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# Effect of CPC micelle on *N*-hetero-aromatic base promoted room temperature permanganate oxidation of 2-butanol in aqueous medium

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#### ABSTRACT

Oxidation kinetics of 2-butanol by permanganate ion under pseudo-first-order conditions,  $[2-butanol]_T \gg [MnO_4^-]_T$ , in aqueous sulfuric acid solutions at 30 °C have been investigated spectrophotometrically. The pseudo-first-order rate constants and half-life were calculated from the ln(Absorbance)<sub>525</sub> versus time plot. The rates were found to be relatively slow in the uncatalyzed path, which increase by the presence of *N*-cetylpyridinium chloride (CPC) micelle and promoters: picolinic acid (PA) and 2,2-bipyridine (bipy). The catalytic effect of CPC on the permanganate oxidation of 2-butanol has been studied spectrophotometrically in the presence of promoter. CMC value of CPC was determined by three different techniques: conductometry, spectro-photometry and kinetics measurements. NMR and FTIR spectra confirmed the oxidized products. The aggregation and morphological changes during reaction were studied by Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). The variation of the reaction rates for the different promoters in the presence and absence of CPC micellar catalyst is discussed qualitatively in the terms of partitioning nature of surfactant, charge of surfactant and reactants. Bipy in association with CPC micellar catalyst exhibited ~100-fold rate enhancements compared to the uncatalyzed reaction path.

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#### 1. Introduction

Oxidation of 2-butanol to 2-butanone, commonly known as methyl ethyl ketone (MEK) is an important transformation in synthetic chemistry. In particular, 2-butanol is used as an intermediate for devulcanizing cured rubber and for the production of alkyl esters for use as a biodiesel fuel. 2-Butanone is an effective and common solvent and is used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films, plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent [1,2].

Chromate and permanganate ions in various forms are used as powerful oxidizing agents in organic and inorganic oxidations in polar media [3]. The contamination of aquatic environment by toxic metals, such as hexavalent chromium is of great concern due to its trends to accumulate on vital organs of human and animals causing several health problems [4,5]. The permanganate oxidation process is eco-friendly compared to other oxidants such as chromates [6–9] and has gained importance in green chemistry. Permanganate ion is a strong oxidizing agent which still remains as one of the most versatile and vigorous oxidant used for oxidation of organic and inorganic compounds in acidic media [10,11]. Permanganate, an important oxidant in many organic and inorganic redox reactions, involves the Mn(VII) entity. In acid solution, permanganate is reduced to  $Mn^{2+}$  by an excess of reducing agent  $(E^0 = 1.51 \text{ V})$ :  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ . The highest oxidation state of manganese corresponds to the total number of 3d and 4 s electrons. The mechanisms for different organic substrates suggested by various authors are not similar, indicating that a variety of mechanisms are possible, depending upon the nature of the reactive manganese species, the reaction environment and the nature of the substrate [10–12].

The 'green chemistry' has encouraged many synthetic organic chemists to use water as the only solvent, because 80% of chemical waste is estimated to be organic solvents. The alternative is to use amphiphiles that formed micelles to accommodate lipophilic environment for the insoluble reactants or reagents. Reaction rates might be faster than those normally observed in organic media, because the effective concentration within the micelle could be quite high. This concept is called micellar catalysis and many researches in this field have been reported [13,14].

Micellar properties have attracted growing attention for use in biochemistry, biological, industrial and chemical research applications. Since the surfactant is providing a very limited amount of an organic medium in which these reactions can take place, reactions occur

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under typically high internal concentrations and under mild, usually room temperature conditions [15]. The salient properties of the surfactants that affect electron transfer reactions are localization and compartmentalization effect, pre-orientational polarity and counter-ion effect and the effect of charged interfaces [16-19]. Mechanistic studies on permanganate oxidation reaction of both organic and inorganic substrates are invariably encumbered by difficulties due to multitude of possible oxidation states [20]. Pyridinium surfactants are often utilized as corrosion inhibitors, as well as being used in emulsion polymerization, the flotation of minerals, and textile processing. Biological applications of these surface-active agents include their antimicrobial activity, as well as their use as drug and gene delivery agents [21]. Cetylpyridinium chloride (CPC) belongs to a class of frequently used cationic surfactants having wide ranging applications, as drug delivery vehicles, for catalysis, as nanoreactors, etc., it is also being used as an antibacterial (antiseptic) drug. It is an active ingredient in mouthwashes [22].

Micellar catalysis oxidation of 2-butanol by CPC in aqueous acidic solutions is usually explained on the basis of a distribution of reactants between water and the micellar "pseudophase". If the solubility of 2butanol is usually greater in the CPC micelles than in water the local concentration is increased in the micelle, often with suitable orientation of the reactants bound in the micelle. This leads to a large increase in the effective concentration leading to an increase in the reaction rate. Comparison to the organic solvents as reaction media modern micellar catalysis involves small amounts of environmentally benign designer surfactants [23,24].

The details of mechanism and oxidation kinetics of permanganate oxidation of 2-butanol are also not yet known in the presence of surface active N-cetylpyridinium chloride (CPC) and N-hetero-aromatic chelating ligands: picolinic acid (PA), 2,2'-bipyridine (bipy). PA and 2,2'bipyridine are *N*-hetero-aromatic chelating agents and form complexes with chromium, zinc, manganese, copper, iron and molybdenum using nitrogen and oxygen atom [25-29]. Furthermore, due to the presence of low-energy  $\pi^*$  orbitals of the ligand, metal complexes can be characterized by strong metal-to-ligand charge-transfer (MLCT) absorption bands in the visible spectrum [30]. In this paper we have for the first time reported the incorporation of permanganate ion into the stern layer of CPC micelles. Mainly, the oxidations are more efficient and selective, the reaction conditions are milder, and the workups are easier. On the other hand, owing to the reaction under aqueous micellar medium, combustion, toxicity, and environmental pollution of solvents are reduced.

#### 2. Experimental

#### 2.1. Materials

2-Butanol (99%, Merck, India), potassium permanganate (99%, Merck, India), sulphuric acid (99%, Merck, India), and CPC (99%, Merck, India) were used. Permanganate solutions were stored in a dark glass bottle and standardized by titration against oxalate. The solvent used was water, previously doubly distilled, deionized and CO<sub>2</sub> free. It was standardized against oxalic acid by following the literature method [31]. PA (AR, Sigma Aldrich), 2, 2'-bipyridine (AR, E Merck), N-cetylpyridinium chloride (AR, SRL), Sulphuric acid (AR, Merck), and all other necessary chemicals used were of highest purity available commercially. Solutions were prepared by using doubly-distilled water. Doubly-distilled water was used throughout the work. Stock solution of 2-butanol was prepared by dissolving the appropriate amount of the sample in doubly-distilled water. The solution of CPC was prepared by using the weighing balance (Sartorius BSA224S-CW) and dissolving calculated amount of CPC in doubly-distilled water through Digital Ultrasonic Cleaner CD 4820 instrument. Surfactant substrate mixture solution and other mixture solution containing surfactant were centrifuged to get a complete mixing through Centrifuge-Z206A (Hermle Labortechnik GmbH).

#### 2.2. Kinetic measurements

Reaction mixtures containing the known quantities of the substrate (2-butanol), and acid under the kinetic conditions,  $[2-butanol]_T \gg$  $10[MnO_4^-]_T$  were thermostated at 30 °C (±0.1 °C). A mixture containing the required amount of permanganate, CPC, water and other reagents (whenever necessary) was thermally equilibrated at a desired temperature and to this was added a measured amount of 2-butanol solution. The absorption measurements were made in a thermostated cell compartment at the desired temperature within (30  $\pm$  0.1 °C) on a UV-VIS-NIR Spectrophotometer (SHIMADZU-3600) automatic scanning spectrophotometer fitted with a Temperature Control System program controller using cells of path length 1 cm. The rate of disappearance of the permanganate ion was monitored at 525 nm  $(\lambda_{max} \text{ of } MnO_4^-)$ [10,11]. It was verified that there is no interference from other reagents at this wavelength. The reaction was started by adding the requisite, and thermally equilibrated, solution of 2-butanol. The pseudo-first-order rate constants ( $k_{obs}$ ;  $s^{-1}$ ) were obtained from the measurements of slopes of the plots (Fig. S1, supplementary file) of log(absorbance) versus time. All experiments were studied in duplicate and the rate constants were found to be reproducible within  $\pm$  3%. The kinetics of the fast reactions was studied by using an Applied Photophysics SX-20 (Kinet Assist) stopped-flow spectrophotometer. Values of the rate constants for the 2-butanol-MnO<sub>4</sub><sup>-</sup> reactions determined from the slopes of the appropriate plots are presented in Table 1.

#### 2.3. Product analysis

The oxidation product of 2-butanol, was qualitatively analyzed. After ensuring completion of the reaction, the oxidized product was separated by fractional distillation of the reaction mixture. The corresponding oxidized product (carbonyl compound) was efficiently separated by fractional distillation [16,25]. The <sup>1</sup>H NMR spectra of the product carbonyl compound in CDCl<sub>3</sub> solvent were obtained on a NMR spectrophotometer (400 MHz, Bruker Ascend) operating at 400 MHz frequency (Fig. S2, supplementary file). In this study the 2-butanone was the main product of oxidation of 2-butanol. Qualitative identifications of the carbonyl products of MnO<sub>4</sub><sup>-</sup> oxidation reactions were made by the formation of yellow or yellow orange colored crystals of 2,4-dinitrophenyl hydrazone derivative precipitated directly by the addition of 2,4dinitrophenyl hydrazene in the reaction mixtures [32]. The hydrazone precipitate was filtered off and was recrystallized to determine the melting points. The melting points 141-142 °C were matched with the earlier reports [33,34]. The crystalline 2,4-DNP derivatives were thoroughly mixed with KBr, pressed into a form of disk (pellet), to record FTIR spectrum by using FTIR spectrophotometer (IR Prestige 21, SHIMADZU) and compared with spectra of the derivatives of known ketone (Fig. S3, supplementary file). Thus, we may safely conclude that carbonyl compound is the main oxidation product.

#### 2.4. Stoichiometry

Stoichiometry of the reaction was determined by analytical method. In this method the reaction mixture containing excess of  $KMnO_4$  over the 2-butanol was allowed to stand at 30 °C for a sufficiently long time. The amount of unreacted permanganate was estimated iodometrically. It has been found that the five molecules of 2-butanol recognize two molecules of permanganate for complete oxidation. On the basis of literature available [35,36] and the work performed, the reaction proceeds as follows:

$$5 \text{ CH}_3 \text{CH}_2 \text{CH}(\text{OH}) \text{CH}_3 + 2 \text{MnO}_4^- + 6 \text{H}^+ \rightarrow 5 \text{CH}_3 \text{CH}_2 \text{COCH}_3 + 2 \text{Mn}^{2+} + 8 \text{H}_2 \text{O}$$

Table 1

Effect of promoters and CPC micelle on pseudo-first-order rate constant and half-life\* for the MnO<sub>4</sub><sup>-</sup> oxidation of 2-butanol.

$10^3 \times Substrate$ (mol dm <sup>-3</sup> )		$\begin{array}{c} 10^4 \times MnO_4^- \\ (mol \ dm^{-3}) \end{array}$	$10^3 \times promoter$ (mol dm <sup>-3</sup> )		$10^3 \times Micellar$ catalyst (mol dm <sup>-3</sup> )		$10^5  imes k_{ m obs}  ({ m s}^{-1})$	Half life $(t_{1/2})$ (h)
2-butanol	1.0	1.0	-		-		$2.75\pm0.02$	7.0
	2.0						$6.816 \pm 0.04$	2.82
	3.0						$7.883 \pm 0.06$	2.44
	4.0						$10.166 \pm 0.05$	1.89
	5.0						$11.12 \pm 0.01$	1.73
2-butanol	1.0	1.0	-		-		$2.75 \pm 0.01$	7.0
		2.0					$2.633 \pm 0.03$	7.31
		3.0					$2.36 \pm 0.01$	8.16
		4.0					$2.416 \pm 0.05$	7.97
		5.0					$2.52 \pm 0.04$	7.64
2-butanol	1.0	1.0	PA	1.0	-		$4.98 \pm 0.02$	3.86
				2.0			$5.716 \pm 0.06$	3.37
				3.0			$6.56 \pm 0.03$	2.93
				4.0			$8.56 \pm 0.04$	2.25
				5.0			$8.766 \pm 0.02$	2.20
2-butanol	1.0	1.0	bipy	1.0	-		$5.85 \pm 0.02$	3.29
				2.0			$7.133 \pm 0.01$	2.70
				3.0			$9.55 \pm 0.01$	2.01
				4.0			$10.1 \pm 0.04$	1.90
				5.0			$13.783 \pm 0.02$	1.40
2-butanol	1.0	1.0	-		CPC	0.3	$98.3 \pm 0.04$	0.19
						0.6	$104.6 \pm 0.04$	0.184
						0.9	$118.3 \pm 0.05$	0.16
						1.2	$124.3 \pm 0.06$	0.155
						1.5	$131.0 \pm 0.05$	0.147
						1.8	$135.0 \pm 0.01$	0.143
						2.1	$140.0 \pm 0.02$	0.138
2-butanol	1.0	1.0	PA		CPC	1.2	$253.8 \pm 0.04$	0.086
2-butanol	1.0	1.0	bipy		CPC	1.2	$281.0\pm0.06$	0.0685

 $[H_2SO_4]_T = 1.0 \text{ mol } dm^{-3}$ , Temp = 30 °C.

The  $t_{1/2}$  values are directly calculated in this table by using the relation  $t_{1/2} = (\ln 2/k_{obs})$ , where  $\ln 2 = 0.693$ ,  $k_{obs} = pseudo-first-order$  rate constant in  $s^{-1}$ .

#### 2.5. Polymerization test

Acrylonitrile [40%] was added to the reaction mixture which was allowed to stand for 2–3 h. No polymer formation was detected. The result indicates the absence of any free radical intermediate and thus the possibility of a one-electron transfer step may be ruled out [37]. The result is in conformity with a one-step two-electron transfer process with no free-radical intermediate.

#### 2.6. Critical micelle concentration (CMC) determination

The CMC of CPC in the presence and absence of permanganate and 2-butanol was determined at break points of nearly two straightline portions of the specific conductivity versus concentration plot [20]. The CMC value of CPC was found to be  $1.0\times10^{-3}$  mol  $dm^{-3}$ by conductometry in the presence of only 2-butanol (1.0  $\times$  $10^{-3}$  mol dm<sup>-3</sup>) (Fig. S4a, supplementary file). The same CMC value was found by the absorbance measurement in UV in the presence of permanganate  $(1.0 \times 10^{-4} \text{ mol dm}^{-3})$  (Fig. S4b, supplementary file). The small change in the CMC could be associated to the formation of ion-pair between permanganate ion and surfactant molecules through electrostatic interactions. To determine the CMC, the conductivity measurements of the surfactant (CPC) solutions were made with conductivity meter (EUTECH Instruments CON 6000, cell constant  $1 \text{ cm}^{-1}$ ), the CMC values of these CPC was determined from plots of the specific conductivity versus [surfactant] in the presence of 2-butanol. The break points at the curve were taken as an indication of micelle formation and this corresponds to the CMC of CPC [38]. The experiments were carried out at 30 °C under varying conditions, that is, water + CPC + 2-butanol (conductometry), water + CPC + 2-butanol +  $MnO_4^-$ (spectrophotometry).

#### 3. Results

#### 3.1. UV-vis spectrophotometric study of the reaction

The MnO<sub>4</sub><sup>-</sup> ion, is a facile oxidant of organic compounds such as alcohol. In that case, 2-butanol, was oxidized into 2-butanone. Due to the excess concentration of alcohol present in the solution as compared to  $MnO_4^-$ , it is expected that the Mn(VII) ion will be totally reduced to Mn(II) at the end of the reaction. The color of the reaction mixture changed from purple to colorless at the end of the reaction. Solutions of Mn(VII) salts were purple in the presence of alcohol, whereas the solutions of Mn(II) salts are colorless. The progress of the oxidation of alcohols with MnO<sub>4</sub><sup>-</sup> in the presence and absence of surfactant and promoters was reflected by marked changes in the electronic spectrum of certain time intervals (Figs. S5-7, supplementary file). The scanned absorption spectra of the different sets of reaction mixtures were taken for both in the presence and absence of surfactant and promoter. Replicate scans of the spectra during the course of the reaction showed a decrease in the absorbance only, with no evidence of any shift in the peaks (Figs. S5–7, supplementary file). Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture 1 min after the start of the reaction with that of the final product within a wavelength of 250-650 nm.

#### 3.2. Dependence of reaction rate on $[MnO_4^-]$

The influence of  $[MnO_4^-]$  was studied at fixed [2-butanol]  $(=1.0 \times 10^{-3} \text{ mol dm}^{-3})$ ,  $[H_2SO_4]$   $(=1.0 \text{ mol dm}^{-3})$ , at different  $[MnO_4^-]$   $(1.0 \times 10^{-4}-5.0 \times 10^{-4} \text{ mol dm}^{-3})$ , at temperature (=30 °C). The kinetic curves were nonlinear showing an initial slow stage (noncatalytic) followed by a fast stage (autocatalytic). It was observed that rate constants of noncatalytic path decrease with increasing

 $[MnO_4^-]$ . These results are against the norms of the kinetics (the pseudo-first-order rate constants should be independent of the initial concentration of the reactant in defect). It may be possible due to the formation and flocculation (coagulation) of colloidal particles of MnO<sub>2</sub> during the course of reaction [20,39]. The independence of pseudo-first-order rate constants obtained from the linear portions of -ln(absorbance)-time plots (Fig. S1, supplementary file) at various [MnO<sub>4</sub>], may confirm that the reaction is first-order with respect to permanganate ion concentration [40]. The first-order dependence with respect to [MnO<sub>4</sub><sup>-</sup>] was confirmed not only from the linearity of the pseudo-first-order plots but also from the independence of the reaction rate (Table 1) on various initial concentrations of permanganate ranging between  $1.0 \times 10^{-4}$  and  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> [41]. The values of  $k_{obs}$  for 2-butanol were found to be almost constant (Table 1) and independent of the initial [MnO<sub>4</sub><sup>-</sup>] indicating that the reaction is first order with respect to  $[MnO_4^-]$  [37].

#### 3.3. Dependence of reaction rates on [2-butanol]

The reaction was studied at different concentrations of 2-butanol without the addition of surfactant within the range  $1.0 \times 10^{-3}$  to  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> concentrations. The plot of velocity constant " $k_{obs}$ " against 2-butanol concentration is found linear (Fig. 1) showing the first order dependency of the rate on 2-butanol concentration in the given range for both stages. It has been observed that the rate of reaction increases with substrate concentration. Velocity constants calculated by different methods are given in Table 1. Under pseudo-first-order conditions, viz. [2-butanol]  $\gg$  [MnO<sub>4</sub><sup>-</sup>], the reaction rate increases with increasing [2-butanol]. The order in [2-butanol] was found to be unity. This can be readily seen from the plot of  $k_{obs}$  versus [2-butanol].

#### 3.4. Dependence of reaction rate on [CPC]

The effect of [CPC]  $(=3.0 \times 10^{-4} \text{ to } 18.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  was studied at constant  $[\text{MnO}_4^-]$   $(=1.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$ , [2-butanol]  $(=1.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ ,  $[\text{H}_2\text{SO}_4]$   $(=1.84 \times 10^{-4} \text{ mol } \text{dm}^{-3})$  and temperature (=30 °C). The  $k_{obs}$ -[CPC] profile shows increase in the rate constants with [CPC] that reaches a limiting value (Fig. 2). It has been observed that the rate of reaction increases with surfactant concentration showing catalytic function of surfactant in the present reaction.

#### 3.4.1. Rate constants–[CPC] profile for oxidation of 2-butanol by MnO<sub>4</sub><sup>-</sup>

In order to see the role of surfactants on the oxidation of 2-butanol by  $MnO_4^-,$  the effects of [CPC] were studied at  $1.0\times10^{-3}$  mol dm $^{-3}$ 



**Fig. 1.** Dependence of  $k_{obs}$  on [2-butanol] for MnO<sub>4</sub><sup>-</sup> oxidation of 2-butanol in aqueous H<sub>2</sub>SO<sub>4</sub> media at 30<sup>9</sup>: [MnO<sub>4</sub><sup>-</sup>]<sub>T</sub> = 2 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [2-butanol]<sub>T</sub> = 2 × 10<sup>-3</sup> mol dm<sup>-3</sup>.



**Fig. 2.** Plot showing the effects [CPC] on  $k_{obs}$  of the oxidation of 2-butanol by permanganate. Reaction conditions:  $[MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ , [2-butanol]<sub>T</sub> =  $1.0 \times 10^{-3} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \text{ mol } dm^{-3}$ , T = 30 °C, the break point of the curve is the CMC (0.9 mM) of CPC.

of 2-butanol and  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> of MnO<sub>4</sub><sup>-</sup>. In our experiment, the kinetic studies were limited in the [CPC] range of  $3.0 \times 10^{-4}$  to  $21.0 \times 10^{-4}$  mol dm<sup>-3</sup>. The plot of  $k_{obs}$  against [CPC] shows gradual increase of rates with the increase in [CPC] (Fig. 2) which clearly demonstrate the CPC catalytic effect not only above but even below CMC, i.e., micellar as well as submicellar catalysis are observed. These observations are most interesting instead of  $k_{obs}$ , attained constant values (for unimolecular reactions) or pass through a maximum (for bimolecular reactions) with [CPC]. The observed catalytic effect may, therefore, be due to (i) presence of premicelles and (ii) preponement of micellization by reactants. The values of rate constants are summarized in Table 1. It is certainly possible that the negative charge on  $MnO_4^$ forms an ion pair  $(Py^+MnO_4^-)$  with the positive pyridinium  $(Py^+;$  $-PyN^+(C_{16}H_{33}))$  head group of CPC molecules which brings the reactants together through electrostatic interactions [42]. Coordination of a Py<sup>+</sup> cation by the permanganate anion would decrease electron density of the  $MnO_4^-$  which, in turn, increases the oxidizing power of the permanganate. Fig. 2 signifies that MnO<sub>4</sub><sup>-</sup> and 2-butanol are interact with the CPC surfactant, and submicellar aggregates are formed [38]. Both the reactants will be preferentially located at the positively charged CPC aggregated molecules and, therefore, the kinetic CMC of CPC is lower than in water. During the oxidation of 2-butanol by permanganate in the presence of CPC micellar catalyst the CMC value obtained for CPC was 0.9 mM by kinetic methods.

#### 3.5. Dependence of reaction rate on added promoters

#### 3.5.1. Effect of PA

The concentration of PA was varied in the range  $1.0-5.0 \times 10^{-3}$  mol dm<sup>-3</sup> keeping all other conditions constant. It was observed that the rate constant was increased with increasing concentration of PA (Table 1, Fig. 3a).

#### 3.5.2. Effect of 2,2'-bipyridine

The concentration of 2,2'-bipyridine was varied in the range  $1.0-5.0 \times 10^{-3}$  mol dm<sup>-3</sup> keeping all other conditions constant. It was observed that the rate constant was increased with increasing concentration of bipy (Table 1, Fig. 3b).

#### 3.5.3. The UV-visible spectra of N-hetero-aromatic base promoters

The electronic spectra of the ligands and there complexes were recorded in water and are given in Fig. 4a. The free ligands picolinic



**Fig. 3.** Dependence of  $k_{obs}$  on [promoter] for MnO<sub>4</sub><sup>-</sup> oxidation of 2-butanol (in absence of surfactant) in aqueous H<sub>2</sub>SO<sub>4</sub> media at 30 °C where  $[MnO_4^-]_T = 2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [2-butanol]\_T =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[H_2SO_4]_T = 1.0$  mol dm<sup>-3</sup>. (a) Dependence of  $k_{obs}$  on [PA]; (b) Dependence of  $k_{obs}$  on [bipy].

acid and 2,2'-bipyridine UV-vis spectral data display two bands ~220–230 nm and ~270–280 nm attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. The electronic spectrum of the Mn(II) complex exhibited three bands in the region near 210-280 nm which may be assigned to the transitions  ${}^6A_{1g} \rightarrow 4T_{1g}$  (4G),  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (4G) and  ${}^6A_{1g} \rightarrow {}^4E_g$ ,  ${}^4T_{1g}$ (4P) respectively, indicating octahedral geometry. The high-energy band 220 nm is due to forbidden ligand  $\rightarrow$  metal charge transfer [43]. Attempts to obtain spectral (UV-visible) evidence for the promoterpermanganate complex was done and presented in Fig. 4b. The UVvis spectrum of Mn(II) solution shows intense bands at  $\lambda_{max} = 215$ and 290. The UV-vis spectra of Mn(II)-PA and Mn(II)-bipy complex are shown in Fig. 4c which shows the spectra has two bands near 200–230 nm are attributed to the  $\pi$ - $\pi$ \* transition of the benzene ring of PA and bipyridine. The n- $\pi^*$  transition of the C=N bond, respectively, while the next band near 230-330 nm, as the most characteristic adsorption band of Mn(II)-promoter complex is due to the MLCT [44].

#### 4. Discussion

#### 4.1. Reaction mechanism of uncatalyzed path

During the oxidation, it is evident that permanganate is reduced to various oxidation states, i.e., Mn(VI), Mn(V), Mn(IV) and Mn(III) in

acidic, alkaline and neutral media. The reactivity of these intermediate states depends on the nature of the reductant and on the pH of the medium. Scheme 1 represents protonation of MnO<sub>4</sub><sup>-</sup>. The next reaction shows the formation of a 2-butanol-Mn(VII) complex. We may assume that the intermediate decomposes in a one-step, two-electron oxidation-reduction mechanism [45] to Mn(V) and other oxidation products. Mn(V) is highly unstable in an acidic medium with respect to disproportionation and immediately gets converted into Mn(IV). An addition to an O-H bond results in the formation of an ester; an addition to a C-H bond gives an organometallic compound. The reducing behavior of methanol and ethanol toward permanganate in a perchloric acid medium has been investigated in the absence and presence of the surfactant Tween-20 [46]. Permanganic acid is the chief oxidizing species, which combines with the alkanol to form an intermediate complex followed by decomposition in the rate-determining step to produce the corresponding aldehyde and Mn(V). The latter disproportionates to Mn(VII) and Mn(II) in the fast step (Scheme 1) [12].

The decomposition of the intermediate complex RCH<sub>2</sub>O.MnO<sub>3</sub> may be thought to occur as follows:



In the case where permanganate serves as an oxidizing agent in an acid medium, the possible intermediate species are Mn(VI), Mn(V), Mn(III) and Mn(IV). On the other hand, Mn(II), the ultimate reaction product, acts as an autocatalyst. The plot of  $k_{obs}$  versus [2-butanol] is linear (Fig. 1), therefore, first-order with respect to [2-butanol]. The formation of a single isosbestic point in the CPC catalyzed path near  $\lambda = 420$  nm confirms the formation of Mn(IV) intermediate during the reaction and as soon as it forms it readily decays to lower valent manganese species. Under the experimental conditions (Figs. S5–7, supplementary file) no manganese(IV) formation was observed in the presence of  $[H^+] \ge 1.0 \text{ mol dm}^{-3}$ . These results are not surprising because Mn(IV) is known to be unstable in acidic medium. Again the presence of Mn(VI) and Mn(V) is ruled out by the fact that they are highly unstable in acidic medium [47]

#### 4.1.1. Rate law

Since the reaction gives a linear plot, it is proposed that the reaction involves a pre-equilibrium with the formation of an intermediate complex between  $HMnO_4$  and the 2-butanol molecule followed by the decomposition of the complex in the rate limiting step to produce the corresponding carbonyl compound and Mn(V). The latter undergoes disproportionation to Mn(VII) and Mn(II) in a fast step (Scheme 1). The existence of Mn(V) as an intermediate species has already been reported by a number of workers [48]. Disproportionation of manganese(V) in a fast step produces manganese(VII). According to the suggested mechanism, the rate of disappearance of  $MnO_4^-$  may be expressed as:

$$-\frac{d[MnO_{4}^{-}]}{dt} = \frac{k_{d}K_{1}K_{2}[H^{+}][CH_{3}CH_{3}CH_{0}(OH)CH_{3}][MnO_{4}^{-}]}{1 + K_{2}[CH_{3}CH_{2}CH_{0}(OH)CH_{3}]}$$

so that the pseudo-first-order rate constant

$$k_{obs} = -\frac{1}{\left[\mathsf{MnO}_{4}^{-}\right]} \cdot \frac{d[\mathsf{MnO}_{4}^{-}]}{dt} = \frac{k_{d}K_{1}K_{2}[H^{+}][\mathsf{CH}_{3}\mathsf{CH}_{3}\mathsf{CH}_{0}\mathsf{OH})\mathsf{CH}_{3}]}{1 + K_{2}[\mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{0}\mathsf{OH})\mathsf{CH}_{3}]}$$

The stable oxidation product of  $MnO_4^-$  in acid medium is Mn(II). Furthermore, because no rise and fall in the absorption was observed at 418 nm, it is concluded that Mn(IV) does not intervene as a possible oxidizing agent since it is short-lived.  $Mn^{2+}$  was identified by UV-visible spectroscopy (Fig. 4c) and spot test [48]. The unstable intermediate



**Fig. 4.** (a) Absorption spectrum of only promoter solution in aqueous medium: (A) Absorption spectrum picolinic acid,  $[PA]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ; (B) Absorption spectrum 2,2'-bipyridine  $[bipy]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ , Temp = 30 °C. (b) Absorption spectrum of reaction mixture with and without promoter (in absence of substrate): (A)  $[MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \text{ mol } dm^{-3}$ , (B)  $[MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[PA]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ , (C)  $[MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \text{ mol } dm^{-3}$ ,  $[Bipy]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[PA]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[PA]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[C] [MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4]_T = 1.0 \times 10^{-3} \text{ mol } dm^{-3}$ , (C) bipy promoted pathway  $[PA]_T = 1.0 \times 10^{-3} \text{ mol } dm^{-3}$ , (C) bipy promoted pathway  $[PA]_T = 1.0 \times 10^{-3} \text{ mol } dm^{-3}$ .



Scheme 1. Oxidation of 2-butanol by MnO<sub>4</sub><sup>-</sup> in absence of catalyst/promoter in aqueous acidic media.

Mn(IV) formed during oxidation reacts with 2 mol of Mn(V) in a fast step to give 2 mol of Mn(II) and Mn(VII), thus satisfying the stoichiometric observations [40]. At the same time, it is well known that, in the reduction process of permanganate ions in strong acid medium while the reducing species is in excess, the  $Mn^{2+}$  ions is the final product.

#### 4.2. Complex formation by the promoters with permanganic acid

The experimental observations indicated that the oxidation rate was increased with the addition of two promoters: PA and bipy. The enhancement in oxidation rate of 2-butanol by  $MnO_4^-$  in the presence of the two promoters is most probably due to the formation of  $MnO_4^-$  promoter complex in pre-equilibrium steps. These complexes are assumed here as Active-oxidant, like the Cr(VI)-promoter complexes in Cr(VI) oxidation kinetics [27–29]. The formation of active oxidants is supported by the proton NMR spectra of  $MnO_4^-$ -promoter complex of the corresponding promoters (Figs. S8 and S9, supplementary file). The corresponding proton NMR signals are assigned in Table S2 (supplementary file).

The UV-vis spectrum (Fig. 4b) clearly confirms the complex formation between the oxidant and promoter. The rate constant of PA and bipy promoted path both in the presence ( $k_{obs} = 253.8 \times 10^{-5} \text{ s}^{-1}$  for 0.005 mol dm<sup>-3</sup> of PA and 281.0 × 10<sup>-5</sup> s<sup>-1</sup> for 0.005 mol dm<sup>-3</sup> of PA and 281.0 × 10<sup>-5</sup> s<sup>-1</sup> for 0.005 mol dm<sup>-3</sup> of bipy) and in the absence ( $k_{obs} = 8.766 \times 10^{-5} \text{ s}^{-1}$  for 0.005 mol dm<sup>-3</sup> PA and 13.786 × 10<sup>-5</sup> s<sup>-1</sup> for 0.005 mol dm<sup>-3</sup> bipy) of CPC is far greater than the aqueous phase path ( $k_{obs} = 2.75 \times 10^{-5}$ ) s<sup>-1</sup> at 30 °C, suggesting a significant ligand participation in complex formation with MnO<sub>4</sub><sup>-1</sup> in the transition state of the oxidation. Furthermore, the transition state is stabilized through coordination with HMnO<sub>4</sub> and the nitrogen lone pair of the ligand (PA and bipy). The cationic species of the promoters are (HA<sup>+</sup>) reactive and major existing species in the presence of 1.0 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> and it may undergo complexation with HMnO<sub>4</sub>.

It is observed that PA and 2,2'-bipyridine display characteristic feature toward the permanganate oxidation of 2-butanol. They promoted the reaction rate. It is well established that the presence of phenyl ring in the permanganate-promoter complex affects the decomposition of the complex. The *N*-hetero-aromatic base promoters may form a complex in the intermediate step probably and it is concluded by the downfield shift of proton signals of promoters during the formation of complex with permanganic acid. The above complexing agents have

the aromatic protons become more deshielded. It is believed that the catalytic activity of complexing agents such as PA and 2,2'-bipyridyl depends on their ability to stabilize intermediate manganese valence states. Quite likely, the complexing agents stabilize the end products, manganese (II) (Fig. 4c), and hence accelerate the whole of the reaction. This is similar to the view reported in the Cr(V) oxidation of sulfides and cyclic ketones in the presence of PA. The reactive nucleophile Cr(VI)-phen complex has been reported in the oxidation of anisole by chromic acid [49,50].

#### 4.3. Association of $MnO_4^-$ with the CPC micelles

Interestingly, the absorbance of reaction mixture ( $MnO_4^- + 2$ -butanol + H<sub>2</sub>SO<sub>4</sub>) changed very rapidly in the presence of CPC (Fig. S4b, supplementary file). This behavior indicates the electrostatic interaction between the positive head group of CPC and permanganate ion or the association of the  $MnO_4^-$  into the stern layer of the CPC micelles and results in the formation of ion-pair complex between  $MnO_4^-$  and CPC. The hyperchromic shift in the absorption spectrum observed at [CPC] below the CMC. Surprisingly, as the [CPC] increased from  $3.0 \times 10^{-4}$ to  $18.0 \times 10^{-4}$  mol dm<sup>-3</sup>, the absorbance decreases with increasing [CPC]. In the presence of CPC, 525 nm represents the  $\lambda_{max}$  of permanganate–CPC ion-pair complex. The initial reaction may be represented as

$$MnO_4^- + CPC \stackrel{R_5}{\rightleftharpoons} MnO_4^- - CPC$$

The following relation is used to determine the value of ion-pair complex formation constant ( $K_s$ ).

$$\frac{[\text{MnO}_{4}^{-}]\text{T}[\text{CPC}]}{\Delta A}\frac{[\text{CPC}]}{\Delta \varepsilon \iota} + \frac{1}{K_{s}\Delta \varepsilon \iota}$$

where  $[MnO_4^-]_T =$  total metal ion concentration,  $\Delta A =$  the difference in the absorbance between the complex and  $MnO_4^-$  at the wave length (525 nm) where both the uncomplexed and complexed forms of the permanganate absorb,  $\Delta \varepsilon =$  the difference in absorption coefficients and l = the path length (1 cm). The values of  $K_s$  and  $\Delta \varepsilon$  were calculated form the slope and the intercept. The values of K<sub>c</sub> and  $\Delta \varepsilon$  are 162 dm<sup>-3</sup> mol<sup>-1</sup> and  $689 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively [20]. The CMC value of CPC in the presence of permanganate was found to be  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> at 30 °C. The premicellar CPC kinetic effects as well as the micellar CPC effects on the oxidation rate can be rationalized by considering the distribution and/or solubilization of the reactants among the different pseudophases present in the reaction medium. The CMC is lower than in water (1.1 mM), suggesting that the active species of  $MnO_4^-$  and/or 2-butanol interacts with a positive head group of CPC aggregates (monomers, dimmers, trimers, etc.) and submicellar aggregates may be formed that bring the reactants together through electrostatic interactions [51]. The binding of permanganate with CPC was also confirmed by the spectral changes observed in proton NMR spectrum of only CPC and CPC with permanganate (Fig. S10, supplementary file). The corresponding proton signals are assigned in Table S2 (supplementary file).

The permanganate interactions with CPC monomers were examined by the chemical shifts in the CPC protons, particularly those on and near the pyridyl ring. Addition of the CPC surfactant, above the cmc (1.2 mM), with permanganate  $(1.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$  displayed distinct upfield shifts in the proton peaks situated near the pyridyl ring, verifying the positioning of permanganate close to the pyridyl ring (Fig. S10). Importantly, the chemical shifts in the proton signals of CPC from normal micelles (Fig. S10, spectrum (a) supplementary file) and that in the presence of permanganate (Fig. S10, spectrum (b) supplementary file) are noticeably different. This is an indication that the CPC micelle structures get modulated by the presence of permanganate. Assuming the interaction of permanganate-CPC complex above the cmc, the binding analysis of the observed (Fig. S4b supplementary file) chemical shifts provided the binding constant value of  $(162 \,\mathrm{dm}^{-3} \,\mathrm{mol}^{-1})$ , which supports the ion–dipole interaction between the polar permanganate and the cationic pyridyl group. On the other hand, similar NMR measurements with permanganate and CPC (1.2 mM, above the cmc of CPC), displayed broader proton peaks, having very little changes in the chemical shifts of the pyridyl protons (Fig. S10b, supplementary file) [22].

#### 4.4. Optical images

The optical micrographs are taken for mixtures of 10:1 concentration ratio of 2-butanol and surfactant CPC in  $100 \times$  magnification in an optical microscope (LEICA DM 1000). The images (Fig. 5) represent the evidence of micelle formation in aqueous medium. The formation of micelles in association with 1-butanol in aqueous medium was clearly identified by the optical images found.

#### 4.5. Scanning electron microscope (SEM) images of CPC micelle

SEM analysis was done by placing a drop of CPC solution on foil paper. Then it was air dried followed by coating with gold, and was observed under Scanning Electron Microscope SEM (S530 HITACHI SEM) instrument using IB 2 ion coater. The SEM picture (Fig. 6a) of pure CPC looked rod-like or cylindrical particles. This also looked like a bilayer structure. Most of the micelles appear to be bent rather than straight cylinders. It has been known for many years that aggregates with different morphologies can form in small molecule surfactant systems. The addition of  $MnO_4^-$  changes the morphologies of the aggregates from bilayers or cylinders to spheres (Fig. 6b, c). At [CPC] > CMC, in the presence of 2-butanol the broken rock-type materials of large size appeared in the SEM picture (Fig. 6d, e). In this concentration of CPC in the medium, the formation of particles of varied geometries and patterns was observed as below:

## 4.6. High resolution transmission electron microscope (HRTEM) images of CPC micelle

The HR-TEM investigation was done at 20 KV acceleration voltage using lacey carbon coated Cu grid of 300 mess size in HR-TEM microscope (JEOL JEM 2100). Samples were prepared by placing sample mixture drops directly on the copper grids using a micropipette. The reactants including the surfactant present in the aqueous mixture were allowed to settle. TEM pictures (Fig. 7) are presented which illustrate the multiple morphologies of the aggregates made from the surfactant CPC. Also, the micrograph suggests a relatively narrow size distribution of the cylindrical micelle (Fig. 7a to c) [52] diameters, but a widely variable length. With the addition of reactants, the morphology changes at some extent may be due to the accumulation permanganate in acidic solution at the micellar surface. Cylindrical vesicles were converted to the spherical micelles in the presence of permanganic acid as depicted in the images. The small particles closely associated with the large spherical micelles (Fig. 7d to f) are permanganate species.

#### 4.7. Analysis of catalytic role of CPC

The formation of an ion-pair complex between permanganate and the positive head group of the CPC micelles was confirmed from the initial absorbance changes at 525 nm (Fig. S2b, supplementary file). The increase in  $k_{obs}$  with [CPC] may be attributed to increasing solubilization/incorporation/association of the reactant species with increase in [CPC]. The plot of  $k_{obs}$  versus [CPC] shows rate constant (Fig. 2) increase monotonically nearly 70-fold with [CPC]. In a micellar system, with CPC as the substrate, both the oxidant and the alcohol are found to be partitioned between the aqueous and the micellar pseudophase. Thus, the reaction may proceed according to Scheme 2.

The attractive electrostatic interaction between the positively charged polar head groups and negatively charged reactants is increased, leading to an increase in the free energy, which are advantages in regards to the energy requirement for the redox reaction. The type of interaction occurring between CPC micelle and reactants determines the locus of the solubilization phenomenon at the micellar interface, in between the hydrophilic head groups and the first few carbon atoms of the hydrophobic fragment (also commonly referred to as the palisade layer), and finally in the core of the micelle. Therefore, the polar -OH functional groups of 2-butanol are mainly solubilized in the outer region of the micelle, whereas nonpolar aliphatic framework are preferentially located in the inner portions of the micelles (Scheme 3a-c) [53]. When concentration of the micelles was less than that in CMC, MnO<sub>4</sub><sup>-</sup> ions are preferentially located at the micellar surface due to the presence of Cl<sup>-</sup> ions. When the concentration of the surfactant becomes greater than or equal to CMC, the aqueous medium is largely populated by surfactant micelles. The MnO<sub>4</sub><sup>-</sup> ion approaches toward the micellar head group region [54]. The electrostatic attraction of the cationic head groups of CPC micelle surface to the nucleophilic anion counterions leads to augmentation of the local concentration of the nucleophile, whereas the incorporation of the substrate 2-butanol in the micelle leads to a higher local concentration of the substrate. This enhanced concentration of the reactants accounts for the higher rate of reaction and thereby leading to a decrease of half-life value (Table 1) [55-57].

#### 4.8. Probable reaction site in micelle

Micellar surfaces are water-rich and polarities of micelle-water interfaces are lower than that of bulk water. The catalysis of the reaction between 2-butanol and permanganate by CPC could be rationalized in terms of both electrostatic and hydrophobic interactions. 2-butanol gets incorporated hydrophobically into the palisade layer and MnO<sub>4</sub><sup>-</sup> may be totally present in the Stern layer due to the electrostatic interactions of negatively charged species may help to stabilize MnO<sub>4</sub><sup>-</sup> and CPC through complexation. It is interesting to note that the reactivity of 2-butanol toward MnO<sub>4</sub><sup>-</sup> is much higher than the corresponding oxidation of many other alcohols in the absence and presence of cationic CPC surfactant. This is not very surprising judging from the fact that side chain alcohol acids play an important role: the oxidation rate increases with hydrophobicity of the side chain as reflected in Table 1. The values of CMC (Fig. S4, supplementary file) suggesting that the MnO<sub>4</sub><sup>-</sup> and 2-butanol interacts with the CPC micellar aggregates (ion pair between positive head group of CPC and reactants) are formed. Therefore, the environment will be less polar than in pure water.

#### 4.9. Probable role of CPC micelle

The hydrophobic, electrostatic and hydrogen bondings are the main factors involved in the rate enhancement of a bimolecular reaction. It was observed that the reaction rate increases with [CPC] (Fig. 2), which clearly demonstrates the CPC catalytic effect not only above but



Fig. 5. Different views of optical micrograph images of mixtures of 2-butanol and surfactant CPC in water: (a) and (b) 2-butanol:CPC = 10:1.

(b)  $CPC+MnO_{4}(2000X)$ 

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5um (e) CPC+2-butanol (500X)

Fig. 6. Different views of SEM images showing micelles formed by CPC in aqueous medium.  $[CPC] = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$  (a) SEM image of only CPC micelles in 6000× magnification; (b) and (c) SEM image of CPC micelles showing the interaction with  $MnO_4^-$  in aqueous acidic medium in  $2000 \times$  and  $6000 \times$  magnification respectively,  $[MnO_4^-] = 1.0 \times 10^{-4}$  mol dm<sup>-</sup>  $[H^+] = 1.0 \text{ mol } dm^{-3};$  (d) and (e) SEM image of CPC micelles showing the interaction with 2-butanol in 2000× and 500× magnification respectively; [2-butanol] =  $1.0 \times 10^{-4} \text{ mol } dm^{-3}$ , Temp =  $30 \degree C$ .

also even below the CMC (i.e., micellar as well as premicellar catalyses are observed) [39]. For 2-butanol- $MnO_4^-$  reactions, the degree of micellar rate enhancement depends largely on the extent of reactive counterion binding to micelles. Reactions occur between the micellar solubilized MnO<sub>4</sub><sup>-</sup> and 2-butanol and the bound counterions in the junctural region of palisade-Stern layers. The frequency of molecular collisions increases as a consequence of the close association of the two reacting species at the micellar interface that enhances the oxidation rate. The promoted reaction pathway in the presence of CPC micelle permanganate-promoter complex affects the rate due to the maximum accumulation of reactants in the stern layer. PA and bipy get complexed with permanganate and thus enhance the catalytic activity of CPC micelle by electrostatic interaction [58] with more number of reactants with CPC micelle. A possible arrangement (although highly schematic) could be that as shown in Scheme 3a-c.

Bunton et al., showed that Cationic micelles of CPC, accelerate the oxidation of thioanisole, by tetraperoxomolybdate ion,  $Mo(O_2)_4^{2-}$  [59]. The acceleration of rate of oxidation of alcohols by KMnO<sub>4</sub> by Lewis acids was carried out by Hongxia Du et al. [60]. The rate is increased by 4 orders of magnitude in the presence of  $Ca^{2+}$ . But in our case the rate has been increased up to 100-fold in the presence of CPC micelle combination with bipy promoters.

It is interesting to point out that micelles can influence the rates of micelle-modified reactions through two different effects.

- The concentration or depletion of reactants in the interfacial region has a major effect on the rates of bimolecular processes, such as the one investigated in this work. This is called the concentration effect.
- $\dot{\mathbf{v}}$ Another effect depends on the transfer of substrate from water to micelles, on the reaction mechanism, and on the properties of the







(a) Only CPC (6000X)





**Fig. 7.** (a) to (c) Different views of TEM images showing micelles formed by CPC in aqueous medium,  $[CPC] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ . (d) to (f) Different views of TEM images of the reaction mixture showing the interaction of MnO<sub>4</sub><sup>-</sup> by CPC micelles in aqueous acidic medium,  $[CPC]_T = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[MnO_4^-]_T = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+]_T = 1.0 \text{ mol dm}^{-3}$ , Temp = 30 °C.

interfacial region, such as local charge, polarity, and water content. The kinetic micellar effects observed in bimolecular processes are mainly due to the concentration of reactants in the small volume of the micelles.

❖ In the reaction studied, the difference between  $k_{obs(w)}$  and  $k_{obs(m)}$  in the presence of  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> bipy is  $278.25 \times 10^{-5}$  s<sup>-1</sup> and accounts for the micellar medium effects in the micellar solutions assuming that no morphological transition occurs [61].

The experimental data in Table 1 describes the half life ( $t_{1/2}$ ) values of the 2-butanol oxidation reaction by MnO<sub>4</sub><sup>-</sup> that gradually decreases upon addition of PA or bipy and CPC micellar catalyst. The decrease in  $t_{1/2}$  value (0.0685 h) becomes more severe when the combined effect of CPC micellar catalyst and bipy promoter has come into play. The overall analysis of our experimental results compared to the literature works are presented in Table 2. The pseudo-first-order rate constants of the oxidation reaction between MnO<sub>4</sub><sup>-</sup> and 2-butanol vary in magnitude in the order of  $k_{(CPC)} > k_{(Aqueous)}$ ,  $k_{(bipy)} > k_{(PA)}$  and  $k_{(bipy)(CPC)} > k_{(PA)(CPC)}$ . The micellar catalysis by CPC in association with bipy promoter exhibited the remarkable ~100-fold rate enhancements (Table 1) as compared to that of uncatalyzed reaction.

#### 5. Conclusion

Our present civilization is highly cursed with ecological pollution, which threatens the very existence of life. Potassium permanganate has long been a suitable oxidant to neutralize some of these pollutants and many studies are progressing in this direction. Permanganate oxidation has gained momentum since more than a century ago. Recently, a large number of studies have been carried out without organic solvent in aqueous micellar medium.

The key facts are:

- (1) The reaction proceeds fast in the presence of PA/bipy promoter in CPC surfactant than in aqueous phase.
- (2) Both the reactants (MnO<sub>4</sub><sup>-</sup> and 2-butanol) proceed toward the cationic head group of CPC micelle.
- (3) The increase in the rate of reaction caused by the presence of micelle is due to the increase in the number of collisions between reactant molecules and stabilizes the intermediate by the opposite charge of cationic surfactant. SEM, TEM and NMR experiments are helpful to determine the interaction of CPC micelle with MnO<sub>4</sub><sup>-</sup> and 2-butanol.



Scheme 2. Partitioning of the oxidant and substrate between the aqueous and micellar pseudo phase. W = aqueous medium, M = CPC micellar medium, S = substrate (2-butanol), O = oxidant.



Scheme 3. (a) Schematic model showing probable reaction site for the cationic (CPC) micellar mediated oxidation reaction between (a) [MnO<sub>4</sub><sup>-</sup>], 2-butanol and proton; (b) [MnO<sub>4</sub><sup>-</sup>], picolinic acid, 2-butanol and proton (c) [MnO<sub>4</sub><sup>-</sup>], 2,2'-bipyridine, 2-butanol and proton.

The proper choice of a surfactant can lead to rate increases of 5- to 1000-fold compared to the same reaction in the absence of a surfactant. Bipyridine exhibited 100-fold rate enhancement of the normal  $MnO_4^-$  oxidation of 2-butanol at room temperature.

In our study the combination of CPC and bipy was the most excellent micellar catalyst and promoter for the  $MnO_4^-$  oxidation of 2-butanol to 2-butanone in acidic medium at room temperature.

#### Table 2

A comparative result for oxidation of 2-butanol using different oxidant and catalyst.

Entry	Catalyst	Ref.	Conditions	Rate constant $(k_{obs})$
1. 2.	$[Cr(III)] = 20 \times 10^{-4} \text{ mol } dm^{-3}$	[62] [63]	$\begin{split} & [2\text{-Butanol}]_{T} = 3 \times 10^{-3} \text{ mol } dm^{-3}, \text{ oxidant} = \text{FeO}_{4}^{2-}, \text{pH} = 9.70, \text{T} = 25 \ ^{\circ}\text{C}. \\ & [2\text{-Butanol}]_{T} = 4.0 \times 10^{-2} \text{ mol } dm^{-3}, [\text{Ce}(\text{IV})] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}, \\ & [\text{Cr}(\text{III})] = 20 \times 10^{-4} \text{ mol } dm^{-3}, [\text{H}_{2}\text{SO}_{4}] = 6.0 \times 10^{-2} \text{ mol } dm^{-3}, \\ & [\text{HCIO}_{4}] = 2.0 \text{ mol } dm^{-3}, \text{u} = 2.1 \text{ mol } dm^{-3}, \text{T} = 30 \ ^{\circ}\text{C}. \end{split}$	$\begin{array}{l} 1.40 \times 10^{-2} \ dm^3 \ mol^{-1} \ s^{-1} \\ 10.47 \times 10^{-4} \ s^{-1} \end{array}$
3.	$[CHAPS] = 8 \times 10^{-3} \text{ mol } dm^{-3},$ [Ir(III)] = 2 × 10 <sup>-6</sup> mol $dm^{-3}$	[18]	[2-Butanol] <sub>T</sub> = $2.0 \times 10^{-3}$ mol dm <sup>-3</sup> , [Ce(IV)] = $2 \times 10^{-4}$ mol dm <sup>-3</sup> , [CHAPS] = $8 \times 10^{-3}$ mol dm <sup>-3</sup> , [Ir(III)] = $2 \times 10^{-6}$ mol dm <sup>-3</sup> , [H <sub>2</sub> SO <sub>4</sub> ] = $0.5$ mol dm <sup>-3</sup> , $\mu$ = [H <sub>2</sub> SO <sub>4</sub> -Na <sub>2</sub> SO <sub>4</sub> ] = $2.0$ mol dm <sup>-3</sup> , T = $30$ °C.	$1.55 \times 10^{-2} \text{ s}^{-1}$
4.	$[Ru(III)] = 4.8 \times 10^{-6} \text{ mol } dm^{-3}$	[64]	$[2-Butanol]_T = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, [K_3Fe(CN)_6] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}, [Ru(III)] = 4.8 \times 10^{-6} \text{ mol dm}^{-3}, [NaOH] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, T = 30 ^{\circ}C.$	$7.29 \times 10^{-5} \text{ mol } dm^{-3} min^{-1}$
5.	$[Ru(VI)] = 4.8 \times 10^{-6} \text{ mol } dm^{-3}$	[65]	$ [2-Butanol]_T = 0.80 \text{ mol } dm^{-3}, [K_3Fe(CN)_6] = 2.0 \times 10^{-3} \text{ mol } dm^{-3}, [Ru(III)] = 4.8 \times 10^{-6} \text{ mol } dm^{-3}, [NaOH] = 0.2 \text{ mol } dm^{-3}, \mu = 0.5 \text{ mol } dm^{-3} \text{ T} = 30 \text{ °C}. $	$13.75 \times 10^{-5} \text{ mol } \text{dm}^{-3} \text{ min}^{-1}$
6.	-	[66]	$[2-Butanol]_{T} = 0.50 \text{ mol } dm^{-3}, [CTADC] = 1.89 \times 10^{-4} \text{ mol } dm^{-3}, medium = DCM, [acetic acid] = 3.24 \text{ mol } dm^{-3}, T = 30 \text{ °C}.$	$3.8 \times 10^{-3} \text{ s}^{-1}$
7.	-	[67]	$[2-Butanol]_T = 2.0 \times 10^{-2} \text{ mol } dm^{-3}$ , $[K_2S_2O_8] = 2.0 \times 10^{-2} \text{ mol } dm^{-3}$ , $pH = 8$ , T = 60 °C.	$6.11\times 10^{-5}\ s^{-1}$
8.	$\label{eq:CPC} \begin{split} [CPC] &= 1.2 \times 10^{-3} \text{ mol } dm^{-3} \text{and} \\ [bipy] &= 5.0 \times 10^{-3} \text{ mol } dm^{-3} \end{split}$	Present work	$\begin{split} & [2\text{-Butanol}]_T = 1.0 \times 10^{-3} \text{ mol } dm^{-3}, \\ & [\text{MnO}_4^-] = 1.0 \times 10^{-4} \text{ mol } dm^{-3}, \\ & [\text{CPC}] = 1.2 \times 10^{-3} \text{ mol } dm^{-3}, \\ & [\text{bipy}] = 5.0 \times 10^{-3} \text{ mol } dm^{-3}, \\ & [\text{H}_2\text{SO}_4] = 1.0 \text{ mol } dm^{-3}, \\ & T = 30 \text{ °C}. \end{split}$	$2.81 \times 10^{-3} \ s^{-1}$

Here, CTADC = Cetyltrimethylammonium dichromate, DCM = Dichloromethane.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.molliq.2014.07.018.

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