Permanganate Transfer and Reduction by D-Glucose in Benzene–Cetyltrimethylammoniumbromide Aqueous Solution: A Kinetic Study

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ABSTRACT: The addition of cationic surfactant, cetlytrimethylammoniumbromide (CTAB), in benzene and aqueous potassium permanganate solution brought the MnO₄⁻ from the aqueous phase to the organic phase. At 525 nm, the absorbance of the organic phase increased until it reached a maximum, and then decreased with [CTAB]. The effect of [CTAB] on the reduction of permanganate by D-glucose in a benzene–CTAB system has been studied spectrophotmetrically. The observed effect on the rate constant is catalytic up to a certain concentration of CTAB; thereafter, a saturation phenomenon is observed with an increased concentration of CTAB. The oxidation reaction obeyed the first-order kinetics with respect to the D-glucose. On addition of H₂SO₄, there was a decrease in the rate constants. There is evidence for the existence of manganese as a water-soluble colloidal MnO₂. A detailed mechanism with the associated reaction kinetics is presented and discussed. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 496–503, 2008

INTRODUCTION

The term phase-transfer catalysis was coined to describe reactions, which are mediated by small quantities of agents, that transfer one reactant across an interface so that a reaction can take place [1]. The reaction at interfaces, in cavities of crown ethers (macrocyclic compound), in the presence of polymers as well as the transfer of reagents across the phase boundaries has been the subject of a large number of investigators [2–10]. In many respects, these systems may be analogous to catalysis by surfactant aggregates [2]. The utilization of surfactants as a reaction media affects rates, products, and in some cases stereochemistry of the reactions. Micellar reactions in some cases have proved superior to organic solvents as reaction media to obtain better yields [11]. It has been established that localization and compartmentalization effects, preorientational

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polarity and counter-ion effects, and effects of charged interfaces are the important factors that affect the rate of electron transfer processes in the presence of surfactants [12–16]. Quaternary ammonium salts used as a phase transfer catalysts have much in common with the surfactant quaternary ammonium salts used in a micellar system. Cordes and Dunlop [17] reported the kinetic effect of certain surface-active quaternary ammonium salts during micelle formation.

Potassium permanganate (a powerful oxidant) solution in crown ether and benzene is stable and has been extensively used in the oxidation of organic compounds. Herriott and Picker [5] investigated the oxidation of organic compounds by MnO_4^- in benzene using tricaprylmethylammonium chloride and suggested that two-phase systems can be used directly in the presence of ammonium ion to maintain $[MnO_4^-]$ in the organic phase. Recognizing the importance of surface-active quaternary ammonium salts in surface chemistry, we carried out the present study with the following aims: (1) to determine the effect of [CTAB] on the transfer of permanganate from aqueous to benzene, (2) to investigate the effect of different variables on the rates of reduction of permanganate by D-glucose in the presence of CTAB-benzene system, and (3) to determine whether the role of CTAB is similar to those of aqueous medium [18]. The observed results and the probable explanations are detailed in this paper. Incidentally, this study appears to be the first report of its kind.

EXPERIMENTAL

Materials

The following analytical-grade chemicals were used without further purification: benzene (99%; Merck, Mumbai, India), potassium permanganate (99%) Merck, India), D-glucose (99% Merck, India), perchloric acid (Fischer Scientific UK; 70% reagent), sulfuric acid (90%; Merck, India), sodium fluoride, cetyltrimethylammonium bromide (Fluka, Germany), and sodium dodecyl sulfate (SDS) (Fluka). Doubly distilled (first time from alkaline permanganate) water was used for the preparation of all reagent solutions. Permanganate solutions were standardized by titration against a standard oxalic acid solution and stored in a dark glass bottle. D-Glucose solutions were prepared just prior to use. Sulfuric acid solutions were prepared and standardized by titration with sodium hydroxide to the phenolphthalein end point. An ELICO LI-120 digital pH meter fitted with a CH-41 combination electrode was used for pH measurements.

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Rate Measurements

The reactions were started in a glass-stoppered twonecked flask fitted with a double-walled condenser to check evaporation. A mixture containing required amount of CTAB, benzene, permanganate, and water was thermally equilibrated at desired temperature $(30 \pm 0.1^{\circ}C)$, and to this was added a measured amount of D-glucose solution, pre-equilibrated at the same temperature. The reaction volume was always 50 cm^3 . Over the entire range of this study, reactions were carried out under pseudo-first-order conditions using an excess of [D-glucose] over $[MnO_4^-]$. The kinetics was followed by monitoring the absorbance of the remaining permanganate in the aqueous phase at known time intervals at 525 nm (λ_{max} for MnO₄⁻ and $\in = 2410 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) on a spectronic 21D spectrophotometer. The cuvettes had a path length of 5 cm. In most cases, the reaction was followed to well over 80% completion. Pseudo-first-order rate constants $(k_{obs}; s^{-1})$ reported here are the slopes of the log(absorbance) versus time plots. The values of the average linear regression coefficient, $\gamma \ge 0.996$, were obtained for each kinetic run. Other experimental details were the same as described elsewhere [18,19]. The pH of the reaction mixture was also measured at the end of each kinetic run, and it was observed that pH drift during the reaction is very small (within 0.05 units).

Product Identification

At the completion of the reaction between D-glucose and permanganate, identification of the reaction product was carried out by paper chromatography [20]. The aqueous phase of the reaction mixture was used as a mobile phase. Lactone was identified against an authentic sample (1,4-D-glucolactone) using 4:1:5 *n*-butanol–acetic acid–water eluent. A three-stage dip of AgNO₃, NaOH, and Na₂S₂O₃ was used to visualize the paper chromatograms. In alkaline or weakly acidic solutions, permanganate changes to Mn(IV), whereas in a strongly acidic medium, permanganate is further reduced, forming Mn(II) as the final reduction product of Mn(VII).

RESULTS AND DISCUSSION

Transfer of MnO_4^- into the Organic Phase

It is well known that quaternary ammonium ions normally permit water-soluble (permanganate) to solubilize in the organic phase [5,21], i.e., benzene. The purple benzene can be separated and used for oxidation reactions under anhydrous conditions. On the other hand, the two-phase system can be used directly for the



Figure 1 Variation of absorbance at 525 nm with the change in [CTAB] in 20 cm³ of benzene. Reaction conditions: MnO_4^- (2.0 × 10⁻⁴ mol dm⁻³) and temperature (30°C).

permanganate oxidation of organic reductants. There is a rapid transfer of the purple cation from aqueous to benzene layer on mixing the required amount of CTAB. Therefore, $[MnO_4^-]$ in the organic phase was established as follows: In a typical experiment, a solution of MnO_4^- (10 cm³, 1.0×10^{-3} mol dm⁻³) was added to a solution containing CTAB (2 cm³; 1.0×10^{-2} mol dm⁻³) and benzene (40%; total volume 50 cm³). After shaking the reaction mixture, the organic layer became purple, indicating the transfer of MnO_4^- from the aqueous to benzene layer. As can be seen from Fig. 1 (a typical example) ($\lambda_{max} = 525$ nm for MnO_4^-), the absorbance of the benzene layer first increased until it reached a maximum and then decreased with [CTAB]. The decrease in $[MnO_4^-]$ in benzene may be due to less partition of MnO_4^- from the aqueous medium owing to a higher aggregate structure of CTAB. This behavior may be attributed to the formation of ion-pair between the positive head group of CTAB and MnO₄⁻ with increasing surfactant concentration, which in turn increases the solubilization of the ion-pair into the organic phase through hydrophobic interactions. The wavelength (525 nm) was chosen to confirm the fulfillment of the Beer-Lambert law and also to calculate MnO_4^- in the benzene phase by monitoring the absorbance of different solutions of MnO_4^- . The law is obeyed for the concentration range used in the present investigations. From the Beer-Lambert plot, MnO_4^- has been calculated to be 0.75×10^{-4} mol dm⁻³ at constant CTAB (8.0×10^{-4} mol dm⁻³). The observed results are summarized in Table I.

It has been established that permanganate transferred into an immiscible phase (benzene) using quaternary ammonium salts and CTAB. In the presence of trimethylammoniumbromide, the transfer of MnO_4^- is

Table I $[MnO_4^-]$ in the Organic Phase at Different[CTAB] at Three Different Time Intervals for the Transferof $[MnO_4^-]$ from the Aqueous $(2.0 \times 10^{-4} \text{ mol dm}^{-3})$ toOrganic Phase

	$10^5 [\text{MnO}_4^-] (\text{mol } \text{dm}^{-3})$			
10 ⁴ [CTAB] ^a	Time (min)			
$(\text{mol } \text{dm}^{-3})$	30	40	50	
2.0	1.0	1.2	1.2	
4.0	1.8	2.1	2.5	
6.0	2.5	2.7	3.8	
7.0	3.0	5.1	5.6	
8.0	5.5	6.1	7.5	
12.0	3.5	5.6	5.8	
16.0	2.5	5.5	4.8	
24.0	1.2	2.6	2.8	
32.0	0.9	2.0	2.3	

^{*a*} Benzene = 40%.

ca. 100%. The absorption spectrum of MnO_4^- in benzene is very similar to that of aqueous MnO_4^- [21,22]. This behavior indicates the transfer of MnO₄⁻ in the benzene (organic phase) and formation of an ionpair complex between the MnO_4^- and $(-N^+(CH_3)_3)$ head group of CTAB through the electrostatic interactions. An increase in absorbance below critical micelle concentration (CMC), that is, submicellar effect, occurred, which may be because small aggregates of CTAB surfactant (dimers, trimers, tetramers, and so on) exist below the CMC. These submicellar aggregates interact physically with the MnO_4^- , forming ionpairs that in turn give some hydrophobic character to permanganate. On the other hand, a hydrophobic tail of small aggregates has a hydrocarbon-like structure. Thus, we may safely conclude that alkyl chains of CTAB aggregates are responsible for the solubilization/incorporation of CTAB-MnO₄⁻ ion-pair into the organic phase (benzene). The cationic surfactant of CTAB acts as an electrostatic sink for the anionic permanganate [23]. This is one of the few examples when MnO_4^- can be dissolved in a nonpolar solvent simply by adding CTAB. Quaternary ammonium salts contain both liphophilic and hydrophilic moieties. Owing to their amphiphilic nature, CTAB distributes itself between the aqueous and organic phase, forms an association complex with the reactive anion (MnO_4^-) , and brings it into the organic phase. A complete understanding of phase transfer (the role of CTAB) is not possible because a number of different interactions, including those associated with the head group of the surfactant, are involved.

The partition of a solute between two immiscible solvents is governed by the distribution law. The ratio

of [solute] in the two phases will be constant and independent of the total quantity of solute. If a solute may exist in different stages of aggregation in the two systems, the law is valid only if the ratio of the concentrations of single molecules in the two phases is taken into consideration. The analytical extractions are complicated by association or dissociation processes that occur in one or both of the solvents. To calculate the partition coefficient of MnO₄⁻ in benzene and aqueous media in different [CTAB], different sets of experiments were performed under different conditions. The values of partition coefficient of MnO₄⁻ in the benzene–aqueous media were found to be 9.8, 17.6, and 37.9×10^{-3} at [CTAB] 4.0, 7.0, and 8.0×10^{-4} mol dm⁻³, respectively.

The observation is not unexpected; aqueous surfactant solution has three components: surfactant monomers in the aqueous solution, micellar aggregates, and monomers absorbed as a film at the interface. There is a dynamic equilibrium between aggregated molecules and monomers. In surfactant solutions, micelles form and break up so rapidly that both aggregation and dissociation of monomers occur at the same time. Therefore, the partition coefficient of MnO_4^- in benzene and aqueous media cannot be constant. On the other hand, it was observed that CTAB is insoluble in benzene. Thus, we may safely conclude that the hydrophobic tails of CTAB aggregates may orient into the benzene layer and polar head group remains in the water phase in the benzene-water system. Benzene also penetrates toward the hydrocarbon-like cores of CTAB micelles, which are responsible for the solubilization of benzene.

Reduction of MnO_4^- by D-Glucose in the CTAB-Benzene System

Preliminary observations showed that the transfer of permanganate from the aqueous to the benzene phase was slow at room temperature $(30^{\circ}C)$. Therefore, the choice of the best conditions for the evaluation of the rate constant is a critical problem that we address first. The requisite amounts of MnO_4^- , CTAB, and benzene were taken in a reaction vessel placed in a thermostat at 30°C for a sufficient time to transfer the maximum $[MnO_4^-]$ from the aqueous to benzene phase. The reaction was initiated with the addition of required volume of the D-glucose solution. The zero time was taken when half of the D-glucose solution had been added. In the present study, it is necessary to point out that the plot of log(absorbance) versus time deviates from linearity. It was noted that the extent of deviation depended on the [D-glucose]. The values of the rate constants of an initial stage were determined

Table II	Effect of CTAB on the Pseudo-First-Order
Rate Cons	tants for the Oxidation of D-Glucose by MnO4
at 30°C	

$10^4 [CTAB]^a$ (mol dm ⁻³)	$\begin{array}{c} 10^4 k_{\rm obs} \\ ({\rm s}^{-1}) \end{array}$	10 ⁴ [CTAB] (mol dm ⁻³)	
0.0	0.0	10.0	7.0
4.0	3.8	12.0	7.6
6.0	5.1	16.0	7.5
8.0	6.6	20.0	7.3

^{*a*} [D-glucose] = 2.0×10^{-3} mol dm⁻³, [MnO₄⁻] = 2.0×10^{-4} mol dm⁻³, and benzene = 40%.

from the slopes of the straight lines of the plots of log(absorbance) versus time.

To see whether the MnO_4^- ion was capable of reacting with CTAB under our kinetic conditions, the same experiments were performed in the absence of Dglucose ($MnO_4^- + CTAB$). No decay in the absorbance of MnO_4^- was observed for the entire range of (CTAB) used in the kinetic experiments. This suggests that there was no oxidation of CTAB by MnO_4^- .

A series of kinetic experiments were carried out in the absence of externally added mineral acids (HClO₄ and H₂SO₄); reduction of permanganate (2.0×10^{-4} mol dm⁻³) by D-glucose (2.0×10^{-3} mol dm⁻³) was not observed under present experimental conditions. Therefore, to see the effect of [CTAB] in the benzene– water system, its concentration varied from 4.0×10^{-4} to 20.0×10^{-4} mol dm⁻³. The rate constant values are summarized in Table II. Figure 2 shows the variation of k_{obs} with [CTAB]. The k_{obs} had been found to increase monotonically, and it became constant with the increase in [CTAB]. The observed catalytic effect may,



Figure 2 Dependence of $k_{\rm obs}$ on [CTAB]. Reaction conditions: MnO₄⁻ (2.0 × 10⁻⁴ mol dm⁻³), D-glucose (2.0 × 10⁻³ mol dm⁻³), benzene (40%), and temperature (30°C).

$\frac{10^4 [MnO_4^-]^a}{(mol \ dm^{-3})}$	10^3 [D-glucose] (mol dm ⁻³)	$10^5 [H_2SO_4]$ (mol dm ⁻³)	$\frac{10^4 k_{\rm obs}}{({\rm s}^{-1})}$	$(k_{\rm obs}-k_{\rm cal})/k_{\rm obs}$
1.2	2.0	0.0	11.8	
1.4			10.7	
1.6			9.6	
1.8			8.3	
2.0			6.8	
2.0	1.0	0.0	$4.4(3.7)^b$	+0.15
	1.6		5.7 (5.7)	0.00
	2.0		6.8 (7.2)	-0.05
	2.6		9.4 (9.3)	+0.01
	3.0		11.0 (10.8)	+0.01
2.0	2.0	3.7	4.2	
		5.6	3.8	
		7.4	2.8	
		9.3	1.5	
		11.2	1.1	

Table III Effect of $[MnO_4^-]$, [D-glucose], and $[H_2SO_4]$ on the Pseudo-First-Order Rate Constants at 30°C

^{*a*} [CTAB] = 8.0×10^{-4} mol dm⁻³ and benzene = 40%.

^b Calculated rate constants (Eq. (11)) are given in parentheses along with the k_{obs} values.

therefore, be due to the (i) presence of free micelles and (ii) micellization of reactants.

The effect of varying $[MnO_4^-]$ on the reaction rate was studied at constant D-glucose $(2.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$, temperature (30°C) , and CTAB $(8.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$. We observed Table III that the k_{obs} values decrease with the increase in $[MnO_4^-]$. The basic trend in chemical kinetics is that the pseudo-first-order rate constants are independent of the initial concentration of the reactant in defect. The same type of defect has earlier been observed in many oxidation reactions of organic oxidants by permanganate and especially in those having an autocatalytic character [24]. Such type of behavior may be due to flocculation of the colloidal particles of MnO_2 [25]. The rate of the reaction can be represented by Eq. (1)

$$\frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-]_T$$
(1)

Table III also contains pertinent data regarding the reaction studied as a function of [Dglucose] $(1.0 \times 10^{-3} \text{ to } 3.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ at $\text{MnO}_4^-(2.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$, and CTAB (8.0×10^{-4} mol dm^{-3}). The k_{obs} values are shown graphically in Fig. 3. By plotting log k_{obs} versus log[D-glucose], a straight line with slope ca. 1.0 was obtained, indicating the order to be 1 with respect to [D-glucose]. Thus, the rate equation experimentally found was

$$\frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-]_T[D-glucose] \quad (2)$$



Figure 3 Dependence of $k_{\rm obs}$ on D-glucose. Reaction conditions were the same as those mentioned in Fig. 2 with CTAB (8.0×10^{-4} mol dm⁻³).

Preliminary observations showed that a reaction mixture containing CTAB and percholoric acid became turbid, which increases with [HClO₄]. Therefore, H₂SO₄ was used to verify the role of [H⁺] on the oxidation rate. The effect of [H⁺] was studied as a function of [H₂SO₄] between 3.7×10^{-5} and 11.2×10^{-5} mol dm⁻³ at constant MnO₄⁻ (2.0×10^{-4} mol dm⁻³), D-glucose (2.0×10^{-3} mol dm⁻³), CTAB (8.0×10^{-4} mol dm⁻³), and temperature (30° C). The rate decreased with the increase in [H₂SO₄] (Table III). In the presence of H₂SO₄, the inhibitory effect is due to the exclusion of reactants from the reaction site (i.e., the Stern layer, as most of the ionic micelle mediated reactions are believed to occur in the region). As we increase the $[H_2SO_4]$, the $[H^+]$ will try to get associated with the MnO_4^- and will thus compete for a site (Stern layer). Consequently, [reactant] is decreased from the reaction site due to the exclusion effect.

To gain insight into the inhibitory role of $[H_2SO_4]$, the effect of [Na₂SO₄] was also investigated under the same kinetic experimental conditions in the absence of H_2SO_4 . The k_{obs} values were found to be 6.6, 6.8, 6.7, and 6.8 10^{-4} s⁻¹ at 10^5 [Na₂SO₄] of 3.7, 5.6, 7.4, 9.3, and 11.2 mol dm^{-3} . These findings indicate that the reaction rate remains the same in the presence of SO_4^{2-} . At higher [Na₂SO₄] (1.8 × 10⁻² to 9.3×10^{-2} mol dm⁻³), k_{obs} increases steeply by increasing $[Na_2SO_4]$ ($k_{obs} \times 10^4 = 1.7, 2.4, 3.0, 3.6, and$ 4.3 s⁻¹ at [Na₂SO₄] 1.8, 3.7, 5.5, 7.4, and 9.3×10^{-2} mol dm^{-3} , respectively). Inert salts, especially the inorganic ones, act as catalysts or inhibitors in the micellemediated reactions [26]. It has also been established that salts of high solubility in the aqueous phase can also increase the binding constant of substrate to the micelles by salting out the substrate from the aqueous pseudophase, and this results in enhancement of the rate [27]. The catalysis of the reaction at higher [Na₂SO₄] could be rationalized in terms of the salting out effect.

To identify the nature of the intermediate(s), the spectrum of the reaction mixture MnO_4^- (2.0 × 10⁻⁴ mol dm⁻³), D-glucose (2.0 × 10⁻³ mol dm⁻³), and CTAB (8.0 × 10⁻⁴ mol dm⁻³) was recorded at the end of the reaction. The plot of log(absorbance) versus log(wavelength) was linear (slope = -5.9; see Fig. 4). The linear relationship between log(absorbance) and log(wavelength) suggests that the soluble Mn(IV) species is present in the form of colloidal particles of MnO₂ [28,29]. To substantiate the formation of Mn(III) as an intermediate, the effect of adding sodium fluoride



Figure 4 Plot of log(absorbance) versus log(wavelength). Reaction conditions were the same as those in Fig. 3.

was also investigated at constant MnO_4^- (2.0 × 10⁻⁴ mol dm⁻³), D-glucose (2.0 × 10⁻³ mol dm⁻³), CTAB (8.0 × 10⁻⁴ mol dm⁻³), and temperature (30°C). The values of k_{obs} were found to be decrease with the increasing amount of [F⁻] ($k_{obs} \times 10^{-4} = 6.4, 6.2, 6.0, 5.7, 5.6, 5.4, and 5.2 s⁻¹ at [F⁻] 0.0, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 × 10⁻⁴ mol dm⁻³, respectively). The observed inhibitory effect suggests the possibility of formation of Mn(III). Therefore, it can be concluded that Mn(IV) (colloidal in nature) and Mn(III) species are formed as the intermediates in the reaction of MnO₄⁻ by D-glucose in the presence of CTAB.$

From these results, the most possible mechanism for the reaction of MnO_4^- by D-glucose can be represented by Eqs. (1)–(7). Under our experimental conditions, MnO_4^- and β -D-glucopyronase are the predominant species in line with the argument presented elsewhere [30, 31]. The mechanism is, therefore, given in Scheme 1.



Scheme 1

Table IV Effect of CTAB, Benzene, and Mineral Acids on the Reactivity of $MnO_4^- + p$ -Glucose Reaction

Reaction Conditions ^a	$10^4 k_{\rm obs} ({\rm s}^{-1})$	Role of CTAB/Benzene/Mineral Acids	Reference
$\overline{(1) \text{ MnO}_{4}^{-} + \text{D-glucose}}$	No reaction		[18]
(2) MnO_4^- + D-glucose + CTAB	No reaction		Present work
(3) MnO_4^- + D-glucose + H ₂ SO ₄	0.2	Catalysis	Present work
(4) MnO_4^- + D-glucose + HClO ₄	No reaction		Present work
(5) MnO_4^- + D-glucose + CTAB + Benzene	6.8	Catalysis	Present work
(6) MnO_4^- + D-glucose + CTAB + Benzene+H ₂ SO ₄	1.1	Inhibition	Present work
(7) MnO_4^- + D-glucose + CTAB + Benzene + HClO ₄	Turbidity	18	
(8) $CTAB + HClO_4$	Turbidity		[18]

 a [MnO₄⁻] = 2.0 × 10⁻⁴ mol dm⁻³, [D-glucose] = 2.0 × 10⁻³ mol dm⁻³, [CTAB] = 8.0 × 10⁻⁴ mol dm⁻³, [H₂SO₄] = 1.12 × 10⁻⁴ mol dm⁻³, benzene = 40%, and temperature = 30°C.

Other contributing steps are as follows:

$$Mn(IV) + \beta$$
-D-Glucopyranose \xrightarrow{fast}
 $Mn(II) + Lactone$ (6)

$$Mn(IV) + Mn(II) \xrightarrow{\text{fast}} 2Mn(III)$$
(7)

 $Mn(III) + \beta$ -D-Glucopyranose \xrightarrow{fast}

Mn(II) + radical (8)

radical + Mn(III)
$$\xrightarrow{\text{rast}}$$
 Lactone + Mn(II) (9)

The complete rate law for the reaction is given by

$$\frac{-d[MnO_4^-]}{dt} = k[MnO_4^-]_T[D-glucose]$$
(10)

where *k* represents the rate constants.

Considering Scheme 1, the rate law (10) can be written as

$$k_{\rm obs} = K_{\rm c} k [\text{D-glucose}] \tag{11}$$

where $k = K_c k$

$$\frac{-d[MnO_4^-]}{dt} = K_c k [MnO_4^-][D-glucose]$$
(12)

The derived rate law clearly accounts for the first-order dependence on [D-glucose] in the absence of H₂SO₄. The value of $K_c k$ obtained from the slope of Fig. 3 was found to be 0.36 mol⁻¹ dm³ s⁻¹. The k_{cal} values are calculated by substituting the $K_c k$ and [D-glucose] values in Eq. (11) and compared with k_{obs} (Table III). A close agreement between k_{obs} and k_{cal} provides a supporting evidence for the mechanism shown in Scheme 1.

Now the kinetic results in the CTAB solution will be considered. The increase in the rate constant with the increase in [CTAB] may be due to the increase in the solubilization and association of the reactant species with the increase in the [CTAB] that reaches a limiting value (Fig. 2). The catalysis of the reaction could be rationalized in terms of the electrostatic effect. Incorporation of MnO_4^- and D-glucose into a limited volume of CTAB micelles decreases the entropy loss that is associated with bringing reactants together in the transition state, leading to an increase in the rate constants in the presence of the surfactant [23].

In micelle-mediated reactions, it is not possible to precisely locate the exact site of the reaction, but reactants' localization can be considered. It is observed that MnO_4^- forms an ion-pair complex with the positive head group of CTAB aggregates. On the other hand, D-glucose is a neutral molecule and has no degree of hydrophobicity due to the high solubility in water. Therefore, its presence in the Stern layer cannot be completely ruled out, thus packing the reactants in a small volume and resulting in the observed catalysis.

Interestingly, the reactivity of D-glucose toward MnO_4^- in the presence of benzene is much higher than its oxidation in the presence of CTAB only (Table IV). Addition of benzene to the reaction mixture containing MnO_4^- , D-glucose, and CTAB increases the reaction rate significantly. The redox reaction probably occurs at the interfacial region of the Gouy-Chapman and Stern layer. In the presence of benzene, the possible reaction site is at the water-hydrocarbon interface. To see the role of anionic surfactant, attempts were made to carry out the oxidation reaction in the presence of SDS. Preliminary observations showed that the benzene layer does not become purple in the presence of SDS. The observation is not unexpected; the anionic head group of SDS, simply based on electrostatic considerations, will repel the MnO_4^- , keeping the $[MnO_4^-]$ unaffected. On the other hand, SDS is unstable [19] in the presence of acidic MnO_4^- . Therefore, [H⁺] cannot be used to neutralize the surface charge of SDS micelles.

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