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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, $[\text{2-butanol}]_T \gg [MnO_4^-]_T$, 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 $\ln(\text{Absorbance})_{525}$ 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, spectrophotometry 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.

## 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 ($E^0 = 1.51$ 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 2-butanol 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 $CO_2$ 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, $[\text{2-butanol}]_T \gg 10[MnO_4^-]_T$ 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 ± 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 ($\lambda_{max}$ 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 ±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-$MnO_4^-$ 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 $^1H$ NMR spectra of the product carbonyl compound in $CDCl_3$ 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 $MnO_4^-$ 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 2,4-dinitrophenyl 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:

$$5\,CH_3CH_2CH(OH)CH_3 + 2\,MnO_4^- + 6\,H^+ \rightarrow 5\,CH_3CH_2COCH_3 + 2Mn^{2+} + 8\,H_2O$$