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Effect of CHAPS and CPC micelles on Ir(III) catalyzed Ce(IV) oxidation of aliphatic alcohols at room temperature and pressure

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ABSTRACT

Kinetics of cerium(IV) oxidation of aliphatic alcohols: ethanol, propanol, propan-2-ol, 1-butanol and 2-butanol were studied at 30 °C in the presence and absence of surfactants in acidic medium. The reaction was studied under pseudo-first-order conditions, $[alcohol]_T \gg [Ce(IV)]_T$. Ir(III)-salt used as catalyst had a significant effect on reaction rate. Cationic surfactant CPC (*N*-cetylpyridinium chloride) inhibits the reaction rate but zwitterionic surfactant CHAPS (3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate) catalyzes the oxidation reaction significantly. CMC value of CHAPS was determined by a spectrofluorometer. The reaction rate increased with increase in the acid concentration of the medium. NMR and FTIR spectra confirmed the oxidized products. The aggregation of surfactants in the reaction condition was studied through Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Dynamic light scattering (DLS) was used to characterize of surfactants and metal ion catalyst are discussed qualitatively in terms of Berezin's model, nature of surfactants, and charge of surfactants. Ir(III) in association with CHAPS micellar catalyst exhibited ~500–2000 fold rate enhancements compared to the uncatalyzed reaction path.

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1. Introduction

Selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in industrial chemistry. Aldehydes and ketones are precursors for many drugs, vitamins, fragrances and it opens up the possibility of using renewable biomass-derived feed stocks. The synthesis of carbonyl compounds is generally carried out in environmentally harmful organic solvents at high temperature and pressure by using stoichiometric oxygen donors (such as chromate and permanganate) producing large amount of wastes [1,2]. The oxidation of alcohols to aldehydes or ketones [3–6] has been traditionally based on the use of stoichiometric amounts of higher valent toxic transition metal oxidants, which renders the catalytic reaction expensive and unattractive from an environmental point of view [7–10] in both the laboratories and industries.

Cerium chemistry is a very broad area of considerable attention through the recent years, resulting in substantial advance both in the synthetic and mechanistic categories. Cerium(IV) is a well known oxidant [11] in acidic media having reduction potential 1.44 V of the couple Ce(IV)/Ce(III) in H₂SO₄ medium and is stable only in a high acid concentration [12]. Most of the cerium(IV) oxidation reactions are catalyzed by transition metals such as Cr(III), Ag(I), Ir(III), Pd(III), Ru(III), Os(VIII), and Mn(II) [13–15]. It is previously reported that a variety of transition-metal-catalyzed transformations can be carried out within micellar media [16]. The potential of iridium(III) chloride as a homogeneous catalyst was best recognized when it was used in an acidic medium for oxidation of a range of alcohols to aldehydes, ketones or carboxylic acids proceeds in good yield. The Iridium(III) catalyzed oxidation of aliphatic and substituted alcohols, diols and aromatic compounds by cerium(IV) in an acidic medium has been investigated early [17,18]. To discover the effect of iridium(III) chloride in catalyzing the oxidation of aliphatic alcohols, we have studied the oxidation of ethanol, propanol, propan-2-ol, butanol and 2-butanol in the presence of iridium(III) chloride by cerium(IV) in an aqueous sulfuric acid medium. However, so far it was not investigated the influence of the metal catalyst on the reaction rates of oxidation reaction in micellar solutions.

Most of the organic substrates are often poorly soluble in water. Micellar systems are often used to overcome the solubility problems of the organic reactants [19,20]. Recently, great attention has been paid to the development of organic reactions in water [21]. Compared with other organic solvents, water is the most abundant "greenest" solvent among all solvents, it is ubiquitous on the earth as well as being a clean, and easy-to-handle [1]. The advantage of using micellar solution as catalyst, avoiding large amounts of organic solvents and the micellar catalyst can be recycled by simple techniques [22]. In addition to the avoidance of organic solvents and the recycling of the aqueous medium,

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the valuable micellar catalyst offers an additional benefit of facile reaction monitoring of room temperature reactions [23]. Nowadays the effect of micellar catalysis on reaction kinetics is growing popularly [6, 24–29]. Micellar catalysis [30] represents a viable solution to solubilization problems; in fact, surfactant aggregation driven by the hydrophobic effect ensures the formation of apolar nano-environments where both substrates as well as catalysts can be efficiently dissolved and interact with higher local concentrations [31,32]. It is to mention here that the most suitable surfactants are still selected for capable of solubilizing all species of proteins is 3-[(3-cholamidopropyl)dimethylammonio]-1propanesulfonate (CHAPS). It has many applications in various fields of biological, medical, and pharmaceutical sciences [33]. CHAPS is a zwitterionic derivative of cholic acid having combined properties of both sulfobetaine type detergents and bile salts. It is frequently used in membrane protein isolation, surface modifier for specific protein adsorption, protein solubilization, purification, and denaturation [34]. But no such experiment was performed about the catalytic efficiency of CHAPS in kinetics. We have thus taken a more precise and detail experimental effort on the catalyzing properties of non-toxic [35] surfactant CHAPS over the N-cetylpyridinium chloride (CPC) in oxidation kinetics.

The important aim of this study was to determine the effects of structural variations of alcohols and effect of various surfactants on the rate of oxidation by Ce(IV). Besides that the other objectives were to find out the main kinetically reactive species (Scheme 1), main oxidation product, deduce the rate law and probable reaction site in the presence of catalyst.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

Ethanol (SRL, AR, Mumbai, India), propanol (SRL, AR, Mumbai, India), propan-2-ol (SRL, AR, Mumbai, India), 1-butanol (SRL, AR, Mumbai, India), 2-butanol (SRL, AR, Mumbai, India), N-cetylpyridinium chloride (CPC) (SRL, AR, Mumbai, India), CHAPS (SRL, AR, Mumbai, India), H₂SO₄ (E. Merck, AR), Na₂SO₄ (E. Merck, AR), HCl (E. Merck, AR), pyrene (SRL, AR, Mumbai, India), iridium(III) chloride (SRL, AR, Mumbai, India), cerium(IV) ammonium sulfate (E. Merck, AR) and all other chemicals used were of the highest purity available commercially. The stock solution of Ce(IV) was obtained by dissolving cerium(IV) ammonium sulfate in 1 mol dm⁻³ sulfuric acid and was standardized with iron (II) ammonium sulfate solution using ferroin as an external indicator [18,36]. Cerium(IV) solution was always made up and stored in a black coated flask to prevent photochemical reaction. A solution of iridium(III) chloride was prepared by dissolving the sample in a minimum amount of concentrated hydrochloric acid. Conductivity water was used throughout the study.

2.2. Instrumentation

The weighing balance (Sartorius BSA224S-CW), sonicator (Digital Ultrasonic Cleaner CD 4820), centrifuge (Z206A, Hermle Labortechnik GmbH), UV–vis NIR spectrophotometer (UV-VIS-NIR-3600, SHIMADZU), stopped flow spectrophotometer (SX20 Stopped-Flow Spectrometer), DLS instrument (Malvern Zetasizer Nano ZS-90 instrument), optical microscope (LEICA DM 1000), SEM (S530 HITACHI SEM) instrument using IB 2 ion coater, HR-TEM microscope (JEOL JEM 2100), FTIR spectrophotometer (RX1, Perkin-Elmer), ¹H NMR (400 MHz, Bruker Ascend) and spectrofluorometer (LS 55, Perkin-Elmer) were used for various purpose of experiments.

2.3. Kinetic measurements

Reaction mixtures containing the known quantities of the substrate (i.e., ethanol, propanol, propan-2-ol, 1-butanol and 2-butanol), and acid under the kinetic conditions, $[alcohol]_T \gg 10[Ce(IV)]_T$ were thermostated at 30 °C (±0.1 °C). The reaction was initiated by mixing the requisite amounts of the oxidant and catalyst [surfactant or Ir(III) in particular case] with the reaction mixture. All kinetic measurements were made at an ionic strength of 2.0 mol dm⁻³ at 30.0 ± 0.1 °C. The progress of the reaction was followed by monitoring the decrease in absorbance of cerium(IV) at 320 nm [37] by the use of a UV-vis spectrophotometer equipped with 1 cm quartz cells in a thermostated cell holder and a Temperature Control System. The surfactant CHAPS was used above the critical micelle concentrations (6.3 mM at 303 K) [35] in all experiments to make sure of the existence of micellar aggregates in solution. The pseudo-first-order rate constants (k_{obs} , s⁻¹) were



Scheme 1. A probable scheme for the main reactive species involved in the oxidation in micellar media.

calculated from the linear plots of -ln(A₃₂₀) versus time at 320 nm wavelength (Fig. 1), (where A₃₂₀ = Absorbance of Ce(IV) at 320 nm wavelength). All the first order plots were linear, with a correlation coefficient of 0.993–0.999. The results were reproducible within an accuracy of \pm 2.5%. The pseudo-first-order rate constants of the present oxidation reactions were measured also in the presence of CPC, CHAPS and Ir(III). The possibility of decomposition of the surfactants CPC and CHAPS by Ce(IV) has been investigated and the rate of decomposition has been found negligible [38]. Values of the rate constants for the alcohol-Ce(IV) reactions determined from the slopes of the appropriate plots are presented in Table 1. The t_{1/2} values are directly calculated in Table 1 by using the relation t_{1/2} = (ln2 / k_{obs}), where ln2 = 0.693, k_{obs} = pseudo-first-order rate constant in s⁻¹.

2.4. Fluorimetry

Fluorescence measurements were performed in a spectrofluorometer using a quartz cell of path length 1 cm at 30 \pm 0.1 °C with an excitation and emission slit width of 3.0 nm and 2.5 nm respectively and a scan speed of 500 nm min⁻¹. Pyrene was used as the fluorescence probe. A series of surfactant solutions were prepared for fluorescence intensities measurement following the procedure used in spectrophotometry. The solutions were excited at 334 nm, and the emission spectra were recorded in the range 360–450 nm. The fluorescence intensities of the peaks at ~372 nm (I₁) and ~383 (I₃) were extracted from the spectra, and the I₃/I₁ value vs. surfactant CHAPS concentration was used for CMC determination. The CMC was found around 6.3 mM from the plot of fluorescence intensity versus CHAPS concentration (Supplementary data).

2.5. Product analysis and stoichiometry

In our experimental condition the concentration of Ce(IV) was kept less than the concentration of alcohols but in the stoichiometric study, a known excess of Ce(IV) was allowed to react completely with a mixed amount of alcohols at 30 °C. After completion of the reaction, the corresponding oxidized products aldehydes and ketones (carbonyl compound) were efficiently separated by fractional distillation [5,6]. The ¹H NMR spectra (Supplementary file) of the product carbonyl compound in CDCl₃ solvent were obtained on an NMR spectrophotometer operating at 400 MHz frequency. In this study the products ethanal, propionaldehyde, and butanal were obtained from the oxidation of ethanol, propanol and 1-butanol respectively. Again the ketones: acetone and 2-butanone were the main products of oxidation of propan-2-ol and 2-butanol. Qualitative identifications of the carbonyl products of cerium(IV) oxidation reactions were performed with the formation of yellow or yellow orange colored 2,4-dinitrophenyl hydrazone derivatives directly by addition of 2,4-dinitrophenyl hydrazine in the reaction mixtures [39,40]. The hydrazone precipitate was filtered off and was weighed out after proper drying. The hydrazones were recrystallized to determine the melting points. The melting points were matched with the earlier reports [41,42]. The crystalline 2,4-DNP derivatives were thoroughly mixed with KBr, pressed into a form of disk (pellet), to record FTIR spectrum and compared with spectra of the derivatives of known aldehydes/ketones (supplementary data). Thus, we may safely conclude that carbonyl compound is the main oxidation product. The spectra of the derivatives of the reaction products were sufficiently different to permit reasonably positive identification of the products [43].

2.5.1. Stoichiometry

Stoichiometry of the reaction was evaluated by taking cerium(IV) in large excess over the organic substrate to ensure its complete oxidation. Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was used in excess over [substrate] at constant ionic strength and acidity were kept for 24 h at 303 K in an inert atmosphere. The results indicated that 2 mol of Ce(IV) was consumed (Fig. 2) per mol of substrate, (i.e. 2:1). In all cases it was assumed that 1 mol of carbonyl product is formed per 2 mol of cerium(IV) reduced by aliphatic alcohols. The calculation of the yield of product from the weight of 2,4-dinitrophenylhydrazone formed requires a knowledge of the reaction product and stoichiometry.

2.6. Test for free radical intermediates

The intervention of free radicals was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 2 h. Upon diluting the reaction mixture with methanol, white precipitate was formed, indicating the presence of free radical intervention in the reaction. The formation of free radicals was confirmed by acrylonitrile polymerization [36,44].



Fig. 1. Representative first-order plot for Ce(IV) oxidation of 2-butanol in CHAPS catalyzed path and propanol in Ir(III) mediated CHAPS catalyzed path. $[Ce(IV)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[CHAPS]_T = 8 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4]_T = 0.5 \text{ mol dm}^{-3}$, $\mu = [H_2SO_4 + Na_2SO_4] = 2.0 \text{ mol dm}^{-3}$, Temp = 30 °C. (a) $[2\text{-butanol}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; (b) $[\text{propanol}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; (b) $[\text{propanol}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[Ir(III)]_T = 2 \times 10^{-6} \text{ mol dm}^{-3}$.

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Table 1

Effect of Ir(III), CPC and CHAPS micellar catalyst on pseudo-first-order rate constant and half-life for the Ce(IV) oxidation of alcohols.

Substrate	$10^6 \times \text{metal catalyst}$ (mol dm ⁻³)		$10^3 imes$ micellar catalyst (mol dm ⁻³)		$10^6 \times k_{\rm obs} ({\rm s}^{-1})$	Half-life $(t_{1/2})$ (h)
Ethanol					30.500 ± 0.02	6.310
Propanol					22.160 ± 0.04	8.680
Propan-2-ol	-		-		6.184 ± 0.06	31.120
1-Butanol					11.870 ± 0.05	16.217
2-Butanol					21.660 ± 0.01	8.887
Ethanol	-		CPC	0.4	4.594 ± 0.09	41.897
				0.6	4.731 ± 0.05	40.689
				0.8	5.342 ± 0.08	36.038
				1.0	5.659 ± 0.07	34.0160
				1.2	5.246 ± 0.03	36.690
				1.4	4.353 ± 0.06	44.210
				1.5	4.231 ± 0.05	45.497
Propanol	-		CPC	0.4	13.150 ± 0.05	14.638
				0.6	10.004 ± 0.08	19.240
				0.8	8.545 ± 0.06	22.527
				1.0	7.569 ± 0.05	25.430
				1.2	7.311 ± 0.06	26.330
				1.4	6.039 ± 0.07	31.870
				1.5	5.015 ± 0.04	38.380
Propan-2-ol	-		CPC	0.4	6.114 ± 0.01	31.480
				0.6	6.669 ± 0.01	28.860
				0.8	7.155 ± 0.03	26.900
				1.0	8.805 ± 0.05	21.860
				1.2	6.898 ± 0.04	27.900
				1.4	4.967 ± 0.05	38.7581
				1.5	4.892 ± 0.05	39.349
1-Butanol	-		CPC	0.4	14.250 ± 0.06	13.510
				0.6	7.455 ± 0.01	25.821
				0.8	6.965 ± 0.03	27.640
				1.0	5.214 ± 0.03	36.920
				1.2	6.931 ± 0.04	27.770
				1.4	6.484 ± 0.01	29.690
				1.5	6.747 ± 0.02	28.530
2-Butanol	-		CPC	0.4	9.468 ± 0.02	20.330
				0.6	6.941 ± 0.06	27.730
				0.8	6.639 ± 0.04	29.0
				1.0	6.267 ± 0.03	30.710
				1.2	8.257 ± 0.07	23.310
				1.4	7.476 ± 0.02	25.750
				1.5	7.356 ± 0.02	26.170
Ethanol	Ir(III)	2	-		84.160 ± 0.01	2.287
Propanol					72.830 ± 0.06	2.640
Propan-2-ol					135.60 ± 0.05	1.420
1-Butanol					89.80 ± 0.04	2.140
2-Butanol					78.50 ± 0.05	2.450
Ethanol	-	-	CHAPS	8	277.0 ± 0.06	0.690
Propanol					237.20 ± 0.03	0.810
Propan-2-ol					403.70 ± 0.03	0.470
1-Butanol					556.7 ± 0.01	0.340
2-Butanol					1732.0 ± 0.02	0.110
Ethanol	Ir(III)	2	CHAPS	8	$22,\!800.0\pm0.08$	30.40 s
Propanol					$12{,}200.0\pm0.05$	56.90 s
Propan-2-ol					$13{,}200.0\pm0.07$	52.60 s
1-Butanol					$12,\!000.0\pm0.07$	58.0 s
2-Butanol					$15,500.0 \pm 0.09$	44.50 s

 $[Ce(IV)]_{T} = 2 \times 10^{-4} \text{ mol } dm^{-3}, [CPC]_{T} = 1.1 \times 10^{-3} \text{ mol } dm^{-3}, [H_2SO_4]_{T} = 0.5 \text{ mol } dm^{-3}, [alcohol]_{T} = 2 \times 10^{-3} \text{ mol } dm^{-3}, \mu = 2.0 \text{ mol } dm^{-3}, Temp = 30 ^{\circ}C.$

2.7. Determination of the size of aggregates by dynamic light scattering (DLS)

The hydrodynamic diameters (D_h) of CPC micelles with and without reactants were determined by DLS experiment. DLS characterization

was performed to obtain micelle/vesicle size and morphology on a DLS instrument with a capillary cell. Size measurements were performed at a 90° angle in triplicate. DLS analyzes the velocity distribution of particle movement by measuring dynamic fluctuations of light



Fig. 2. Conversion of alcohol to corresponding carbonyl compound by Ce(IV) at 30 °C.



Fig. 3. (a) to (c) Different views of TEM images showing micelles formed by CPC in aqueous medium, $[CPC]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$. (d) to (f) Different views of TEM images of the reaction mixture showing the interaction of Ce(IV) by CPC micelles in the aqueous acidic medium. $[CPC]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[Ce(IV)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 0.5 \text{ mol dm}^{-3}$, $\mu = 2.0 \text{ mol dm}^{-3}$, Temp = 30 °C.

scattering intensity caused by the Brownian-motion of the particle. The light scattering study was done with CPC surfactant by taking concentration above its CMC value in an acidic medium.

2.8. High resolution transmission electron microscope (HR-TEM) images of CPC micelle

The HR-TEM investigation was done at 20 kV acceleration voltage using a lacey carbon coated Cu grid of 300 mess size. 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. 3) 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 diameters, but a widely variable length. With the addition of reactants, the morphology changes at some extent may be due to the accumulation of a small amount of reactant at the micellar surface.

2.9. Scanning electron microscope (SEM) images of CHAPS micelle

SEM analysis was done by placing a drop of CHAPS solution on a foil paper. Then it was air dried, coated with gold, and was observed under a Scanning Electron Microscope. The SEM picture (Fig. 4) of pure CHAPS looked like rod-like or cylindrical particles. This also looked like a bi-layer 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 reactants changes the morphologies of the aggregates from bi-layers or cylinders to spheres. At [CHAPS] > CMC, the broken rock-type materials of large size appeared in the SEM picture. In this concentration of CHAPS in the medium, the formation of particles of varied geometries and patterns was observed as below:

3. Results

3.1. Spectrophotometric study of the reaction

3.1.1. UV-vis spectra

The ceric(IV) ion, is a facile oxidant of organic compounds such as alcohol. In that case, ethanol, propanol and 1-butanol, are oxidized into ethanal, propionaldehyde and 1-butanal respectively, itself susceptible to further oxidation to corresponding acids. Due to the excess concentration of alcohol present in solution as compared to ceric(IV), it is expected that the ceric(IV) ion will be totally reduced to Ce(III) at the end of reaction. Indeed, solutions of Ce(IV) salts are yellow in the presence of alcohol, whereas solutions of Ce(III) salts are colorless [45]. The progress of the oxidation of alcohols with cerium(IV) in the presence and absence of surfactant and Ir(III) (Fig. 5, 6, 7) is reflected by marked changes [46] in the electronic spectrum of certain time intervals. The



Fig. 4. (a) to (c) Different views of SEM images showing micelles formed by CHAPS in aqueous medium. $[CHAPS]_T = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$.



Fig. 5. Sequential scans of absorption spectra during the course of the uncatalyzed reaction of alcohol with Ce(IV) in sulfuric acid media for 5 min time interval, with $[Ce(IV)]_T = 2.0 \times 10^{-4} \text{ mol } dm^{-3}$, $[H_2SO_4]_T = 0.5 \text{ mol } dm^{-3}$, $\mu = [H_2SO_4 + Na_2SO_4] = 2.0 \text{ mol } dm^{-3}$, Temp = 30 °C. (a) $[ethanol]_T = 2.0 \times 10^{-3} \text{ mol } dm^{-3}$, (b) $[2-butanol]_T = 2.0 \times 10^{-3} \text{ mol } dm^{-3}$.

scanned absorption spectra of the different set of reaction mixtures were taken for both in the presence and absence of surfactant and Ir(III) (Figs. 6, 7). 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. 5, 6 and 7).

The spectra presented in Figs. 5 to 7 reveal one absorption band of cerium(IV) at 320 nm with a molar absorption coefficient depending

on acid concentration used. The absorbance maximum at 320 nm due to the electronic transitions of the cerium(IV) complexes. The color of Ce(IV) compounds in presence of anion in aqueous medium is due to the LMCT bands. The absorption spectrum of Ce(IV) species in aqueous sulfuric acid solution differs from that of Ce(III) species[14]. However, Ce(III) complexes produced after completion of reaction have an absorption band near 250 nm (Fig. 8). The reason for these changes is



Fig. 6. Sequential scans of absorption spectra during the course of the Ir(III) catalyzed reaction of alcohol with Ce(IV) in sulfuric acid media. $[Ce(IV)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}, [H_2SO_4]_T = 0.5 \text{ mol dm}^{-3}, [Ir(III)]_T = 2 \times 10^{-6} \text{ mol dm}^{-3}, \mu = [H_2SO_4 + Na_2SO_4] = 2.0 \text{ mol dm}^{-3}, Temp = 30 ^{\circ}C. (a) [propan-2-ol] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (b) [1-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 2 min, (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Inte$



Fig. 7. Sequential scans of absorption spectra during the course of the CHAPS catalyzed reaction of alcohol with Ce(IV) in sulfuric acid media. $[Ce(IV)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}, [H_2SO_4]_T = 0.5 \text{ mol dm}^{-3}, [CHAPS]_T = 8 \times 10^{-3} \text{ mol dm}^{-3}, \mu = [H_2SO_4 + Na_2SO_4] = 2.0 \text{ mol dm}^{-3}, Temp = 30 \text{ °C}. (a) [ethanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (b) [1-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (b) [1-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (b) [1-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (b) [1-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{ min}; (c) [2-butanol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, Interval time 3 \text{$

the disappearance of the intensive yellow colored cerium(IV), which is reduced to a pale green cerium(III). Cerium(III) complexes, under conditions used in this work, are practically transparent in visible spectral



Fig. 8. Absorption spectra of Ce(III) solution from Ce(IV) after completion of the uncatalyzed reaction at 30 °C. $[Ce(IV)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4]_T = 0.5 \text{ mol dm}^{-3}$, $\mu = [H_2SO_4 + Na_2SO_4] = 2.0 \text{ mol dm}^{-3}$, $[alcohol]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$. (a) ethanol, (b) propanol, (c) propan-2-ol, (d) 1-butanol, (e) 2-butanol.

region and exhibit only less intensive absorption bands at 295, 254, 241, 223 and 212 nm respectively in UV region. In contrast, with cerium(III) the lowest energy electronic absorption bands in the UV regions corresponding to the $4f^n \rightarrow 4f^{n-1}d^1$ transition. The electronic spectrum of Ce(III) is corresponding to a single transition between $^2F_{5/2}$ (ground state) and $^2F_{7/2}$.

3.2. Dependence on [Ce(IV)]

The oxidation reaction of the alcohols is of first order in [Ce(IV)] in the absence and presence of surfactant as indicated by the linearity of a plot of $-\ln(A_{320})$ versus time (t) (Fig. 1) [47].

3.3. Dependence on [H₂SO₄]

The reaction was carried out at a various initial concentration of sulfuric acid at a fixed CPC concentration as in Table 2. It was observed that the rate of oxidation reaction of each alcohol increased with an increasing sulfuric acid concentration (Fig. 9). The plots of k_{obs} versus [H⁺] (Fig. 9) for the aliphatic alcohols are found to be linear in nature. This indicates that the reaction order with respect to [H⁺] is first. From the hydrogen ion dependence on rate constants for the various aliphatic alcohols it is clear that the rate is increased with the increasing concentration of H⁺. The half-life value (Table 2) of the corresponding reaction decreases in usual way.

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Table 2

Effect of hydrogen ion concentration on reaction rate for different alcohol oxidation by Ce(IV).

Substrate	${\rm H^{+}} \ ({\rm mol} \ {\rm dm^{-3}})$	$10^6 \times k_{\rm obs} ({ m s}^{-1})$	Half-life $(t_{1/2})$ (h)
Ethanol	0.5	5.659 ± 0.01	34.0
	1	9.376 ± 0.05	20.530
	1.5	9.538 ± 0.03	20.180
	2	10.622 ± 0.02	18.120
	2.5	12.290 ± 0.06	15.660
Propanol	0.5	7.311 ± 0.03	26.330
	1	8.123 ± 0.03	23.70
	1.5	9.489 ± 0.04	20.280
	2	11.074 ± 0.05	17.380
	2.5	12.10 ± 0.01	15.90
Propan-2-ol	0.5	8.392 ± 0.02	22.930
	1	12.430 ± 0.05	15.480
	1.5	13.670 ± 0.06	14.080
	2	14.80 ± 0.05	13.0
	2.5	17.110 ± 0.03	11.250
1-Butanol	0.5	6.931 ± 0.05	27.770
	1	9.60 ± 0.06	20.0
	1.5	9.770 ± 0.02	19.70
	2	11.220 ± 0.04	17.150
	2.5	11.80 ± 0.04	16.30
2-Butanol	0.5	8.257 ± 0.01	23.30
	1	11.80 ± 0.02	16.30
	1.5	13.0 ± 0.06	14.80
	2	14.50 ± 0.03	13.270
	2.5	15.40 ± 0.05	12.50

 $[Ce(IV)]_T=2\times 10^{-4}$ mol dm^-3, $[CPC]_T=1.1\times 10^{-3}$ mol dm^-3, $[alcohol]_T=2\times 10^{-3}$ mol dm^-3, Temp=30 °C.

4. Discussion

4.1. Reaction mechanism of uncatalyzed path

In the uncatalyzed path the proposed mechanism involves the formation of complex in a reversible manner to form [Ce(IV)-S] (S = alcohol) complex followed by a slow redox decomposition (Scheme 2) giving rise to aldoxide radical which is rapidly oxidized by Ce(IV). An example of this type was the oxidation of DMSO by Ce(IV) [48] which involves a reversible rapid complex formation between them with a kinetic proof yielding the final products in the rate determining step. Cerium(IV) forms 1:1 complexes of the type [ROH.Ce(IV)]⁴⁺ with the alcohols [12, 49] by the elimination of cerium(III) and H⁺ ions. Here the complex [Ce(IV)-alcohol] (C₁) may undergo deprotonation with the transfer of single electron from the substrate to Ce(IV)-sulfato species at the rate-



Fig. 9. Dependence of k_{obs} on $[H^+]$ for the Ce(IV) oxidation of alcohol in the presence of constant CPC concentration in aqueous H_2SO_4 media at 30 °C. $[Ce(VI)]_T = 2 \times 10^{-4} \text{ mol dm}^{-3}$, $= 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[CPC]_T = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$, a for [ethanol]_t = $2 \times 10^{-3} \text{ mol dm}^{-3}$, b for [propanol]_T = $2 \times 10^{-3} \text{ mol dm}^{-3}$, c for [propan-2-ol]_t = $2 \times 10^{-3} \text{ mol dm}^{-3}$, d for [1-butanol]_t = $2 \times 10^{-3} \text{ mol dm}^{-3}$, e for [2-butanol]_T = $2 \times 10^{-3} \text{ mol dm}^{-3}$, e for [2-butanol]_T = $2 \times 10^{-3} \text{ mol dm}^{-3}$.

determining step to give Ce(III) and free radical (C_2) so as to participate at the faster steps to yield the carbonyl product. The free radical generated during the reaction was evident from the acrylonitrile polymerization test [36,44,47,48]. The effects of structural variations of alcohols were investigated in our present system and in most cases everything except the alcohol was kept constant and thus the cerium(IV) species should be the same for all alcohols [50]. The rate law of the uncatalyzed reaction path [12,51] has been expressed as:

$$k_{\rm obs} = \frac{kK[{\rm RR'C HOH}]}{1 + K[{\rm RR'C HOH}]}$$

4.2. Reaction mechanism of iridium(III) catalysis

It is known that $IrCl_3$ in hydrochloric acid medium gives $IrCl_6^{3-1}$ species. During the oxidation of alcohols to carbonyl compounds, $[IrCl_5H_2O]^{2-}$ has been considered as the reactive species of Ir(III)catalyst in our present kinetic study [19]. The possibility of the association of alcohol and Ir(III) leading to a certain interaction between alcohol and Ir(III) in the first pre-equilibrium step (Scheme 3), was detected by UV-vis absorption spectra of different alcohol-Ir(III) mixture solutions. The UV-vis spectrum of the mixing solution is distinctly different from those of the individual alcohols and Ir(III) solution (supplementary data) [19]. Spectral evidence suggesting that 1:1 type complex formation between alcohol and Ir(III) in the first equilibrium step. The second equilibrium probably involves the outer-sphere association (C₃) of the alcohol and Ir(III) catalyst followed by the electron transfer leading to the complex (C_4) which may be Ce(III) \cdot (alcohol) \cdot Ir(IV). Subsequently electron transfer occurs within the complex to give Ir(III) and the free radical which is rapidly oxidized by Ce(IV) at a fast step. Thus the oxidation of alcohol occurs through the Ir(III)/Ir(IV) catalytic cycle [52]. The reaction mechanism involving an association of the oxidant, substrate and catalyst in some pre-equilibrium steps before the electron transfer step [18,53,54]. The rate expression [53,55] of the Ir(III)-catalyzed reaction pathway has been expressed as follows:

$$k_{\text{obs}} = \frac{k_1 K_1 K_2 [\text{RR'CHOH}] [\text{Ir(III)}]}{1 + K_1 [\text{RR'CHOH}] (1 + K_2 [\text{Ir(III)}])}$$

4.3. Dependence of rate constant on structural variation of alcohols

It is believed that the amount of covalent bonding between rare earth ions and electronegative atoms is guite small since high energy; diffuse orbitals (4f, 5d, 6s, or 6p) would have to be involved in the bonding. The paucity of stable complexes of rare earth metal ions supports the postulate of weak electrostatic bonding rather than stronger covalent bonding [50]. Several factors must be considered in attempting to rationalize the changes in the observed rate constants for the alcohol oxidation with changes in the alcohol structures. These are electronic effect, steric effect, size of cerium(IV)-alcohol and Ir(III)-alcohol complexes and the location of the reactants in the nano-reactor (micellar surface). The relative rates of chromic acid oxidation of many stereo isomeric pairs of alcohols have been reported previously [50]. In general, the more sterically crowded alcohol oxidizes at a faster rate in aqueous solvent. The steric factor mainly arises from the step up (Scheme 4) of a single - CH₂ group from ethanol to propanol and then butanol (Scheme 4). In fact, a trend in rate constant of the Ce(IV) oxidation of different alcohol was observed. It does seem to exist as the crowded alcohol in the Ce(IV)-alcohol complex for more sterically hindered alcohol of a pair of alcohols of comparable polar nature is greater than that for the less crowded alcohol. Although sometimes discrepancy have been also observed. Such was reflected from our study by the k_{obs} for ethanol $(3.05 \times 10^{-5} \text{ s}^{-1})$ and propanol $(2.216 \times 10^{-5} \text{ s}^{-1})$, propan-2-ol $(0.6184 \times 10^{-5} \text{ s}^{-1})$ and 1-butanol $(1.187 \times 10^{-5} \text{ s}^{-1})$, and



Scheme 2. Oxidation of aliphatic alcohol by Ce(IV) in the absence of catalyst in aqueous acidic media.

2-butanol $(2.166 \times 10^{-5} \text{ s}^{-1})$ [48]. Therefore, ethanol and propanol were oxidized at a faster rate (Table 1) in comparison to propan-2-ol, 1-butanol, and 2-butanol in the uncatalyzed path. Again, propan-2-ol and 1-butanol were oxidized at a more faster rate compared to the ethanol, propanol, and 2-butanol in Ir(III) catalyzed path. The trend is slightly discontinued here. But in the case of CHAPS and CHAPS-Ir(III) systems the larger oxidation rate constants were obtained (Table 1) for more sterically hindered alcohols over less sterically hindered alcohols. The magnitude of the rate constants for the Ce(IV)-oxidation of alcohols with different chain length is different.

4.4. Structural difference between CPC and CHAPS surfactants

The head groups of zwitterionic (or amphoteric) detergents are hydrophilic and contain both positive and negative charges in equal numbers, resulting in zero net charge. Thus, 3-[(3-cholamidopropyl) dimethylammonio]-1-propanesulfonate, better known as CHAPS behaves differently from N-cetylpyridinium chloride (CPC: containing a pyridinium moiety and cetyl group) because of the presence of OH groups in the CHAPS molecule, it possibly interacts with the aliphatic alcohols through conformation changes of the amphiphile [40]. The zwitterionic amphiphile CHAPS (Fig. 11a) interacts fairly by way of hydrogen bonding and hydrophobic interaction. Its hydrophobic group is the same as that of cholic acid, i.e., a trihydroxy bile acid. During aggregate formation, the hydrophobic faces are considered to contact with each other, while the hydrophilic ones remain exposed to the aqueous environment [56]. Therefore, the nonpolar part of CHAPS micelle cannot be simply ascribed as a methyl group along with the number of methylene groups like a classical surfactant tail (here CPC, Fig. 11b). During micellization only a very small part of the cholesterol-like skeleton of bile salt derivative is fully removed from contact with water molecules [57]. All these effects strongly explain that CHAPS increases in both the affinity of cerium(IV) and Ir(III) reactive species to react with alcohol consequently increases the velocity of reaction in micelles.

4.5. Micellar effect on reaction rate

The surfactant concentration presents higher than the critical micelle concentration (cmc) in water results in the formation of micelles [58] consisting of a hydrophobic core and a hydrophilic head groups. In the case of oxidation of all the alcohols, the cationic surfactant *N*-cetylpyridinium chloride (CPC) has been found (Fig. 11b) to retard the rate and the rate levels off at a higher CPC concentration. However the most characteristic zwitter-ionic surfactant CHAPS has been found to accelerate the rate process.

4.5.1. Rate accelerating effect by CHAPS

The oxidation reaction rates observed (Table 1) in CHAPS micellar media can differ from those observed in conventional media. This is accounted for the solubilization as well as in the orientation of the reactants, reduction of their effective concentrations through their segregation in different 'compartments' within the bulk medium. The faster oxidation rate is attributed to the higher reactant concentration within CHAPS micelles, the changes in the polarity and physicochemical properties of the medium [59,60].

The zwitterionic micellar surface of CHAPS attracts the cationic species $\text{Ce}(\text{SO}_4)^{2+}$ and Ir(III)-alcohol positive complex due to electrostatic or coulombic interactions. Again the hydrophobic interactions [61] can bring about the incorporation of the reactants (substrate) into micelles. Thus, overall increment of rate occurs due to the increased



Scheme 3. Oxidation of aliphatic alcohol by Ce(IV) in the presence of Ir(III) catalyst in aqueous acidic media.

concentration of both alcohol and $Ce(SO_4)^{2+}/Ir(III)$ -complex in the Stern layer (Scheme 5) of micelle [62]. Reactants in the close vicinity of the hydrophobic parts respond to the changes of properties in medium by showing enhanced reaction rate [63]. Moreover, it should be noted that the different hydrophobic alkyl chain length of the five different alcohols is also expected to affect the partitioning effects (Scheme 5a) and hence, the extent of the accelerating effects of the micelle. Micellar catalysis by CHAPS was found to be more sensitive towards Ir(III)-salt [64]. The incorporation of metal-substrate complex into the micelles of CHAPS enhances almost kilo fold rate acceleration for different alcohol oxidation. Based on electrostatic [4–6,13,15, 26–29] considerations, the reactive species $Ce(SO_4)^{2+}$ (presence of positive charge cloud around it) and the substrate alcohol (presence of electron cloud around on it) come closer to the zwitter-ionic CHAPS micellar



Scheme 4. Structural variation of the representative aliphatic alcohols.

surface (containing a sulfobetaine group), which increases the local molarities in the Stern layer [65]. Addition of Ir(III)-salt caused neutralization of micellar surface charge (Scheme 5b), consequently catalyzed the reaction by virtue of increased concentration of reactants in the Stern layer [65].

4.5.2. Rate retarding effect by CPC

The inhibiting effect of CPC micelles is related to the different positions of the localization of substrate and oxidant in cationic micelles. The rate data presented in Table 1 clearly reveals that the rate decreased with increase in concentration of CPC. This indicates that there is a charge development in the transition state involving a more polar activated complex [66] than in the reactants. From the plot of k_{obs} versus CPC concentration the rate constant value at the maxima or minima is smaller than the rate constant value [67] in bulk water. This maxima or minima point is the CMC value of CPC ranging from ~1.0 to 1.2 mM for different alcohols. Addition of CPC leads to a slight increase in the reaction rate after which further addition of CPC inhibits the observed rate constant k_{obs} value up to the minimum (Fig. 10a to e). In this path, CPC restricts the positively charged alcohol-Ce(IV)-sulfate complex in an aqueous phase and thus the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction [4,6,26]. The plot of k_{obs} versus [CPC] (Fig. 10, Table 1) shows a continuous decrease



Fig. 10. Influence of the surfactant CPC on the k_{obs} for the Ce(IV) oxidation of alcohol in aqueous H₂SO₄ media at 30 °C. [Ce(VI)]_T = 2 × 10⁻⁴ mol dm⁻³, [H₂SO₄]_T = 0.5 mol dm⁻³, $\mu = [H_2SO_4 + Na_2SO_4] = 2.0 mol dm^{-3}$. For (a) [ethanol]_T = 2 × 10⁻³ mol dm⁻³, (b) [propanol]_T = 2 × 10⁻³ mol dm⁻³, (c) [propan-2-ol]_T = 2 × 10⁻³ mol dm⁻³, (d) [1-butanol]_T = 2 × 10⁻³ mol dm⁻³, (e) [2-butanol]_T = 2 × 10⁻³ mol dm⁻³.

in rate up to the concentration of CPC used. Positive hydrophilic groups of CPC micelles directed towards the exterior of the micelle which strongly repels (Scheme 6) the approaching reactive species $Ce(SO_4)^{2+}$ in an aqueous acidic medium. Hence relative lowering of the local concentration of the reactants in the micellar phase which results observed decreases in rate constants [38].

4.6. The kinetic model to explain the micellar effects

Micellar catalysis generally depends on the interactions of the micelle with the substrate (s) and the intermediate complex. This is an enormously complicated problem because a number of different interactions are concerned including those associated with the head groups of the surfactant, different segments of the alkyl chain and the counterions. By considering the Berezin's model, a solution above the CMC may be regarded as a two-phase system (Scheme 7), consisting of an aqueous phase and a micellar pseudophase. A quantitative model for a bimolecular reaction occurring only in the aqueous (k_W path) and micellar (k_M path) phase [38] has been given as:

 $R \, or \, R' = -H, -CH_3, \, -CH_3CH_2$

W = aqueous medium, M = CPC/CHAPS micellar medium, S = substrate (alcohol), O = oxidant.

The catalytic effect is more pronounced in the presence of CHAPS in comparison to CPC. Hence the rate of reaction is increased by the addition of both CHAPS and Ir(III) metal catalyst. The experimental data in Table 1 describes the half life $(t_{1/2})$ values of the alcohol oxidation reaction by Ce(IV) gradually decreases upon addition of Ir(III) and CHAPS micellar catalyst. The decrease in $t_{1/2}$ value becomes more severe when combined effect of CHAPS micelle and Ir(III) catalysts has come into play.

4.7. Optical micrographs for micelle

The optical micrographs are taken for the substrate–surfactant mixtures at 10:1 ratio in $100 \times$ magnification in an optical microscope. The images (Fig. 12) represent the evidence of micelle formation in the aqueous medium. The formation of micelles in association with the alcohols in aqueous medium was clearly identified from optical images.

4.8. DLS explanation of micellar aggregate

It was found from the plot (Fig. 13) that, in the case of CPC the size or diameter of micelle changes when alcohol and Ce(IV) are added into the micellar medium. The plot informs us about the changes in micellar diameter when reactants are present in the reaction medium. This is also evident from the SEM images (Fig. 4) of CPC micelle. The changes in size or diameter of the micelle help us to understand that an interaction



Fig. 11. (a) Molecular structure of surfactant CHAPS; (b) Molecular structure of surfactant CPC.



Scheme 6. Schematic model showing probable location of reactants for the cationic micellar mediated oxidation reaction between [Ce(IV)] complex and alcohol.

occurs between the substrate (alcohol) and Ce(IV) with the "stern layer" of CPC micelle. The overall charge of CPC micelle is cationic, therefore positive Ce(IV) species that interacts less with the aggregates and alcohol molecules reside in the "stern layer" of the micelle. The size of

CPC was 5.6 nm as found in the plot. Upon the interaction of oxidant and substrate with the outer surface of the aggregates the diameter of the CPC micelle increases from 5.6 nm to 7.6 nm and 6.61 nm respectively corresponding to Ce(IV) and alcohol (propanol) system.



Scheme 5. Schematic model showing probable location of reactants for the zwitter-ionic micellar mediated oxidation reaction between (a) [Ce(IV)] species, alcohol and proton; (b) [Ce(IV)], Ir(III)-alcohol and proton.







Scheme 7. Partitioning of the oxidant and substrate between the aqueous and micellar pseudo phase.

4.9. Reactive species of cerium(IV)

Both Ce(III) and Ce(IV) ions are reported to form a number of complexes in sulfuric acid media (Eqs. (1) to (4)) depending upon the concentrations of H^+ , HSO₄⁻, and SO₄²⁻. The stepwise equilibria of Ce(III)– sulfato and Ce(IV)–sulfato species, and the corresponding formation constants [14] are as follows:

$$\operatorname{Ce}^{3+} + \operatorname{SO}_{4}^{2-} \rightleftharpoons \operatorname{Ce}(\operatorname{SO}_{4})^{+} \quad K_{1}{}' = 43 \tag{1}$$

$$\operatorname{Ce}(\operatorname{SO}_4)^+ + \operatorname{SO}_4^{2-} \rightleftharpoons \operatorname{Ce}(\operatorname{SO}_4)_2^- \quad K_2' = 5$$
⁽²⁾

$$Ce(SO_4)_2^- + SO_4^{2-} \rightleftharpoons Ce(SO_4)_3^{3-} K_2' = 5.5$$
 (3)

$$Ce^{4+} + HSO_4^- \rightleftharpoons Ce(SO_4)^{2+} + H^+ K_1' = 3500$$
 (4)

$$Ce(SO_4)_2^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ K_2' = 200$$
 (5)

$$Ce(SO_4)_2 + SO_4^{2-} \rightleftharpoons Ce(SO_4)_3^{3-} + H^+ \quad K_2' = 20$$
 (6)

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+.$$
(7)



Fig. 12. Optical micrograph images of mixtures of alcohol and surfactants in water: (a) 1-butanol:CHAPS = 10:1 (b) propan-2-ol:CPC = 10:1.



Fig. 13. (a) Variation of particle size distribution of CPC (1.1 mM) micelles/vesicles determined by dynamic light scattering (DLS). The average particle sizes for only (\blacksquare) CPC is 5.6 nm and ceric(IV) incorporated (\bullet) CPC is 7.6 nm. [Ce(IV)] = 2×10^{-4} mol dm⁻³, $\mu = 2$ mol dm⁻³. (b) The average particle sizes for only (\blacksquare) CPC is 5.6 nm and propanol incorporated (\bullet) CPC is 6.6 nm. [propanol] = 2×10^{-3} mol dm⁻³.

Table 3

The enhancement in rate of oxidation for different alcohol catalyzed by CHAPS-Ir(III) system compared to the uncatalyzed reaction.

$10^4 \times substrate$ (mol dm ⁻³)		Catalyst (mol dm ⁻³)	Enhancement in rate
Ethanol	20	CHAPS = 8×10^{-3} and Ir(III) = 2×10^{-6}	747 fold
Propanol	20		549 fold
Propan-2-ol	20		2130 fold
1-Butanol	20		1013 fold
2-Butanol	20		719 fold

The exact nature of the complexes of ceric(IV) with the alcohol is not known, but the variation in the first-order rate constant for ceric(IV) disappearance as a function of hydrogen ion for the different alcohols (Fig. 9) is in agreement with the stated equilibria of Eqs. (5) to (7). According to Eq. (7), with increasing sulfate concentration the amount of HSO₄ increases. This pushes the equilibria 3, 4, and 5 toward the right. to result in an increase of concentration of the more highly sulfated complexes. The observed faster rate for the disappearance of ceric(IV) ions with increasing hydrogen ion concentration (Fig. 9) is also in accordance with the foregoing conclusion. Although the effect of increasing hydrogen ion (Eq. (7)) is to bring about an increase in HSO₄, the excess of $\rm H^+$ over SO₄²⁻ minimized this factor. From the hydrogen-sulfate dependence, $Ce(SO_4)^{2+}$ has been identified as kinetically (Table 2) active among the different sulfato-cerium(IV) species under the experimental conditions. In aqueous-micellar media, the different sulfato complexes of Ce(IV) are expected to be partitioned in different ways. This partitioning behavior of CPC and CHAPS may be helpful and reliable probe to identify the kinetically reactive species [13,15]. It is also evident from Scheme 5 that CHAPS can accelerate the rate process by involving the reactive species $Ce(SO_4)^{2+}$ in the kinetics of the alcohol oxidation.

The pseudo-first-order rate constants of the oxidation reaction between Ce(IV) and alcohol vary in magnitude in the order of $k_{(CHAPS)} >$ $k_{(Aqueous)} > k_{(CPC)}$. The micellar catalysis by CHAPS in association with Ir(III)-salt exhibited the remarkable ~ 500-2000 fold rate enhancements (Table 3) as compared to that of uncatalyzed reaction. However as seen in Table 3, the catalytic activity of the Iridium(III)-mediated CHAPS micellar catalyst has a highest significant 2000 fold rate enhancement in the Ce(IV) oxidation of propan-2-ol compared to the rest of the alcohol oxidations.

The overall key analysis of our present work comparing to the previously reported works has been summarized in Table S15 of supplementary data. The dramatic difference in the catalytic activity of iridium(III)-mediated CHAPS micellar catalyst in contrast to the CPC is mainly due to the electrostatic interaction between the oppositely charged species [68] in a pseudo-micellar phase. Preliminary experiments indicate that the absorbance of the Ce(IV)-CHAPS mixture is shifted compared with the free CHAPS surfactant and free Ce(IV) solution respectively. Whereas the wavelength of maximum absorbance remains unchanged (vide supra); these observations suggest a strong association/incorporation of the reactive species at the CHAPS micelles (Supplementary data).

5. Conclusion

The oxidation reaction of aliphatic alcohols by Ce(IV) is very sluggish in the sulfuric acid medium. From the analysis of various kinetic experiments, $Ce(SO_4)^{2+}$ suggested the kinetically main reactive species of cerium(IV). CPC inhibits the reaction rate compared to the uncatalyzed path. Ir(III)-Ce(IV) system in CHAPS micellar medium is highly efficient to oxidize both the primary and secondary alcohols from the kinetic and synthetic points of views.

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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.2014.03.037.

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