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Mixed Anionic-Nonionic Micelle Catalysed Oxidation of Aliphatic Alcohol in Aqueous Medium

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Abstract

Oxidation of isoamyl alcohol was carried out under pseudo 1st order reaction condition in aqueous medium by chromic acid. In addition to single micelle, mixed anionic-nonionic micelle (SDS-TX 100) was found to be effective catalyst. Promoters in presence of micelle catalyst showed almost million fold rate acceleration. The product was confirmed by IR and NMR study. UV and NMR analysis were carried out to establish the formation of mixed micelle. Formation of active oxidant was confirmed by fluorescence measurement. Interactions between surfactant and substrate were analysed by NMR spectra. In addition to SDS catalysed Bpy promoted reaction combination of mixed micelle with Bpy promoter was found to show higher rate of oxidation. For single micelle catalysed path the observed rate constants follow the order $k_{\text{obs}}(\text{SDS}) > k_{\text{obs}}(\text{TX 100})$ and $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$ was observed for promoted reactions. In SDS micelle and mixed micelle $k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{PA})$ was observed while in TX 100 micelle $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$ was found.

Keywords: Mixed micelle; catalysed; promoter; surfactant; active oxidant (AO^+); rate constant.

Abbreviations:

CMC - Critical Micelle Concentration

SDS - Sodium dodecylsulphate

TX 100 - Triton X 100

Bpy - 2, 2'-Bipyridine

Phen - 1, 10-Phenanthroline

PA - 2-Picolinic acid/ Pyridine-2-carboxylic acid

2, 4-DNP - 2, 4-Dinitrophenylhydrazine

AO⁺ - Active Oxidant

UV - Ultraviolet

IR - Infrared

NMR – Nuclear magnetic resonance

TMS – Tetramethylsilane

k_{obs} – Pseudo 1st order rate constant.

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1 Introduction

The revolutionary observation of McBain in 1913 had introduced a paradigm shift in the field of chemical science [1]. At present micelle is efficiently used to carry out organic reactions in water [2-6]. Many organic reactions are reconstructed in aqueous micellar medium to eliminate toxic, volatile organic solvents and to mould the process in a green envelop [7-15]. Moreover micelle has a unique property of catalysing chemical reaction due to close proximity of reactants in micelle core or stern region depending on substrate [16-31]. Micelles are formed by surfactants. Actually at critical micelle concentration or maximum aggregation number surfactant molecules assemble to form different nano-like aggregates such as spherical micelle, vesicles, lamellar, unilamellar, rodlike, disklike, threadlike micelle etc. and significantly alter different physiochemical properties of the solution such as surface tension, viscosity, ionic conductance, refractive index, molecular adsorption, diffusion coefficient etc. [32-34]. So physiochemical properties study of daily life inevitable surfactant solution is an important research topic [35-40].

Sometimes better performance in practical application is achieved by using mixed micelle instead of single one due to synergistic effect of constituent blocks and effectively used in emulsification, dispersion, detergency, cleaning, targeted drug delivery, synthesis of advanced nano-material, cosmetics, wastewater treatment, oil recovery and food industries [41-49]. Properties of mixed micelle solution are significantly different from single micelle and hence their physiochemical aspects are interesting research topic for last two decades [50-53]. Though properties of the mixed micelle are well studied by different techniques such as viscosity measurement, surface tension measurement, conductometry, capillary electrophoresis, NMR, small angle neutron scattering, dynamic light scattering, fluorescence anisotropy measurements, 2D- NOESY etc., the application of such system in the field of oxidation kinetics is limited [54-58]. Herein we report for the first time effect of mixed micelle on the oxidation kinetics and catalysis from our end.

Oxidation by Cr(VI) is well established and has been used for years [59]. In spite of toxic and carcinogenic effect, preference of chromic acid as oxidant is due to its definite aqueous chemistry in sulfuric acid medium and formation of kinetically non-labile Cr(III) on completion of reaction, which can be used as nutritional supplement in definite form such as chromium(III) picolinate [60-62]. It has been seen for years that chromic acid oxidation of different organic

compounds are catalysed by micelle and the rate can further be enhanced by using some heteroaromatic bases [63-71]. These bases during the course of reaction are transformed as Cr(III)-base complex and hence better called as promoter instead of catalyst [72-73].

In this paper we have reported oxidation of isoamyl alcohol in aqueous medium under pseudo 1st order reaction condition by chromic acid at 30°C. Isoamyl alcohol on oxidation produces isovaleraldehyde which is used as precursor of 2, 3-dimethyl-2-butene and butizide [74]. The reaction is catalysed by anionic, nonionic and mixed anionic-nonionic micelle. Additional increment in rate is obtained by using promoters such as Bpy, Phen and PA. A tremendous increment of rate is observed in SDS catalysed Bpy promoted reaction and mixed SDS-TX 100 micelle catalysed and Bpy promoted reaction.

2 Experimental

2.1 Materials and reagents

Isoamyl alcohol (99.0 %, AR, Merck, India), K₂Cr₂O₇ (99.9 %, AR, BDH, India), H₂SO₄ (98%, AR, Merck, India), Sodium dodecylsulfate (>90%, AR, Merck, India), Triton X-100 (98%, AR, SRL, India), 2-Picolinic acid (99%, AR, Sigma Aldrich, UK), 2, 2'-Bipyridine (99%, AR, Spectrochem, India), 1, 10-Phenanthroline (99.5%, AR, Merck, India), Deuterium oxide (D₂O) (99.9%, AR, Sigma-Aldrich, USA), Chloroform-d (CDCl₃) (99.8%, AR, Sigma-Aldrich, USA). Double distilled water (conductivity 2 μS cm⁻¹) was used for the preparation of required solutions. All the chemicals were used as received without further purification.

2.2 Instrumentation and Kinetic measurement

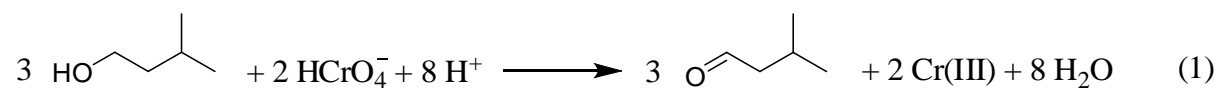
A double beam UV-Visible spectrophotometer, SHIMADZU UV-1800 (Japan) fitted with temperature controller TCC 240A was employed to follow the progress of reactions using quartz cuvettes of cell length 1 cm. Mettler Toledo ME204 chemical balance having readability of 0.1 mg and digital ultrasonic cleaner CD 4820 were used for preparation of solutions. Specific conductances were measured by Eutech Instrument (CybarScan PCD 6500, cell constant 1 cm⁻¹, accuracy 0.5%). Steady state fluorescence measurements were carried on Hitachi FL -7000 Spectrofluorometer. IR spectra were recorded by Perkin Elmer Spectrum Two FT-IR spectrometer, JEOL 400 MHz and Bruker Ascend 400 MHz spectrophotometers were utilized for ¹H-NMR study.

Under pseudo 1st order reaction condition kinetic data were collected by keeping concentration of isoamyl alcohol excess (15 times) over the concentration of oxidant potassium dichromate in 0.40 mol dm⁻³ H₂SO₄ medium in absence and presence of surfactants (SDS, TX 100). All the solutions were thermostated at 30°C (± 0.1°C) separately before the reaction and the oxidation was initiated by mixing the required solutions. Promoters (PA, Bpy and Phen) were used in the concentration range [oxidant]_T ≤ [promoter]_T ≥ [substrate]_T. The decrease in absorbance of Cr(VI) at wavelength 450 nm was followed at regular time interval at 30°C. Each experiment was carried out for three times. Completion of the reaction is indicated by appearance of pale blue colour solution (unpromoted reaction) or pale violet colour solution (promoted reaction).

2.3 Product analysis and stoichiometry

After completion of reaction solvent extraction with diethyl ether (thrice) followed by fractional distillation resulted in two liquids with boiling points 132°C (isoamyl alcohol, literature value 131.5°C) and 93°C (isovaleraldehyde 92°C). 2, 4-DNP derivative was made with a small portion of the lower boiling liquid in sulfuric acid medium [75]. The yellow coloured recrystallized derivative showed melting point 123°C [75]. Product isovaleraldehyde was also confirmed by IR and ¹H- NMR spectral analysis.

As pseudo 1st order condition is employed so it is expected that Cr(VI) ion will be totally reduced to Cr(III) at the end of reaction. The absorption maximum found at 580 nm is in agreement with the existence of Cr(III) in the reaction mixture (⁴A_{2g}(F) → ⁴T_{2g}(F)) [76-77]. The constant absorbances at 580 nm, over a period of three days after the completion of the reaction in spectrophotometric titration with fixed concentrations of Cr(VI) and varying concentrations of isoamyl alcohol solutions at constant [H⁺] = 0.4 mol dm⁻³ showed that 2 mol of chromic acid was consumed by 3 mol of isoamyl alcohol (Equation 1).



2.3.1 IR spectral analysis

IR spectrum of isovaleraldehyde shows characteristic carbonyl (C=O) stretching frequency of aldehyde group at 1724 cm^{-1} (Fig. 1(a)), its 2, 4-DNP derivative shows peaks at 1618 cm^{-1} and 3293 cm^{-1} for C=N and N-H symmetric stretching frequency respectively (Fig. 1(b)).

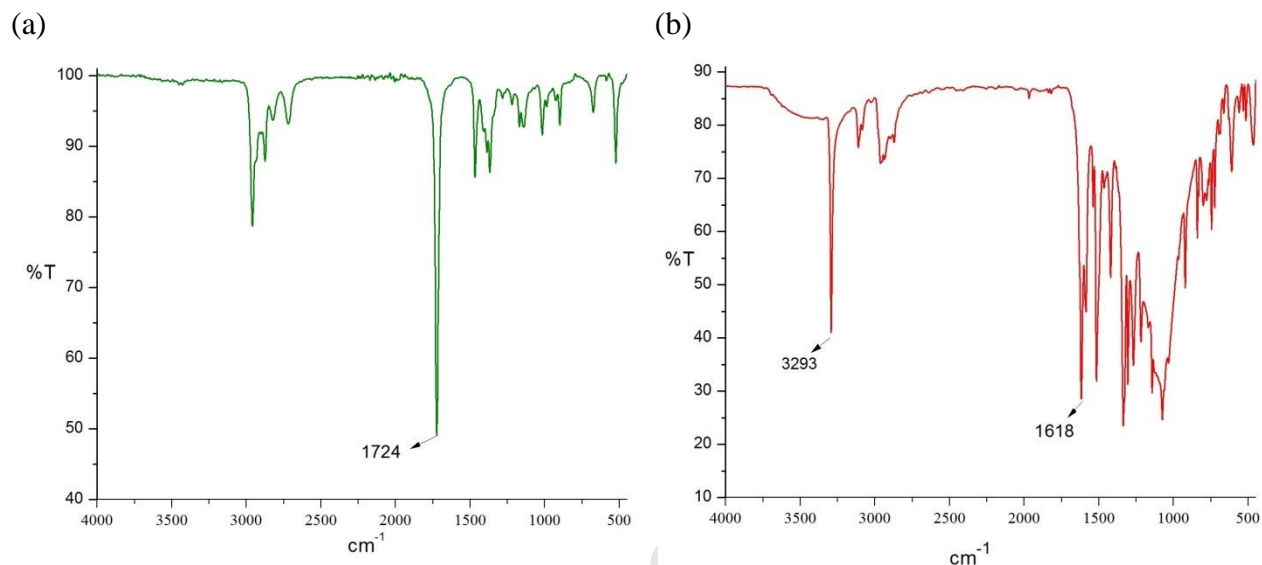


Fig. 1 IR spectrum of (a) isovaleraldehyde and (b) 2, 4-DNP derivative of isovaleraldehyde

2.3.2 $^1\text{H-NMR}$ spectral analysis

$^1\text{H-NMR}$ spectrum (Fig. 2) of isovaleraldehyde was recorded at 400 MHz in CDCl_3 solvent. Chemical shifts (ppm) were internally referenced to the TMS are reported in Table 1. Peak at 9.39 ppm confirms the presence of aldehyde functionality.

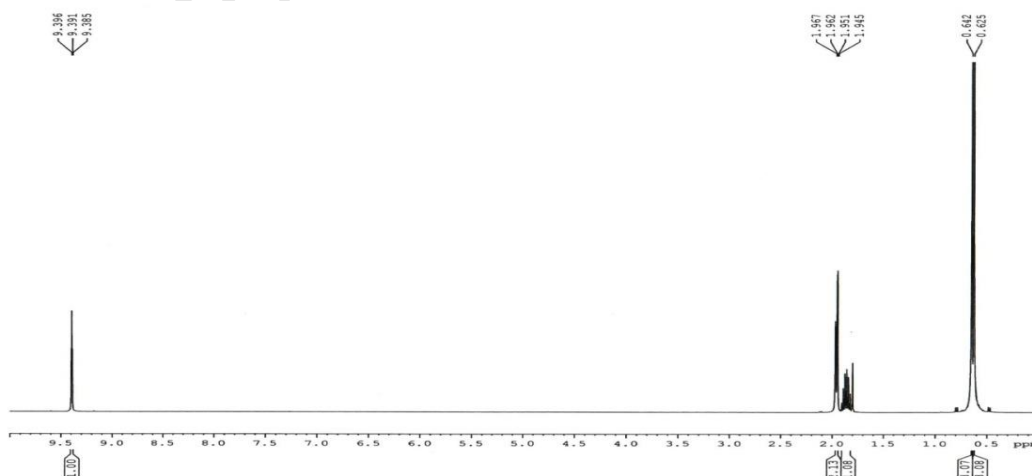
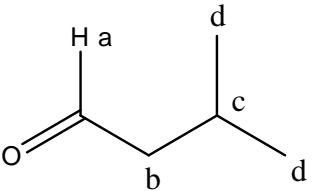


Fig. 2 The $^1\text{H-NMR}$ spectrum of isovaleraldehyde in CDCl_3 solvent

Table 1 Chemical shift values for different protons of isovaleraldehyde

Isovaleraldehyde	Atom	Chemical shift (δ ppm)
	a	9.39 (t)
	b	1.96 (dd)
	c	1.80 (m)
	d	0.64 (d)

2.4 Precautions

As Cr(VI) is highly toxic and carcinogenic, hence special precaution been taken so that no Cr(VI) is discarded through drainage. Due excessive usages of surfactants in different sectors presently surfactant pollution becomes alarming, surfactants containing waste water discharge to the water bodies causing serious harm to the aquatic animals and plants [78-79]. Hence, the used surfactants were recycled after the completion of the reaction to eliminate such effect from environment [21]. SDS was recycled using CaCl_2 and precipitated as Ca-salt whereas TX 100 was separated using thermal method of precipitation [21].

3. Result and Discussion

As previously mentioned, the progress of reactions was followed spectrophotometrically by observing the decrease in absorbance (A_{450}) of Cr(VI) at 450 nm at regular time interval (Fig. 3). From the slope of the plot $-\ln(A_{450})$ vs. time in second pseudo 1st order rate constants (k_{obs}) were calculated and half life for each reaction was evaluated from the relation $t_{1/2} = 0.693/k_{\text{obs}}$ (Fig. S1), (Table 2). It is clearly seen in table 2 that micelle catalysed and promoted reactions complete in much shorter time than uncatalysed reaction. Evidently the final species in uncatalysed and micelle catalysed reaction is Cr(III) (Fig. S2) [80-81]. In promoted reaction the final species is different from pure Cr(III), it is expected that Cr(III)-promoter complex are formed [66]. Here, ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition shows a hypsochromic shift ($\lambda_{\text{max}} = 546, 552$ and 565 nm for Bpy, Phen and PA-promoted reactions) due to the presence of strong field hetero aromatic ligands. A single isobestic point in each reaction suggest that the probability of formation of intermediate species like Cr(V) and Cr(IV) is of very low concentration (fig. S3) [82].

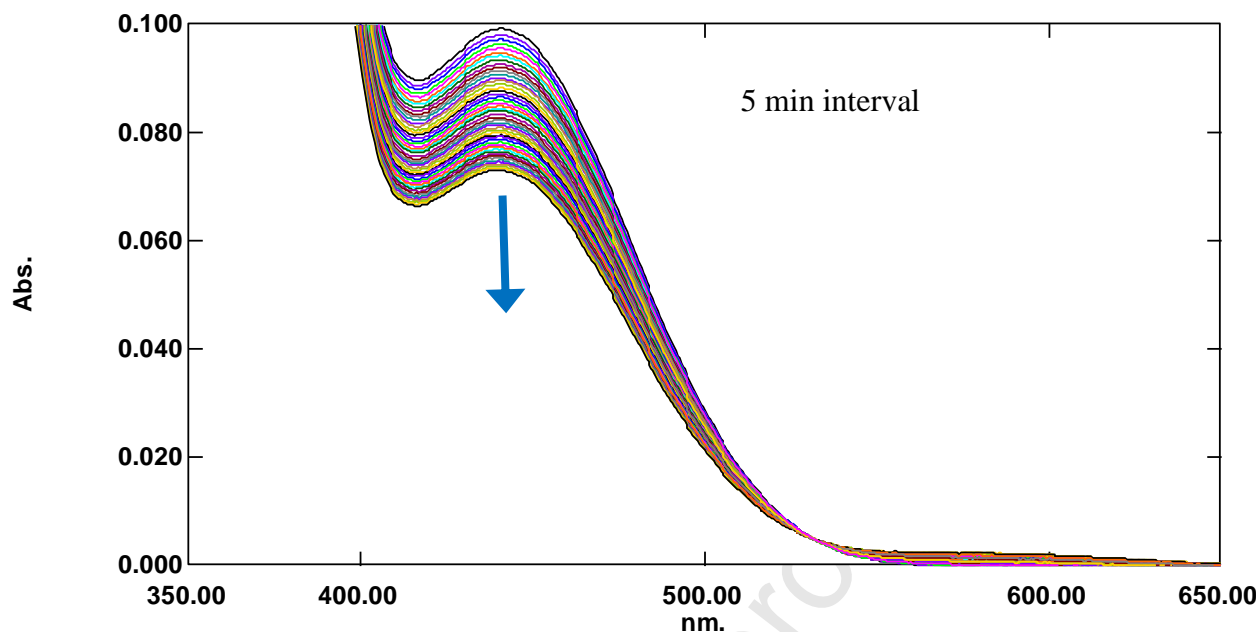


Fig. 3 Scanned absorption spectra of uncatalysed reaction at regular time interval (5min): $[\text{Isoamyl alcohol}]_{\text{T}} = 75 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.40 \text{ mol dm}^{-3}$, Temperature = 30°C .

Table 2 k_{obs} and half life of the reaction in presence and absence of promoter and micellar catalysts.

SDS [mol dm^{-3}] $\times 10^3$	TX 100 [mol dm^{-3}] $\times 10^3$	Promoter [mol dm^{-3}] $\times 10^4$	$10^4 \times k_{\text{obs}}$ [s^{-1}]	$t_{1/2}$ [h]
None	None	None	0.209 ± 0.001	9.21
10	None	None	0.423 ± 0.003	4.55
20			0.479 ± 0.005	4.01
30			0.496 ± 0.005	3.88
40			0.589 ± 0.007	3.26
50			0.639 ± 0.006	3.01
None	10	None	0.321 ± 0.004	5.99
	20		0.333 ± 0.004	5.78
	30		0.365 ± 0.003	5.27
	40		0.477 ± 0.002	4.04
	50		0.525 ± 0.007	3.66
10	10	None	0.271 ± 0.001	7.10
20			0.480 ± 0.003	4.01
30			0.556 ± 0.003	3.46
40			$0.651 \pm .0004$	2.95
50			0.739 ± 0.004	2.60

10	20	None		0.285 ± 0.004	6.75
	30			0.304 ± 0.005	6.33
	40			0.336 ± 0.007	5.73
	50			0.392 ± 0.005	4.91
None	None	2-Picolinic acid	5	0.410 ± 0.005	4.69
			25	0.840 ± 0.009	2.29
			50	1.186 ± 0.006	1.62
			75	1.490 ± 0.013	1.29
		1, 10-Phenanthroline	5	1.058 ± 0.009	1.82
			25	3.783 ± 0.030	0.51
			50	7.526 ± 0.070	0.25
			75	10.80 ± 0.061	0.18
		2, 2'-Bipyridine	5	0.909 ± 0.007	2.11
			25	3.296 ± 0.010	0.58
			50	5.094 ± 0.040	0.38
			75	7.604 ± 0.015	0.25
10	None	2-Picolinic acid	5	0.802 ± 0.006	2.40
			25	2.151 ± 0.010	0.89
			50	3.423 ± 0.023	0.56
			75	4.569 ± 0.030	0.42
None	10	2-Picolinic acid	5	0.630 ± 0.006	3.05
			25	1.918 ± 0.021	1.00
			50	3.031 ± 0.024	0.64
			75	4.624 ± 0.050	0.42
10	10	2-Picolinic acid	5	0.617 ± 0.007	3.12
			25	1.612 ± 0.010	1.19
			50	2.790 ± 0.025	0.69
			75	4.010 ± 0.070	0.48
10	None	1, 10-Phenanthroline	5	0.852 ± 0.001	2.26
			25	3.062 ± 0.009	0.63
			50	7.058 ± 0.060	0.27
None	10	1, 10-Phenanthroline	5	1.232 ± 0.011	1.56
			25	4.991 ± 0.060	0.39
			50	10.60 ± 0.055	0.18
			75	16.10 ± 0.020	0.12
10	10	1, 10-Phenanthroline	5	0.997 ± 0.001	1.93
			25	4.362 ± 0.010	0.44
			50	6.360 ± 0.027	0.30
			75	9.094 ± 0.050	0.21
10	None	2, 2'-Bipyridine	5	28.40 ± 0.070	0.07
			25	191.2 ± 0.100	0.01
None	10	2, 2'-Bipyridine	5	1.181 ± 0.016	1.63
			25	5.312 ± 0.020	0.36
			50	10.10 ± 0.091	0.19

			75	15.80 ± 0.010	0.12
10	10	2, 2'-Bipyridine	5	6.355 ± 0.009	0.30
			25	21.10 ± 0.010	0.09
			50	40.80 ± 0.030	0.05
			75	68.00 ± 0.090	0.03

[Isoamyl alcohol]_T = 75×10^{-4} mol dm⁻³, [Cr(VI)]_T = 5×10^{-4} mol dm⁻³, [H₂SO₄] = 0.40 mol dm⁻³, Temperature = 30°C.

Data in table 2 suggest that Phen promoted reactions are faster than other two promoters, while SDS shows highest rate among the micelle. Bpy promoted SDS catalysed reaction is the fastest one and it is so fast that at higher concentration of Bpy the reaction cannot be studied. Mixed micelle shows an intermediate rate of oxidation but with increase in concentration rate increases and combination of mixed micelle-Bpy is suitable one.

3.1 Mechanism of the reaction.

Product analysis shows that isovaleraldehyde is the product of chromic acid oxidation of isoamyl alcohol. The mechanism of the reaction can be divided into four categories (i) unpromoted and uncatalysed path, (ii) promoted path, (iii) micelle catalysed path and (iv) micelle catalysed promoted path.

3.1.1 Unpromoted and uncatalysed path

Chromic acid in aqueous medium predominately exists as HCrO_4^- (B) as the protonation constant of B is very low [83]. Under pseudo 1st order reaction condition this species reacts reversibly with the substrate to form neutral chromate ester (1). In the subsequent steps the so formed neutral ester undergoes acid catalysed decomposition to form isovaleraldehyde and Cr(III) (Scheme S1).

3.1.2 Promoted path

Rate of reactions in promoted path are greater than unpromoted one. The observed rate constant values vary in the order $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$ (Fig. 4). Completion spectra of promoted reactions indicate that some Cr(III)-promoter complexes are formed at the end of the

reaction (Fig. S2). Cr(III) is kinetically inert, so such type complex formation is difficult. Hence, we may expect that during the reaction at first Cr(VI)-promoter complex (AO^+) is formed which then reduced to Cr(III)-promoter complex. In fact, absorption and emission spectral analysis with Cr(VI) and promoters suggest such type of complex formation (Fig. S4 and S5). Previous NMR analysis also supports Cr(VI)-promoter complex formation [84]. In the proposed mechanism (Scheme 2, 3) active oxidant forms a neutral ester which undergoes acid catalysed decomposition to the product. The observed rate variation with different promoters can be explained if we consider the formation of active oxidants. All the three-promoter used here are chelating agents with N, N or N, O donors and can form chelated complex with Cr(VI). Rate of formation of active oxidant (AO^+) is higher in case of Phen as in 1, 10-Phenanthroline both the donating N atom are always *cis* with three stable aromatic ring. This may be attributed to the enhanced rate of oxidation in case of Phen. Stable conformer for 2, 2'-Bipyridine is *s-trans* and hence an activation barrier is there to change the conformation to *s-cis* prior to the formation of active oxidant. This may results a relative reduction in the rate of reaction. 2-picolinic acid is depriving of more aromatic stabilization (in Bpy two aromatic rings and in Phen three aromatic rings) and the presence of more electronegative O atom may affect the rate.

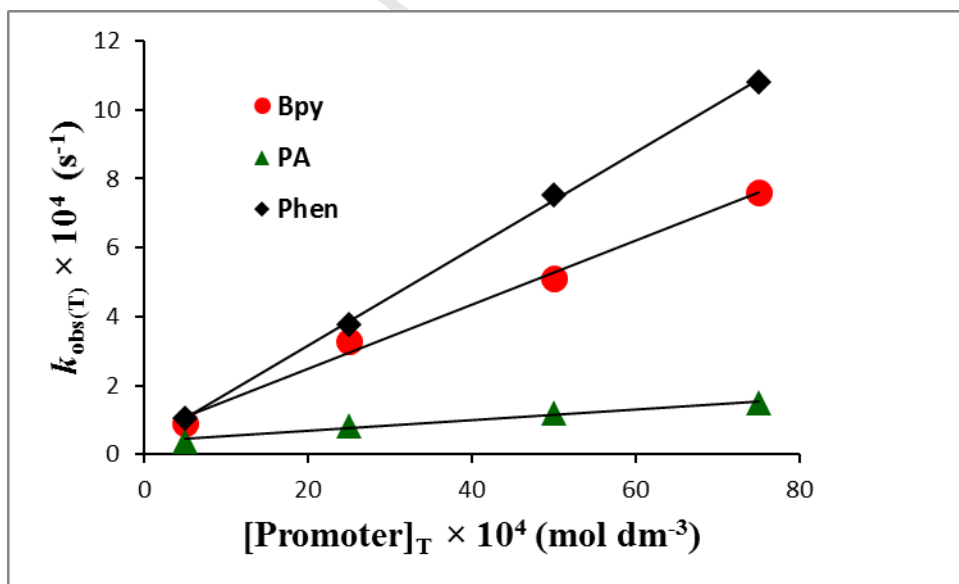


Fig. 4 Dependence of k_{obs} on $[Promoter]_T$ for Cr(VI) oxidation of isoamyl alcohol (in absence of surfactant) in aqueous H_2SO_4 media at $30^\circ C$. $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.4 \text{ mol dm}^{-3}$, $[Isoamyl\ alcohol]_T = 75 \times 10^{-4} \text{ mol dm}^{-3}$.

3.1.3 Micelle catalysed path

Micelle catalysed path can be subdivided in to two categories (i) single micelle catalysed path and (ii) mixed micelle catalysed path.

3.1.3.1 Single micelle catalysed path

Both SDS and TX 100 used here are at post CMC and the observed rate constants follow the order $k_{\text{obs}}(\text{SDS}) > k_{\text{obs}}(\text{TX 100})$ (Fig. 5). To explain this trend we must look at the mechanism part (Scheme S4), in proposed mechanism once again a neutral ester is formed which undergoes acid catalysed decomposition to form the product. Unlike the unpromoted path here in presence of micelle, to facilitate binding of Cr(VI) through ion-dipole interaction and H bonding interaction to the micellar surface the active species of chromic acid is H_2CrO_4 [83]. UV spectroscopic analysis of Cr(VI)-micelle system also suggests a definite interaction between Cr(VI) and micelle surface (stern layer) as broadening of Cr(VI) absorbance band occurs with red shift of λ_{max} (Fig. 6) [85]. Interaction between substrate (alcohol) and micelle was also investigated by NMR. Modulated chemical shifts of surfactant in presence of substrate strongly suggest a definite interaction between them (Fig. S6). Upfield chemical shifts of head group region protons of either surfactant in presence of alcohol indicates that polar -OH group of alcohol orients itself toward the stern layer of micelle, while hydrophobic chain buried in palisade layer. The upfield shift may be due to the increased electron density by the presence of alcoholic -OH group in vicinity of head group protons of surfactant. The upfield shift of other protons can be explained considering hydrophobic interaction between hydrocarbon chains of alcohol and surfactant [21]. The observed greater slope of rate constant in SDS can be explained considering the acid catalysed decomposition of neutral chromate ester. H^+ can approach neutral ester present in the negatively charged SDS micelle with greater ease (attractive interaction) compare to neutral TX 100. This may lead to observed higher rate in SDS micelle (Scheme S5).

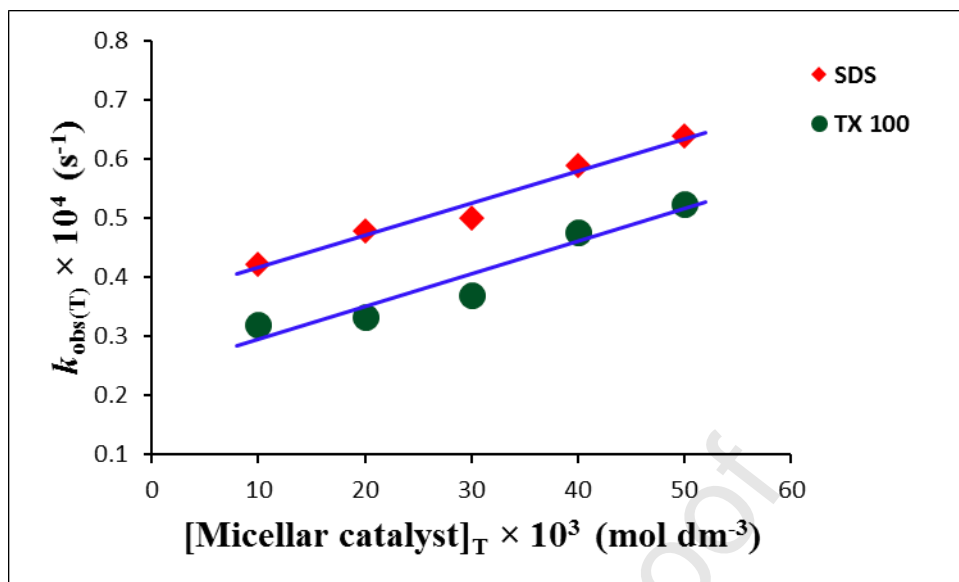


Fig. 5 Dependence of k_{obs} on $[\text{Surfactant}]_{\text{T}}$ for Cr(VI) oxidation of isoamyl alcohol (in absence of promoter) in aqueous H_2SO_4 media at 30°C . $[\text{Cr(VI)}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.40 \text{ mol dm}^{-3}$, $[\text{Isoamyl alcohol}]_{\text{T}} = 75 \times 10^{-4} \text{ mol dm}^{-3}$.

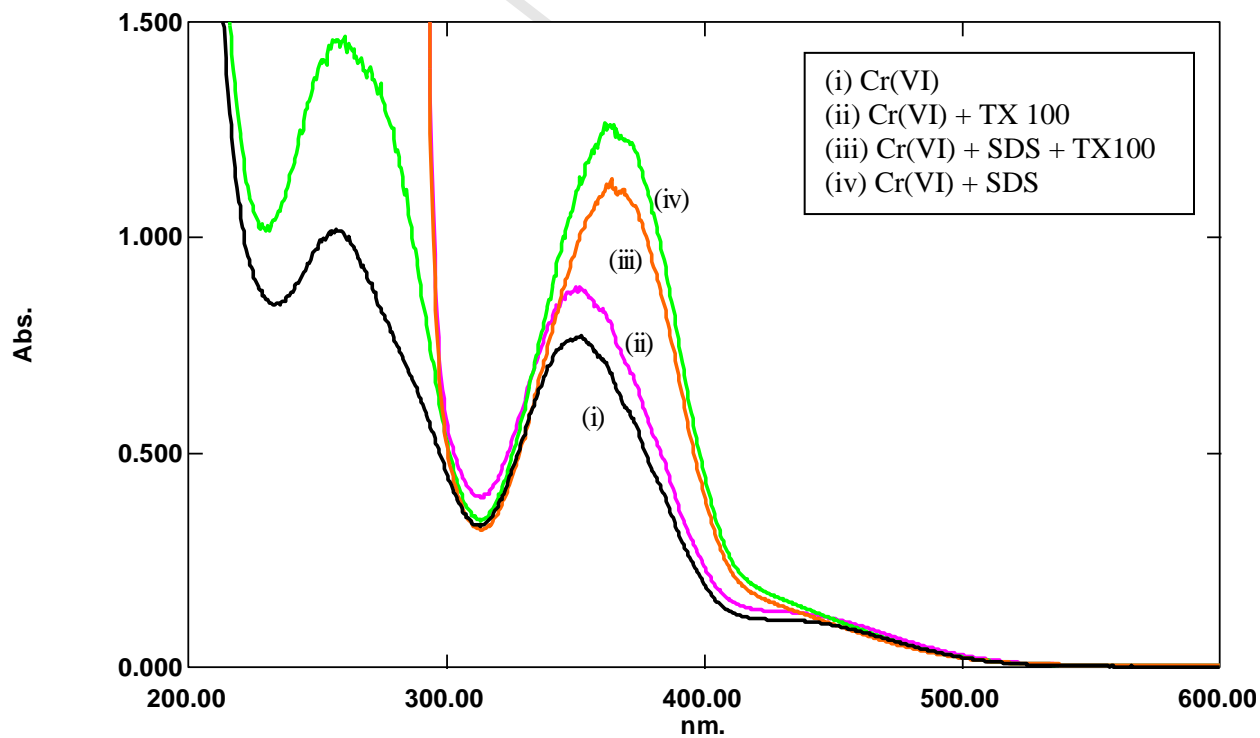


Fig. 6 UV-Vis study of interaction between Cr(VI) and different surfactant above CMC. $[\text{Cr(VI)}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = [\text{TX 100}]_{\text{T}} = 20 \times 10^{-3} \text{ mol dm}^{-3}$ in aqueous media at 30°C .

3.1.3.2 Mixed micelle catalysed path

UV spectrum of SDS + TX 100 with Cr(VI) suggests that in solution they do not exist as discrete unit rather a mixed micelle may form (Fig. 6). In fact, UV spectral analysis at 276 nm (λ max of TX 100 absorbance) with varying concentration of TX 100 and fixed post CMC of SDS suggest a definite interaction between them as hypochromic shift is observed (Fig. 7). We further determine CMC of SDS in presence of TX 100 with constant mole fraction (0.5) of both the surfactants by conductometry method. CMC was found to be 0.15 mM, which is much lower than CMC of SDS (8.2 mM) and higher than CMC of TX 100 (0.24 mM) (Fig. S7) but is consistent with literature value [58, 86]. This observation once again suggests that discrete single micelle is not present in the solution rather true mixed micelle is present. NMR study with 1:1 surfactant solution shows following type of modulated chemical shifts with δ values for SDS are shifted to upfield while that of TX 100 are downfield (Table 3) (Fig. 8 and S8). This observation is quite similar in trend with available data in literature [55]. So, we may conclude in present case too that methylene group of SDS (alpha protons) are situated near the phenoxy ring of TX 100 in mixed micelle, the hydrophobic part of SDS does not extended much into the micellar core while hydrophilic part of TX 100 remain coiled in the mixed micellar solution.

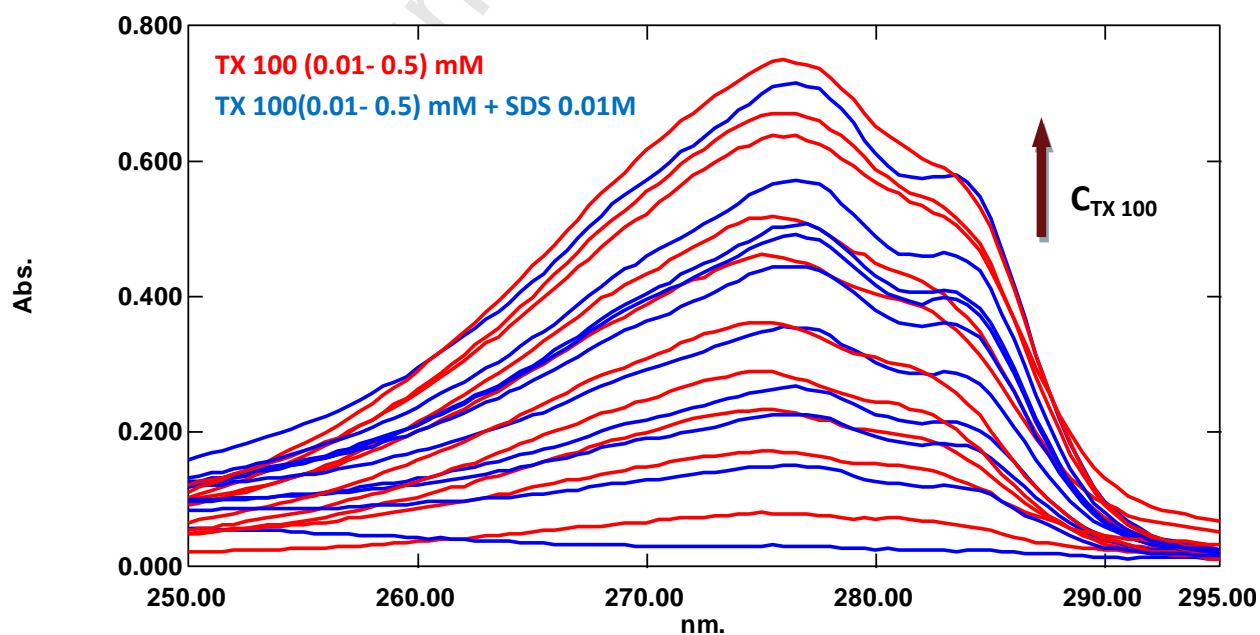


Fig. 7 Interaction between TX 100 and SDS micelle at 30°C in aqueous medium, $[\text{SDS}]_{\text{T}} = 0.01 \text{ mol dm}^{-3}$, $[\text{TX 100}]_{\text{T}} = 0.01\text{-}0.5 \text{ mM}$.

Table 3 ^1H chemical shifts (ppm) of mixed SDS and TX 100 in D_2O .

	α -H's	β -H's	Bulk-H's	Terminal-H's	a-H's	b-H's	c-H's	d-H's	e-H's	f-H's	g-H's	h-H's
SDS(0.01M)	3.91	1.54	1.15	0.735								
SDS (0.01M) + TX100(0.01M)	3.81	1.45	1.05	0.730	0.565	1.52	1.15	7.055	6.655	3.92	3.66	3.45-3.55
TX 100(0.01M)					0.535	1.47	1.11	7.05	6.65	3.85	3.62	3.4-3.6

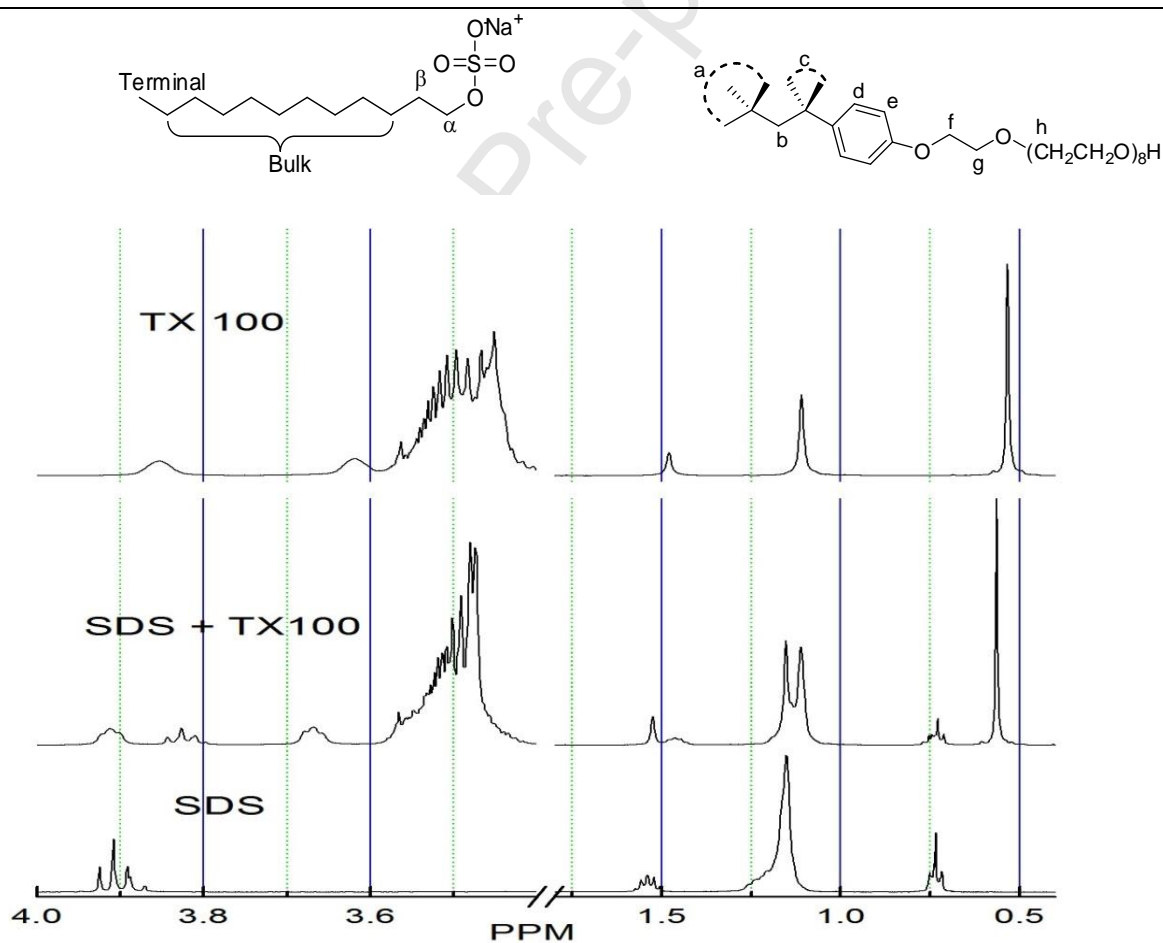


Fig. 8 Selected region of SDS-TX 100 interaction ^1H NMR.

The observed rate with 1:1 SDS-TX 100 mixed micelle is somewhat lower than that observed in single micelle catalysed reaction (Table 2). With increase in concentration of either the surfactant keeping the other surfactant constant at post CMC showed rate increment and at higher concentration rate are comparable to that of single micelle catalysed reaction (Fig. 9). The mechanism of reaction here is same as that of single micelle catalysed path. The observed result can be explained if we consider the above mentioned fact with observation that in mixed micelle of SDS-TX 100 at first TX 100 micelle is formed then with increase in total micelle concentration SDS micelle shows aggregation behavior [58]. As TX 100 micelle is populated by SDS at lower concentration so available space for alcohol to penetrate into micelle is reduced (steric factor) and hence a slow rate is observed. With increase in concentration of either the surfactants single micellar aggregate may form in addition to the mixed micelle, resulting higher rate of oxidation. NMR investigation of mixed micelle (1:1) alcohol interaction shows hardly any change in chemical shift values. This suggests that alcohol could not effectively penetrate the mixed micelle at specified concentration to modulate the chemical shift values (Fig. S9).

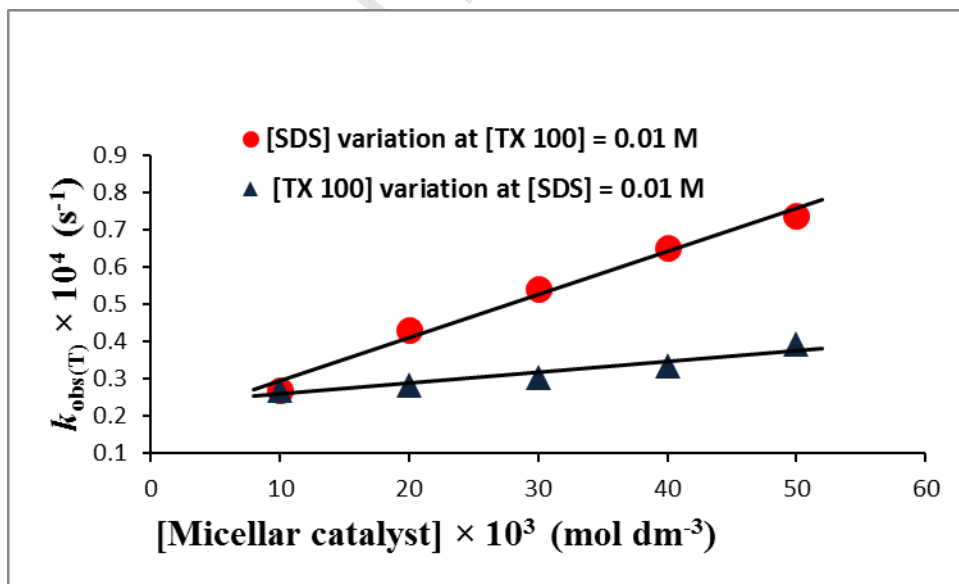


Fig. 9 Dependence of k_{obs} on mixed micelle for Cr(VI) oxidation of isoamyl alcohol (in absence of promoter) in aqueous H_2SO_4 media at 30°C . $[\text{Cr(VI)}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.40 \text{ mol dm}^{-3}$, $[\text{Isoamyl alcohol}]_{\text{T}} = 75 \times 10^{-4} \text{ mol dm}^{-3}$.

3.1.4 Micelle catalysed promoted path

We have already seen the order of rate constant in promoted path with reasoning and the order is $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$. Here in the micelle catalysed promoted path the mechanism is same as that of promoted path and the observed rate depends on how easily active oxidant (AO^+) reacts with substrate present in micelle to form chromate ester (Scheme S6). In TX 100 micelle catalysed path there exists pi-pi interaction in between aromatic sextet of TX 100 and the active oxidants. This facilitates congregation of active oxidants in stern layer leading to higher rate of oxidation. The number of pi electrons is highest in Phen so it shows higher rate followed by the other two. So the observed rate follow the order $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$ in TX 100 medium (Fig. S10a). In SDS medium there is no pi-pi interaction present, rather attractive electrostatic interaction is present between positively charged active oxidant and negatively charged SDS micelle. The active oxidant formed by Phen and Bpy are bipositive while that of PA is unipositive. So, considering the attractive interaction Phen and Bpy promoted reaction should show same rate followed by PA promoted one ($k_{\text{obs}}(\text{Bpy}) \approx k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{PA})$). Beside attractive interaction there exists repulsive interaction between pi electron cloud of AO^+ and negative charge surface of SDS micelle. Pi electron density is highest in Phen and Lowest in PA. So the repulsive interaction is highest in Phen promoted reaction and lowest in PA promoted reaction. Hence considering repulsive interaction $k_{\text{obs}}(\text{PA}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen})$ should be observed. The actual order of rate constant in SDS micelle is $k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{PA})$, can be explained considering both the attractive and repulsive interaction simultaneously (Fig. S10b). The observed order of rate constants $k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{PA})$ in mixed micellar system can be explained considering above discussed factors with steric factor discussed in the mixed micelle catalysed path (Fig. S10c.). Variation of micellar system for a fixed promoter is shown in fig. S 11.

4 Conclusions

In this study we have presented a green approach of alcohol oxidation with utilisation of mixed micelle and single micelle. Use of promoters in combination with micellar catalyst completes the reaction almost instantly. In addition to SDS-Bpy combination mixed SDS-TX 100 micelle in combination with Bpy found to be efficient catalyst. Use of relatively low cost mixed micelle may open new avenue and suppose to be beneficial for industry [58]. In future such type of study

with cationic-neutral and anionic-cationic micelle may lead to some new findings. Beside the effect of mixed micelle on oxidation some physiochemical properties study such as shape and size of mixed micelle system may be of immense importance for scientific community.

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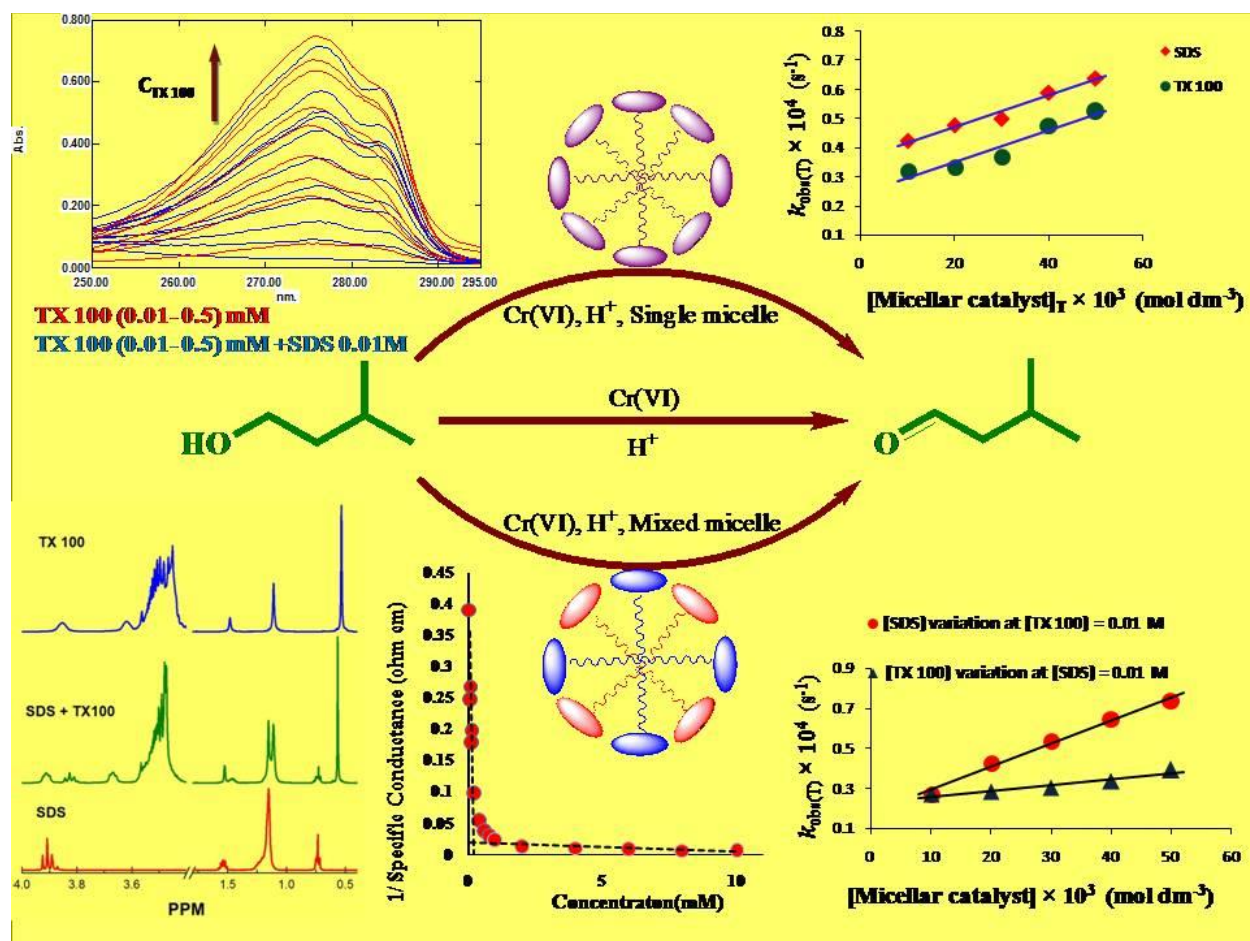
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Journal Pre-proof

Graphical Abstract



Highlights

1. Greener efficient method of oxidation of isoamyl alcohol.
2. SDS catalysed reactions are faster than TX 100 catalysed reactions.
3. Mixed micelle (SDS + TX 100) found to be efficient catalyst.
4. Rate constants in promoted path follow the order, $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$.
5. SDS catalysed and Bpy promoted reaction showed million folds rate acceleration.

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