the k_{obs} decreases.

The reactions have also been studied at different temperatures (35, 40 and 45° C) to investigate the



Fig. 1. Plots of $1/k_{obs}$ versus 1/[Substrate] in aqueous medium (1), in the presence of anionic microemulsion (2) and cationic microemulsion (3). $[KMnO_4] = 4.0 \times 10^{-4} \text{ mol/dm}^3$, $[NaOH] = 10.0 \times 10^{-3} \text{ mol/dm}^3$, $[NaNO_3] = 0.2 \text{ mol/dm}^3$, 35° C.

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Fig. 2. Plots of $1/k_{obs}$ versus $1/[OH^-]$ in aqueous medium (1), in the presence of anionic microemulsion (2) and cationic microemulsion (3). [Substrate] = 20.0×10^{-3} mol/dm³, [KMnO₄] = 4.0×10^{-4} mol/dm³, [NaNO₃] = 0.2 mol/dm³, 35°C.

	$k_{\rm obs} \times 10^4, {\rm s}^{-1}$						
[H ₂ O]/[Surfactant]	glucose			fructose			
	35°C	40°C	45°C	35°C	40°C	45°C	
Aqueous medium	6.15	6.70	7.29	6.50	6.92	7.86	
33.25	5.71	6.10	6.38	6.00	6.60	7.21	
15.95	5.50	5.65	5.85	5.79	6.36	6.60	
10.11	4.70	5.18	5.45	5.01	5.83	6.41	
7.28	4.10	4.85	5.20	4.83	5.75	6.01	
5.55	3.83	4.41	4.90	4.60	4.82	5.41	

Table 3. Effect of [H₂O]/[Surfactant] ratio in cationic microemulsion on the observed rate constants at different temperatures

 $[Substrate] = 20.0 \times 10^{-3} \text{ mol/dm}^3, [KMnO_4] = 4.0 \times 10^{-4} \text{ mol/dm}^3, [NaOH] = 10.0 \times 10^{-4} \text{ mol/dm}^3, [NaNO_3] = 0.2 \text{ mol/dm}^3.$

Table 4. Effect of $[H_2O]/[Surfactant]$ ratio in anionic microemulsion on the observed rate constants at different temperatures

	$k_{\rm obs} imes 10^4, { m s}^{-1}$						
[H ₂ O]/[Surfactant]	glucose			fructose			
	35°C	40°C	45°C	35°C	40°C	45°C	
Aqueous medium	6.15	6.70	7.29	6.50	6.90	7.86	
10.65	5.80	6.33	6.90	6.14	6.71	7.48	
5.10	5.20	5.80	6.33	6.01	6.52	6.71	
3.25	5.00	5.37	5.80	5.90	6.20	6.33	
2.33	4.60	5.20	5.60	5.80	6.00	6.14	
1.78	4.41	4.80	5.37	5.70	5.60	6.00	

 $[Substrate] = 20.0 \times 10^{-3} \text{ mol/dm}^3, [KMnO_4] = 4.0 \times 10^{-4} \text{ mol/dm}^3, [NaOH] = 10.0 \times 10^{-4} \text{ mol/dm}^3, [NaNO_3] = 0.2 \text{ mol/dm}^3.$

 Table 5. Second-order rate constants at different temperatures

Temperature, K	Second-order rate constants, $dm^3 mol^{-1} s^{-1}$							
		glucose		fructose				
	aqueous medium	anionic microemulsion	cationic microemulsion	aqueous medium	anionic microemulsion	cationic microemulsion		
308	1.53	1.10	0.95	1.58	1.34	1.15		
313	1.67	1.11	1.10	1.72	1.39	1.20		
318	1.82	1.34	1.22	1.96	1.48	1.35		

 $[Subdtrate] = 20.0 \times 10^{-3} \text{ mol/dm}^3, [KMnO_4] = 4.0 \times 10^{-4} \text{mol/dm}^3, [NaOH] = 10.0 \times 10^{-4} \text{mol/dm}^3, [NaNO_3] = 0.2 \text{ mol/dm}^3.$

effect of temperature and to evaluate the activation parameters. The second order rate constants $(k_{obs}/[MnO_4^-])$ at different temperatures are reported in Table 5. The activation parameters $\Delta E^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$, evaluated with the help of Arrehenius and Eyring plots can be also found in Table 6. The large values of $\Delta E^{\#}$ and $\Delta H^{\#}$ obtained in microemulsion in comparison to those found in aqueous medium are consistent with the accepted view that slower reactions (in microemulsion) would require higher $\Delta E^{\#}$ or $\Delta H^{\#}$. A lower negative value derived from experiments in microemulsions indicates a relatively higher extent of rigidness for the reactants in microemulsions. Nearly the same value of $\Delta G^{\#}$ is in favour of suggestion that a

		Glucose		Fructose			
Parameter	aqueous medium	anionic microemulsion	cationic microemulsion	aqueous medium	anionic microemulsion	cationic microemulsion	
$\Delta E^* \pm 0.25$, kJ/mol	17.5	21.4	24.2	19.6	22.0	23.0	
$\Delta H^{\#} \pm 0.25$, kJ/mol	14.8	18.8	21.4	17.0	19.4	20.5	
$-\Delta S^* \pm 1.00$, J K ⁻¹ mol ⁻¹	243.4	235.5	229.7	236.2	236.5	228.7	
$\Delta G^{\#} \pm 0.50$, kJ/mol	91.0	92.6	93.0	90.9	93.2	92.0	

 Table 6. Activation parameters evaluated by the Arrenius and Eyring plots

common mechanism is operative in the oxidation reactions.

In alkaline medium, the formation of enediol anion of monosaccharides proceeds as follows:

$$\begin{array}{cccc} H & H & OH & H & O^{-} \\ H - C - OH & C & C \\ L & C = O & H & C & OH \\ R & R & R & R \\ Fructose & Enediol (E) & Enediol anion (E^{-}) \end{array}$$

In the absence of other reactants these anions undergo epimerization and isomerization to form a mixture of aldoses and ketoses (Lobry de Bruyn– Alberda–van Ekenstion transformation). Aldoses and ketoses generally yield a mixture of Z- and E-enediols, the proportion of which differs from one sugar to another and are dependent on experimental conditions such as the strength and the nature of alkali and temperature. In the presence of an oxidant or a catalyst, the enediol anion was considered as a reactive species of the reducing sugar. A higher rate of fructose enolization was explained [19] on the basis of an easy attack on the two active primary H atoms at C(2) of aldoses. The observed rate constants follow the order: k_{obs} (fructose) > k_{obs} (glucose).

The oxidation of reducing sugars by alkaline KMnO₄ in aqueous medium and in the presence of anionic, cationic and non-ionic surfactants was reported [14–16]. The presence of the surfactant in the reaction mixture retards the rate of oxidation of reducing sugars by KMnO₄. The formation of an inactive complex between the surfactant and oxidant, KMnO₄ was responsible for the inhibition effect of surfactant on the rate of oxidation. A spectrophotometric evidence for the complexation/association between surfactant and MnO_4^- also confirmed this suggestion. The inhibition effect of cationic surfactant (CTAB) on the rate of oxidation was more pronounced due to a more favourable association/complexation between negatively charged MnO_4^- and positively charged surfactant.

From the results obtained in the present investigation, i.e. in the oxidation of reducing sugars by KMnO₄ in microemulsions, the following observations can be emphasized:

(1) The kinetic results are similar to those observed in the presence of surfactants. The reaction order in oxidant was always unity while that in alkali and substrate was found to decrease from unity to zero at higher [Alkali] and [Substrate]. The effect of ionic strength on the rate of oxidation was positive.

(2) When a reaction occurs in the microemulsion, its rate is lower than when it takes place in a conventional aqueous medium or in the presence of surfactant. The inhibition effect was also found to be greater in microemulsion medium.

(3) With decreasing $[H_2O]/[Surfactant]$ ratio in the microemulsion, the k_{obs} (and hence the rate of oxidation) also decreases indicating that an increase in the surfactant contents in microemulsion is responsible for decreasing in k_{obs} .

(4) The inhibition effect is more pronounced in case of cationic microemulsion in comparison to that in anionic microemulsion.

On the basis of the above facts and making use of known mechanism for the oxidation process in aqueous surfactant medium, a common mechanism for oxidation in microemulsion may be proposed as

Sugar + OH⁻
$$\stackrel{K_1}{\longleftrightarrow}$$
 E⁻, (I)
(Enediol anion)

$$E^- + MnO_4^- \stackrel{K_2}{\longleftarrow} I^-$$
, II)
(Intermediate)

$$I \xrightarrow{\kappa_3} \text{Products (slow)}, \qquad (III)$$

 $\begin{array}{c} \text{Surfactant} + \text{MnO}_{4}^{-} \xrightarrow{\kappa_{2}} X. \\ \text{(in microemulsion)} & \longleftrightarrow & (\text{Complex}) \end{array} \tag{IV}$

On the basis of above mechanism, the rate of disappearance of $KMnO_4$ may be obtained as

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

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

where $[MnO_4^-]_T = [MnO_4^-] + [I] + [X].$

This rate law explains all the experimental results such as the first-order dependence of reaction rate with respect to MnO_4^- , decrease in the order of reaction from unity to zero in each alkali and substrate and an inhibition effect of surfactant content in micro-emulsion.

It has been observed that the size of the droplets and aggregation number of the surfactants and water molecules depends on molar ratio only. An increase in the surfactants concentration in the medium results in an increased concentration of droplets of the same size and characteristics. And when the concentrations of the other reactants referring to the total system is kept constant, the distribution of the reactants between greater numbers of droplet causes a more strong complexation/association between the surfactant and oxidant ($KMnO_4$). This in turn results in a more pronounced effect on retardation that experiences the reaction rate in microemulsion compared to that observed in aqueous surfactant medium. The greater inhibition effect of surfactant in cationic microemulsion in comparison to that in anionic microemulsion is also observed, which is expected due to a more strong complexation/association between cationic surfactant

and negatively charged oxidant (MnO_4^-) caused by the attractive forces developed between these species.

So, the rate of oxidation of reducing sugars by $KMnO_4$ in anionic and cationic microemulsions was found to be lower than when it takes place in aqueous medium or in the presence of a conventional surfactant. On decreasing $[H_2O]/[Surfactant]$ ratio in the microemulsion, the k_{obs} was found to decrease. The inhibition effect was greater in the case of cationic microemulsion in comparison to that an anionic microemulsion. The association between surfactant

and MnO_4^- has been found to be responsible for the retarding effect on the rate of oxidation.

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