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Effect of ionic and non-ionic surfactants on the reduction of water soluble colloidal MnO_2 by glycolic acid

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Abstract Kinetics of the redox reaction between colloidal MnO_2 and glycolic acid have been studied spectrophotometrically by monitoring the decay in the absorbance of colloidal MnO_2 in absence and presence of surfactants. Anionic sodium dodecyl sulfate has no effect, non-ionic Triton X-100 catalyzed the reaction and experiments were not possible in presence of cationic cetyltrimethylammonium bromide due to the precipitation of MnO_2 . The reaction followed the same type of kinetic behavior, i.e., fractional-, first- and fractional-order dependencies, respectively, in [glycolic acid], $[\text{MnO}_2]$ and $[\text{H}^+]$ in both the

media. Effects of gum arabic and manganese(II) have also been studied and discussed. Mechanisms in accordance with the experimental data are proposed for the reaction.

Keywords Micelles · TX-100 · Glycolic acid · Colloidal MnO_2 · Reduction

Introduction

Manganese dioxide is an oxidant, which has been known for a long time and also as a catalyst in many inorganic and organic reactions [1]. Generally, solid manganese dioxide is prepared from solutions of manganous sulfate, sodium hydroxide and potassium permanganate [2]. Due to the heterogeneity of the manganese dioxide aqueous solution, the kinetics and mechanism of its reactions have not been satisfactorily clarified [3]. It has been established that reduction of permanganate by a number of reductants proceeds through the formation of a brownish-yellow colored intermediate with +4 oxidation state [4–8]. Manganese(IV) is known to form a number of water soluble complexes with organic and inorganic ligands [9–12]. The use of colloidal solutions has been quite successful

to study fast interfacial processes [13]. Perez-Bento et al. [14] had reported a method for the preparation of water soluble colloidal form of manganese dioxide. Consequently, colloidal MnO_2 -organic acid reactions have been studied in some depth focusing on the determination of kinetic parameters [15–17]. Some reports are also available on the reduction of colloidal MnO_2 by carboxylic acids in presence of micelle-forming surfactants [18–21]. The role of surfactants is quite different in micellar catalysis and surface reactions. In such type of reactions, reactants are adsorbed on the surface of the colloidal particles. In continuation to our investigations of micellar effects on the electron-transfer reactions of different metal ion oxidants with a variety of organic reductants [19–27], we undertook the present investigation with a view to gaining an insight into the glycolic acid-colloidal MnO_2 reaction.

Experimental

Materials

Sodium dodecyl sulfate (Sigma, USA, 99%), cetyltrimethylammonium bromide (BDH, UK, 98%), Triton X-100 (Fluka, Switzerland, 99%), potassium permanganate (E. Merck, India, 98.5%), sodium thiosulfate (s.d. fine, India, 99%), glycolic acid (Lancaster, UK, 98%) and manganese(II) sulfate-1-hydrate (E. Merck, India, 99%) were used as received. Double distilled (first time from alkaline KMnO_4), deionized and CO_2 free water was used as solvent. Perchloric acid (E. Merck, India, 70% solution) was used to maintain the $[\text{H}^+]$ constant.

Preparation of water soluble colloidal MnO_2

To prepare the stock solution of colloidal MnO_2 , standardized KMnO_4 ($=5.0 \times 10^{-4} \text{ mol dm}^{-3}$) and sodium thiosulfate ($=1.87 \times 10^{-4} \text{ mol dm}^{-3}$) were used [15, 16]. The resulting solution was dark brown and perfectly transparent and remained stable for several weeks.

Kinetic measurements

The kinetics of MnO_2 -glycolic acid redox reaction was performed under pseudo-first-order conditions with at least a tenfold excess of reductant over oxidant concentration. The reaction vessel containing requisite amounts of reactants was kept immersed in a water bath thermostated at $30 \pm 0.1^\circ\text{C}$ (unless stated otherwise). The progress of the reaction was monitored spectrophotometrically upto not less than 80% completion. The absorbance for disappearance of colloidal MnO_2 was measured at 390 nm with Baush & Lomb Spectronic 20 spectrophotometer. The values of pseudo-first-order rate constants (k_{obs} or k_{ψ} , s^{-1}) were estimated from the slope of log (absorbance) versus time plots.

Results and discussion

Reaction in absence of surfactants

Results of the reduction of water soluble colloidal MnO_2 by glycolic acid are summarized as follows:

(a) The plots of log(absorbance) versus time show that the reaction has complex kinetic features (Fig. 1). Deviation from linearity clearly indicates that the reaction proceeds through the formation of an intermediate which has higher reaction rate in comparison to the parent reaction. The values of pseudo-first-order rate constants were calculated

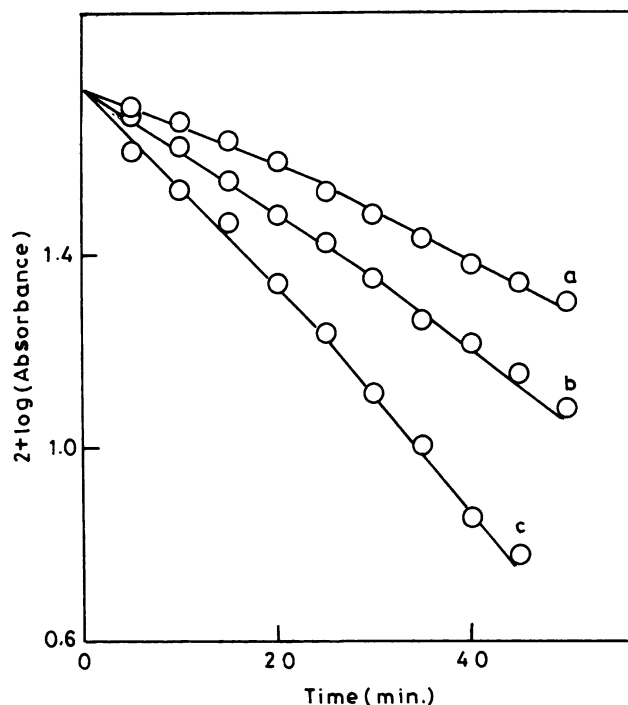


Fig. 1 Plots of log(absorbance) versus time. Reaction conditions: $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, [glycolic acid] = 24(a), 48(b), $96 \times 10^{-3} \text{ mol dm}^{-3}$ (c), $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 30°C

from the slopes of both straight lines (k_{obs1} and k_{obs2} refer to the rate constants of initial and autoacceleration reaction pathways, respectively).

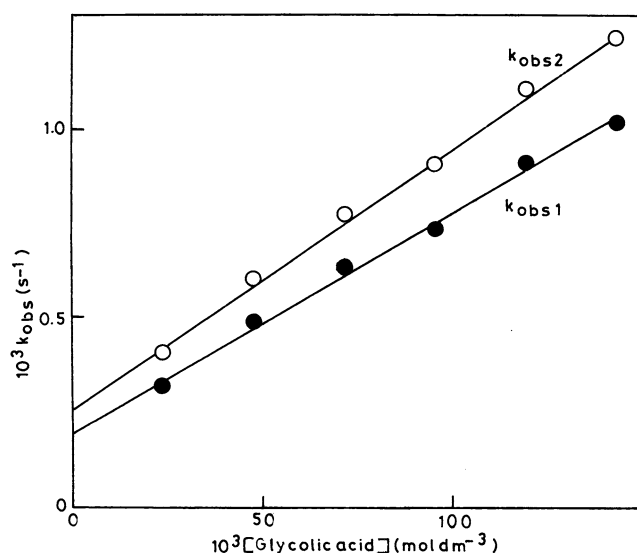
- (b) The k_{obs1} and k_{obs2} decreased with an increase in the initial $[\text{MnO}_2]$ at constant [glycolic acid], $[\text{H}^+]$ and temperature (Table 1). These findings are not in accordance with the norms of pseudo-first-order kinetics. Therefore, a series of kinetic runs were performed in presence of gum arabic but the values were again found to decrease with gum arabic (Table 1). The decrease in rate constants may be due to possible flocculation of colloidal MnO_2 particles.
- (c) The order with respect to glycolic acid was deduced from the values of rate constants obtained at several [glycolic acid] (Table 1, Fig. 2). The plots of log (rate constants) versus log [glycolic acid] are linear with positive slopes = $0.67(k_{\text{obs1}})$ and $0.63(k_{\text{obs2}})$. Thus, the order with respect to [glycolic acid] is fractional each for k_{obs1} and k_{obs2} .
- (d) It was observed that the reaction rate increased markedly with increasing $[\text{HClO}_4]$ (Table 2). The plots of k_{obs1} and k_{obs2} versus $[\text{HClO}_4]$ are shown in Fig. 3. The plots of log (rate constants) versus log $[\text{HClO}_4]$ are linear with slopes = 0.25 and 0.27 for k_{obs1} and k_{obs2} , indicating fractional order dependence on $[\text{H}^+]$ for each step. On the other hand,

Table 1 Pseudo-first-order rate constants for the reduction of colloidal MnO_2 by glycolic acid in the absence and presence of TX-100 ($=15.0 \times 10^{-3} \text{ mol dm}^{-3}$) at $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$ and temperature $= 30^\circ\text{C}$

10 ⁵ [MnO ₂] (mol dm ⁻³)	[gum arabic] (g dm ⁻³)	10 ³ [glycolic acid] (mol dm ⁻³)	Aqueous		TX-100	
			10 ⁴ <i>k</i> _{obs1} (s ⁻¹)	10 ⁴ <i>k</i> _{obs2} (s ⁻¹)	10 ⁴ <i>k</i> _{ψ1} (s ⁻¹)	10 ⁴ <i>k</i> _{ψ2} (s ⁻¹)
2.0	0.0	96.0	9.2	12.8	12.8	16.8
3.2			8.9	12.2	11.5	16.2
4.0			8.7	11.6	11.3	16.0
4.8			8.1	11.0	11.1	15.9
6.0			7.7	10.2	10.5	15.8
7.2			—	—	9.6	15.3
8.0			7.3	9.0	8.3	15.1
10.0			6.6	7.1	—	—
8.0		24.0	3.1	4.0	4.1	6.6
		48.0	4.8	6.0	5.1	9.2
		72.0	6.4	7.7	7.0	11.5
		96.0	7.3	9.0	8.3	15.1
		120.0	9.0	11.0	10.2	16.7
		144.0	10.8	12.3	11.6	19.7
1.0		4.8	Not obsd.			
2.0		4.4	Not obsd.			
3.0		4.2	Not obsd.			
4.0		3.7	Not obsd.			
5.0		3.2	Not obsd.			
6.0		3.0	Not obsd.			

intercepts on y-axis in Fig. 3 clearly suggest the involvement of acid-dependent and acid-independent reaction paths in the reduction of colloidal MnO_2 by glycolic acid. Thus, the rate equation experimentally found was

$$v = \frac{-d[\text{MnO}_2]}{dt} = (k + k'[\text{H}^+]^{0.25})[\text{MnO}_2][\text{glycolic acid}]^{0.67} \quad (1)$$

**Fig. 2** Effect of glycolic acid on the pseudo-first-order rate constants. Reaction conditions: $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature $= 30^\circ\text{C}$

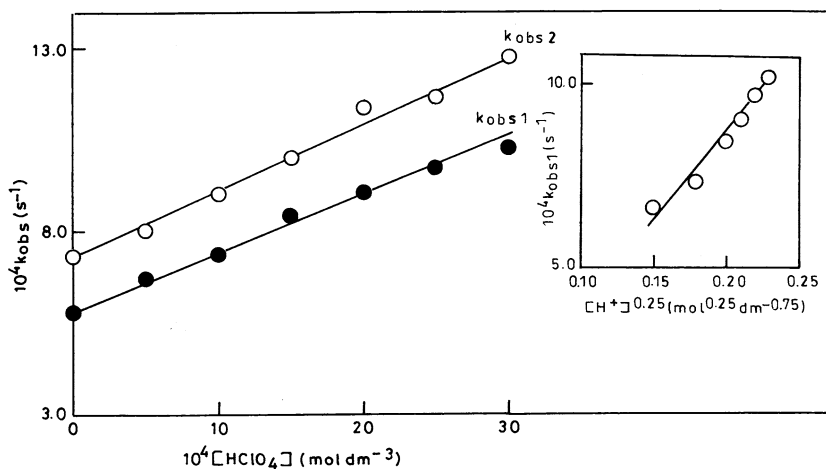
- (e) In order to obtain activation parameters, a series of kinetic runs were also performed at different temperatures ($25\text{--}40^\circ\text{C}$). Arrhenius and Eyring equations were used in evaluating these parameters. The results are summarized in Table 3 along with k_{obs1} and k_{obs2} obtained at different temperatures.
- (f) The effect of externally added Mn(II) was studied over fixed $[\text{glycolic acid}]$, $[\text{MnO}_2]$ and $[\text{H}^+]$ at 30°C . The results (Table 2) indicate that both k_{obs1} and k_{obs2} increase with increase $[\text{Mn(II)}]$. Interestingly, the plot of rate constants versus $[\text{Mn(II)}]$ are sigmoid for the

Table 2 Pseudo-first-order rate constants for the reduction of colloidal MnO_2 by glycolic acid

$10^4 [\text{HClO}_4]$ (mol dm^{-3})	$10^6 [\text{Mn(II)}]$ (mol dm^{-3})	$10^4 k_{\text{obs1}} (\text{s}^{-1})$	$10^4 k_{\text{obs2}} (\text{s}^{-1})$
0.0	0.0	5.8	7.3
5.0		6.6	8.0
10.0		7.3	9.0
15.0		8.4	10.0
20.0		9.0	11.4
25.0		9.7	11.7
30.0		10.2	12.8
0.0	5.0	8.1	10.7
	10.0	8.3	12.1
	20.0	8.5	12.8
	30.0	9.7	14.1
	40.0	10.3	15.5
	50.0	10.7	16.2

$[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature $= 30^\circ\text{C}$

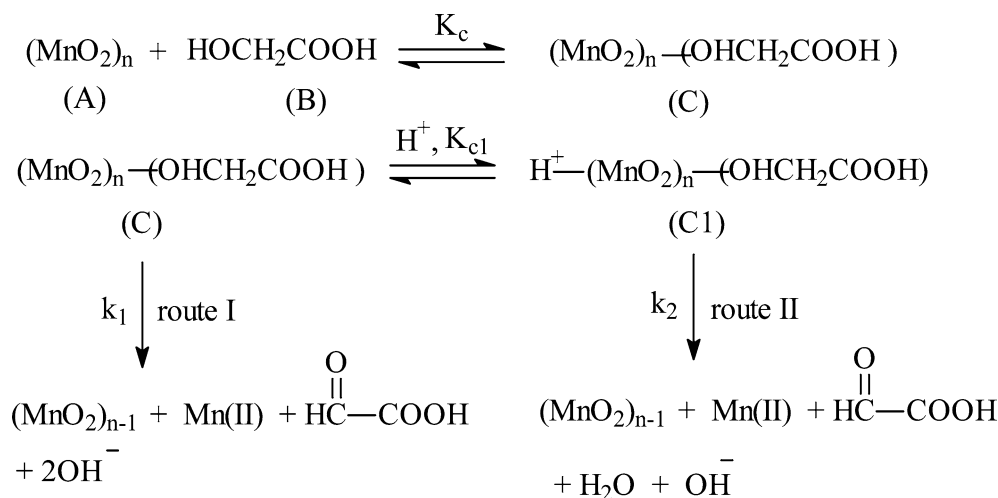
Fig. 3 Effect of HClO_4 on the pseudo-first-order rate constants. *Reaction conditions:* $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, temperature = 30°C . *Inset plot* showing the effect of hydrogen ion concentration on the pseudo-first-order rate constant



oxidation in presence of manganese(II) (Fig. 4) which suggests that Mn(II) has an autocatalytic role.

On the basis of above results the following mechanism is proposed for the first-step reaction pathway:

Scheme 1



The following rate law is derived from Sch. 1

Table 3 Pseudo-first-order rate constants and activation parameters for the reduction of colloidal MnO_2 by glycolic acid in the absence and presence of TX-100 ($= 15.0 \times 10^{-3} \text{ mol dm}^{-3}$)

Temperature($^\circ\text{C}$)	Aqueous		TX-100	
	$10^4 k_{\text{obs1}} (\text{s}^{-1})$	$10^4 k_{\text{obs2}} (\text{s}^{-1})$	$10^4 k_{\psi 1} (\text{s}^{-1})$	$10^4 k_{\psi 2} (\text{s}^{-1})$
25	5.5	7.0	6.6	10.0
30	7.3	9.0	8.3	15.1
35	12.2	16.2	14.0	20.6
40	17.0	22.4	19.2	34.8
Activation parameters				
$E_a (\text{kJ mol}^{-1})$	63	67	58	66
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	61	64	58	63
$\Delta S^\ddagger (\text{J K}^{-1} \text{mol}^{-1})$	-104	-91	-112	-90
$\Delta G^\ddagger (\text{kJ mol}^{-1})$	92	91	92	91

$[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$

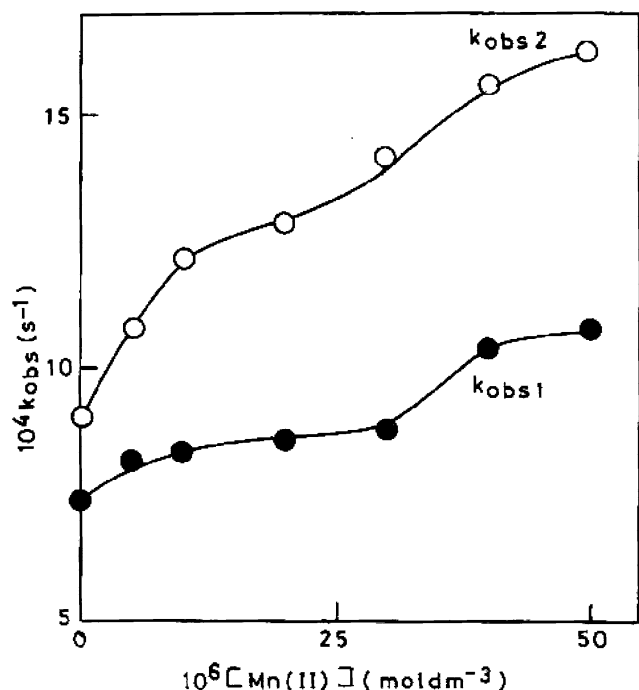


Fig. 4 Effect of Mn(II) on the pseudo-first-order rate constants. Reaction conditions: $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 30°C

Fig. 5 Effect of TX-100 on the pseudo-first-order rate constants. Reaction conditions: $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 30°C

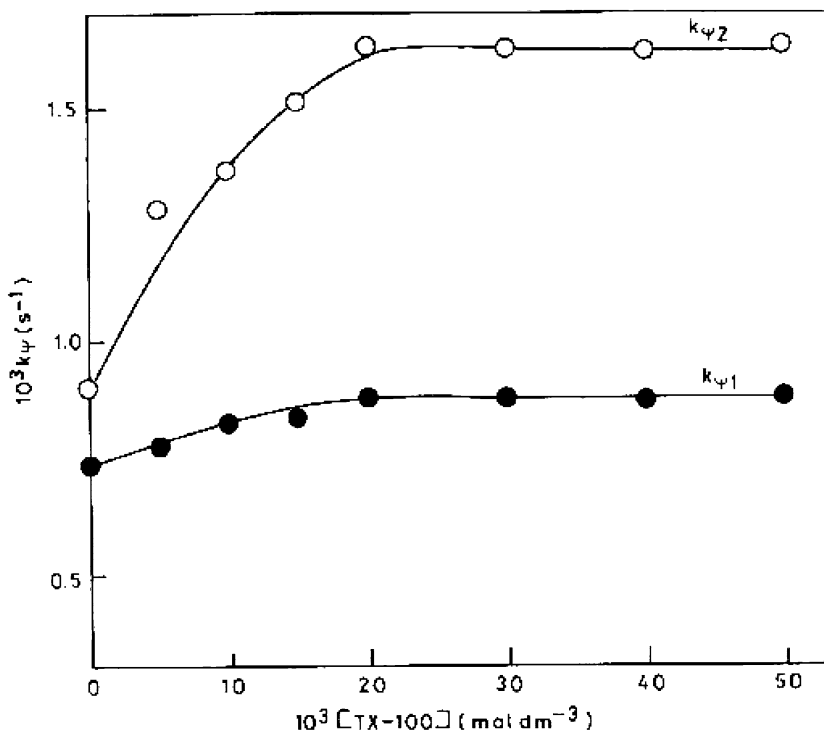


Table 4 Pseudo-first-order rate constants for the reduction of colloidal MnO_2 by glycolic acid in presence of TX-100

$10^3 [\text{TX-100}] (\text{mol dm}^{-3})$	$10^4 k_{\psi 1} (\text{s}^{-1})$	$10^4 k_{\psi 2} (\text{s}^{-1})$
0.0	7.3 (7.3, 7.3)	9.0 (9.1, 9.0)
5.0	7.7	12.8
10.0	8.2	13.6
15.0	8.3	15.1
20.0	8.7	16.3
30.0	8.7	16.3
40.0	8.7	16.2
50.0	8.7	16.3

$[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 30°C . The values quoted in parentheses were obtained, respectively, at $[\text{SDS}] = 4 \times 10^{-3}$ and $20 \times 10^{-3} \text{ mol dm}^{-3}$

$$v = \frac{-d[\text{MnO}_2]}{dt} = \frac{(k + k'[\text{H}^+]_s)[\text{MnO}_2][\text{glycolic acid}]_s}{1 + (K_c + K_c K_{c1}[(\text{H}^+)_s])([\text{glycolic acid}]_s)} \quad (2)$$

where $k = k_1 K_c$ and $k' = k_2 K_c K_{c1}$, whereas $(\text{H}^+)_s$ and $(\text{glycolic acid})_s$ stand for concentrations of hydrogen ions and glycolic acid adsorbed on the colloid surface.

Under our experimental conditions ($[\text{HClO}_4] = 5.0$ – $30.0 \times 10^{-4} \text{ mol dm}^{-3}$), the $[\text{H}^+]$ – independent path (route I) can be neglected in comparison to $[\text{H}^+]$ – dependent path. Thus, Eq. 2 reduces to Eq. 3

$$k_{\text{obs1}} = \frac{k'[(\text{H}^+)_s][(\text{glycolic acid})_s]}{1 + K_c K_{c1}[(\text{H}^+)_s][(\text{glycolic acid})_s]} \quad (3)$$

Here adsorption isotherm can be used to explain the observed results. Applying Freundlich adsorption isotherm for the species present in the bulk solution and adsorbed on colloidal MnO_2 , we get the following equilibrium

$$[(\text{H}^+)]_s = m[\text{H}^+]^n \quad (4)$$

$$[(\text{glycolic acid})_s] = m'[\text{glycolic acid}]^{n'} \quad (5)$$

where m , n and m' , n' are the Freundlich adsorption parameters for hydrogen ions and glycolic acid, respectively, whereas $[\text{H}^+]$ and $[\text{glycolic acid}]$ represent the concentrations of the corresponding species in the bulk solution. Eq. 3 can now be written as

$$k_{\text{obs1}} = \frac{k' m m' [\text{H}^+]^n [\text{glycolic acid}]^{n'}}{1 + K_c K_{c1} m m' [\text{H}^+]^n [\text{glycolic acid}]^{n'}} \quad (6)$$

Equation 6 is in perfect agreement with the experimental results with $n=0.25$ and $n' = 0.67$, which totally satisfy the applicability of the Freundlich isotherm, since for that isotherm the exponent must be a number in the 0–1 interval.

In view of the results obtained in presence of added Mn(II) , Sch 1 mechanism is modified as Sch 2. Both glycolic acid and Mn(II) compete for the reduction of colloidal MnO_2 . As a result, we may say that the values of k_{obs1} and k_{obs2} quoted in Table 2 are the sum of paths I and II and, therefore, exact dependence of k_{obs1} or k_{obs2} on $[\text{Mn(II)}]$ cannot be predicted.

Reaction in presence of surfactants

Preliminary experiments, which were followed in presence of anionic micelles of SDS, indicated that the rate of disappearance of colloidal MnO_2 remained unchanged (see the k_ψ values quoted in parentheses, Table 4). On the other hand, precipitate formation was

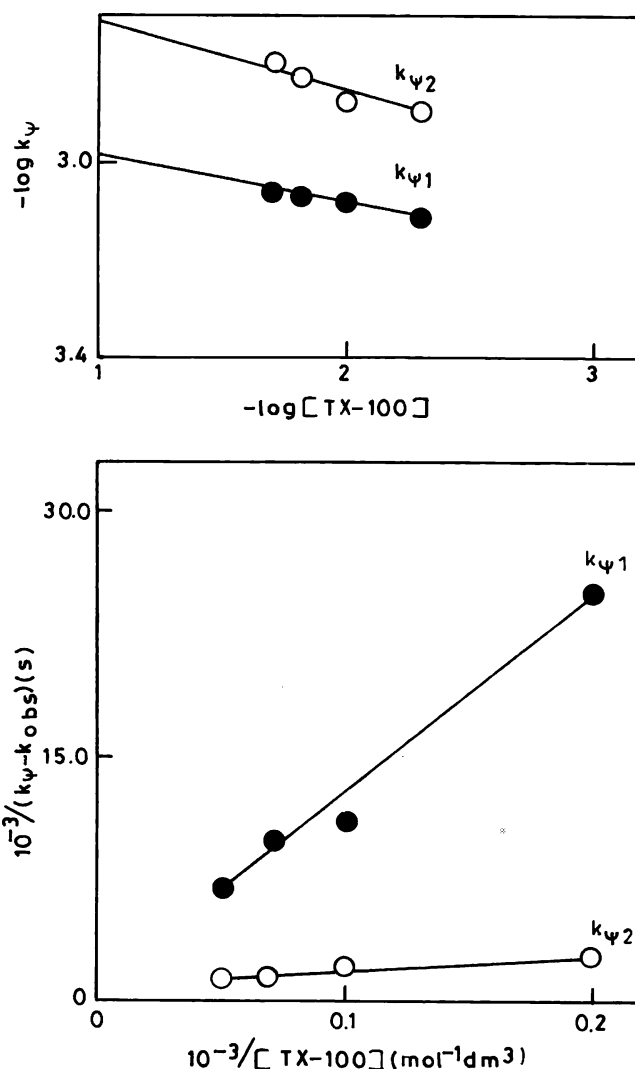


Fig. 6 Log-log plots between k_ψ and $[\text{TX-100}]$ (A) and $(1/k_\psi - k_{\text{obs}})$ against $1/[\text{TX-100}]$ (B). Reaction conditions: $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 9.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 30°C . The data belong to the part up to which the effect of TX-100 was catalytic (cf. Fig. 5)

Scheme 2

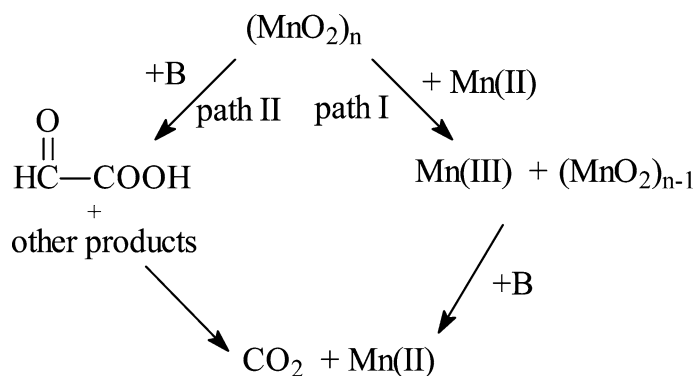


Table 5 Comparison of second-order-rate constants ($k_{\text{obs}}^{\text{II}}$) for the reduction of colloidal MnO_2 by different reductants at 25°C

Reductant	Medium	$10^2 k_{\text{obs}}^{\text{II}} / \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$	Reference
Citric acid ^a	Aqueous neutral	38.1	[20]
Oxalic acid ^b	HAc–NaAc	23.0	[16]
Lactic acid ^c	Aqueous acidic	1.7*	[17]
Glycolic acid ^d	HClO_4	0.57	Present work

^a $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{citric acid}] = 16 \times 10^{-4} \text{ mol dm}^{-3}$

^b $[\text{MnO}_2] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{oxalic acid}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$

^c $[\text{MnO}_2] = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{lactic acid}] = 0.3 \text{ mol dm}^{-3}$, * at 30°C

^d $[\text{MnO}_2] = 8 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{glycolic acid}] = 96 \times 10^{-4} \text{ mol dm}^{-3}$

observed in presence of cationic CTAB. As no quantitative explanation of the role of these surfactants can be provided, non-ionic TX-100 surfactant was chosen. The kinetic experiments were carried out in dilute HClO_4 medium. The conditions employed are given in Table 4. As $[\text{TX-100}]$ increased, the reaction rate increased up to certain $[\text{TX-100}]$ (Fig. 5) and then remained constant.

The following relations were found to hold good to explain the catalytic role of the surfactant

$$\log k_{\psi 1} = 0.0822 \log [\text{TX} - 100] - 2.9192 \quad (r = 0.9933) \quad (7)$$

$$\log k_{\psi 2} = 0.0822 \log [\text{TX} - 100] - 2.5166 \quad (r = 0.9509) \quad (8)$$

According to Eqs. 7 and 8, the plot of $\log k_{\psi 1}$ or $\log k_{\psi 2}$ versus $\log [\text{TX-100}]$ should be linear and this was found to be so (Fig. 6a). These findings are in good agreement with the observations of Tuncay et al. Furthermore, Lineweaver-Burk method was also used to explain the catalytic role of TX-100. According to this, the Michaelis-Menton type of enzyme catalysis equation can be arranged as

$$\frac{1}{k_{\psi 1} - k_{\text{obs}1}} = \frac{a}{[\text{TX} - 100]} + b \quad (9)$$

$$\frac{1}{k_{\psi 2} - k_{\text{obs}2}} = \frac{a'}{[\text{TX} - 100]} + b' \quad (10)$$

The values of empirical parameters a (a') and b (b') have

been calculated from the slopes and intercepts of Fig. 6b, and these values are $1.19 \times 10^2 \text{ mol dm}^{-3} \text{ s}$ ($0.07 \times 10^2 \text{ mol dm}^{-3} \text{ s}$) and $0.83 \times 10^3 \text{ s}$ ($1.13 \times 10^3 \text{ s}$).

Role of TX-100

The catalytic effect of ionic and non-ionic surfactants on reaction rates of bimolecular reactions is due to the association/incorporation through electrostatic/hydrophobic and hydrogen bonding interactions between the reactants within a small volume of the self-assemblies [22, 28–30]. As TX-100 is a non-ionic surfactant, any type of electrostatic interaction is not possible. Also, MnO_2 and glycolic acid have no hydrophobicity. Thus, only hydrogen bonding is left to play its role for the catalytic action of TX-100. The surfactant contains a number of oxyethylene chains and hydrogen bonding between MnO_2 sols and polyoxyethylene chains of TX-100 seems responsible for its adsorption on the surface of colloidal MnO_2 . In case of glycolic acid, which has one each of $-\text{COOH}$ and $-\text{OH}$ groups, hydrogen bonding may also take place. As a number of donor groups are present in one molecule of TX-100, more number of molecules of glycolic acid may bind to form multiple hydrogen bonds thereby increasing the number of bound glycolic acid molecules. Thus, hydrogen bonding between the polar polyethoxyethylene chains of TX-100 and the reactants appears to be responsible for the catalytic role of TX-100. The surfactant (i.e., TX-100) has thus the tendency of bringing the molecules (reactants) closer, which may orient in a manner suitable for the redox reaction followed by rearrangement of TX-100 molecules.

According to Tuncay et al. [18], hydroxyl ions bonded to colloidal MnO_2 are considered the active sites for substrate adsorption on the colloidal surface. On the basis of experimental observations, the reactivity of different reductants (citric, oxalic, lactic and glycolic acids) towards colloidal MnO_2 are compared (Table 5). Based on their reactivity, the reductants can be ordered as follows: citric > oxalic > lactic > glycolic which indicates that as the number of hydroxyl group increases, the reaction rate also increases. As in case of citric acid four hydroxyl groups are contained in each molecule, the reaction rate is higher as compared to others (Table 5).

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