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Surface phenomenon in micellar media: An excellent controlling factor for oxidation of fatty aldehyde in aqueous medium

Suman Chowdhury¹, Atanu Rakshit¹, Animesh Acharjee^{1,2}, Kalachand Mahali³ and Bidyut Saha^{1*}

¹Homogeneous Catalysis Laboratory, Department of Chemistry, The University of Burdwan, Burdwan 713104, WB, India

²Department of Chemistry, Hooghly Mohsin College, Chinsurah, WB, India

³Department of Chemistry, University of Kalyani, Kalyani, 741235, WB, India

*Corresponding author, E-mail Id: b_saha31@rediffmail.com (B. Saha) Mobile: +91 9476341691

Abstract

Oxidation of long chain aldehydes is truly tough in aqueous medium. So, an attempt has been made to oxidise octanal, a fatty aldehyde, by Cr(VI) in acidic aqueous media with the assistance of surfactants. The detailed kinetics of this successful micellar oxidation reaction has been studied spectrophotometrically under pseudo 1st order condition at 25°C ($\pm 0.1^\circ\text{C}$). In promoting the oxidation reaction three hetero-aromatic bases i.e. 1, 10 – phenanthroline (Phen), 2-picolonic acid (PA) and 2, 2' – bipyridine (Bpy) have been used in combination with the surfactants. Mixture of SDS and Bpy has come out to be the most effective among the others to enhance the oxidation rate maximum. Necessary spectral analysis and thermodynamic facts have also been produced in support of the whole process.

Keywords

Fatty aldehyde oxidation; aqueous micellar media; homogeneous catalysis; pi-pi interaction.

Abbreviations

CMC – Critical Micelle Concentration

SDS – Sodium dodecylsulphate

CPC – Cetylpyridinium chloride

Bpy – 2, 2'-Bipyridine

Phen – 1, 10-Phenanthroline

PA – 2-Picolinic acid

rds – Rate Determining Step

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1. Introduction

Organic synthesis is one of the most successful segments of chemical science to define the necessity, applicability, viability and favour of science to mankind. It is inevitable that the products obtained from organic syntheses have provided us numerous benefits from commercial to survival purposes. Chronologically, many advancements have been made by the heirs of researchers keeping parallelism and compatibility with the desire of human beings but in few cases compatibility with the green requirements of reaction procedures cannot be retained. Usages of hazardous organic solvents in those synthetic procedures has made them refractory to eco-friendly green principles.[1-3] So, in the present era the growing concern of environment has led us find an approach with non-violation of green principles. For some past years surfactants are in good agreement with those green principles replacing hazardous organic solvents in organic syntheses. Its amphiphilic nature [4] has gifted us the privilege of solubilizing many hydrophobic organic species and continue the reaction procedures in hazardless aqueous medium. Many popular organic reactions e.g. Diels-Alder reaction, Friedel-Crafts reaction, Suzuki coupling, Epoxidation reaction, Heck coupling, Ether synthesis etc. have also been revised successfully in micellar media formed by surfactants.[5-7] In many cases surfactants, above their critical micelle concentration, have also been obtained with some additional power of catalysing reaction rates.[8-15]

In this paper also the 'like dissolves like' mechanism and surface phenomena of micellar media of reducing interfacial tension [4] has been exploited to solubilize octanal, an eight carbon saturated fatty aldehyde, in aqueous medium which is an eco-friendly and easily available solvent. Not only that, but also an considerable catalysing power of the surfactants has been come across in our experiment of oxidising octanal by hexavalent chromium Cr(VI) and a detailed kinetics of the octanal oxidation has been studied spectrophotometrically under pseudo^{1st} order condition at 25°C ($\pm 0.1^\circ\text{C}$). It is truly a great achievement that such a long chain aldehyde has been oxidised to octanoic acid in aqueous medium though oxidation of another fatty aldehyde, comparatively of short chain, has been reported previously [16]. Octanoic acid, also popularly known as caprylic acid, is commercially used in the production of esters which is used in the preparation of perfumes and dyes. In addition, it has plenty uses as antimicrobial pesticide in food, dairy, breweries, wineries, beverage processing plants and also as disinfectant, algaecide, bactericide, fungicide, and herbicide in nurseries, greenhouses. For epilepsy, tremors, renal failure, digestive disorders also octanoic acid is taken by mouth. [17-21] Therefore,

preparation of octanoic acid is very important for its so many unavoidable usages. In our experiment, we have also used some organic hetero-aromatic bases in the micellar media to reinforce the catalysing power of the surfactants. The organic hetero-aromatic bases i.e. 1, 10 – phenanthroline (Phen), 2-picolonic acid (PA), 2, 2' – bipyridine (Bpy) should better be termed as 'promoter' due to the formation of Cr(III)-Phen, Cr(III)-PA and Cr(III)-Bpy after the oxidation reaction is over which is discussed in detail latter. [9-10] At the end of the introductory part it is essential to mention that using Cr(VI) as an oxidising agent in our experiment no green principle is violated because after the reaction is over the toxic Cr(VI) is reduced entirely to non-toxic Cr(III) which is also useful in dietary supplements. [22] There is also no chance of staying Cr(VI) unreduced in the reaction medium as the fatty aldehyde, octanal, is taken 15 times higher than the concentration of Cr(VI) which is mentioned latter.

2. Experimental

2.1. Materials and reagents

Octanal (99.0 %, AR, SRL, India), $K_2Cr_2O_7$ (99.9 %, AR, BDH, India), H_2SO_4 (98%, AR, Merck, India), sodium dodecylsulfate (SDS) (> 90.0 %, AR, Merck, India), N-cetylpyridinium chloride (CPC) (98.0 %, AR, SRL, India), Triton X-100 (98.0 %, AR, HIMEDIA, India), 1, 10 – phenanthroline (99.5 % AR, Merck, India), 2, 2' – bipyridine(99.0 %, AR, Spectrochem, India), Pyridine-2-carboxylic acid (99.0 %, AR, Sigma Aldrich, UK), deuterium oxide (D_2O) (99.9 %, AR, Sigma-Aldrich, USA), chloroform-d ($CDCl_3$) (99.8%, AR, Sigma-Aldrich, USA). In preparation of all requisite solutions double distilled water has been used. All the chemicals were used as received without further purification.

2.2. Procedures and kinetic measurements

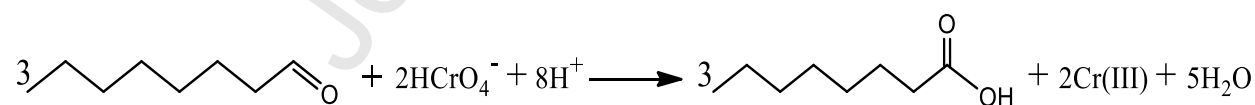
The process of this experiment is mainly based upon spectrophotometric analysis where a double beam UV-visible spectrophotometer [UV-vis 1600 (SHIMADZU)] has been used which is attached with a temperature controller. In preparation of homogeneous aqueous solution of fatty aldehyde, octanal, measured volume of octanal has been taken in three different micellar media (SDS, CPC and TX-100) of different concentrations separately and then the solutions are acidified with concentrated H_2SO_4 to keep its acidity 0.3 (M), i.e. $pH < 1$. It is very necessary to mention here that in every reaction Cr(VI) and octanal has been taken 2.5×10^{-4} (M) and 3.75×10^{-3} (M) respectively ([Octanal] = 15 [Cr(VI)]) to keep the whole process go on under pseudo 1st order reaction condition at a temperature $25^\circ C (\pm 0.1^\circ C)$. Then for kinetic measurements the decreasing absorption intensities of reaction solutions have been recorded at $\lambda_{max} = 438nm$ at a regular time interval starting from the moment of addition of Cr(VI) solution (aqueous solution of $K_2Cr_2O_7$) to the homogeneous solution of octanal. Some experiments have also been

performed using three promoters 1, 10 – phenanthroline (Phen), 2-picolonic acid (PA) and 2, 2' – bipyridine (Bpy) at a concentration range of 10^{-3} to 10^{-4} (M). Sartorius BSA 224S-CW balance and Digital Ultrasonic Cleaner CD 4820 Sonicator have been used for the preparation of reaction solutions. DLS study has been done using Horiba nano partica SZ-100 instrument. Various ^1H -NMR has been recorded by Bruker Ascend 400 MHz spectrometer. For detail study of kinetics the activation parameters have also been calculated and reported below at three different temperatures 25°C , 35°C and 40°C .

2.3. Product analysis and stoichiometry

After recording the absorption intensities of reaction solution till the pale yellow colour goes off, it has been stored in a safe place for 3 days to assure complete reduction of Cr(VI) by octanal with the appearance of faint colour solution caused by Cr(III). The bluish solution on solvent extraction (using diethyl ether) followed by fractional distillation gives two organic liquids of boiling points 171°C (literature value 170°C corresponds to octanal) and 238°C (literature value 239°C corresponds to octanoic acid) [23-24]. The ^1H -NMR spectroscopy of this high boiling liquid proves the product of the oxidation reaction to be octanoic acid. (Fig. S1a, S1b)

UV-Visible spectra of the bluish coloured solution in three different micellar media show λ_{max} at 581nm which confirms Cr(III) to be produced in the reactions. [25] For the determination of stoichiometry of the reaction a Cr(VI) solution of known concentration has been reacted with various concentrations of octanal in micellar media of fixed concentration and at a constant H^+ concentration of 0.3(M). The recorded absorbances of the solutions after 4 days gives the following stoichiometry of the reaction.

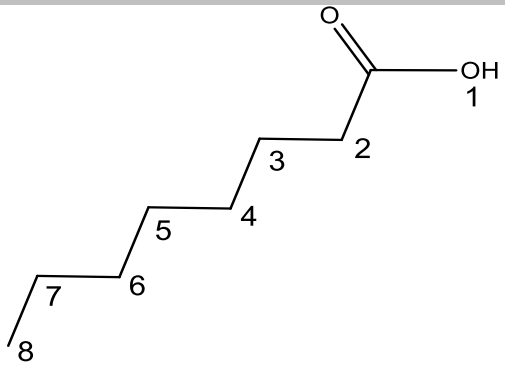


^1H -NMR spectral analysis

To record the ^1H -NMR spectrum of the product TMS has been taken as reference and CDCl_3 solution of the product has been prepared. The recorded ^1H -NMR spectrum at 400 MHz shows a peak at 11.837 ppm corresponding to carboxylic acid and other chemical shift values have also been produced here in support of the product. (Fig. S1a, S1b) (Table 1)

Table 1 Chemical shift values for different protons of Octanoic acid.

Octanoic acid	Atom	Chemical shift (δ ppm)
---------------	------	--------------------------------

	1	11.837 (1H, s)
	2	2.34 (2H, t)
	3	1.633 (2H, m)
	4 - 7	1.311-1.299 (8H, m)
	8	0.884 (3H, t)

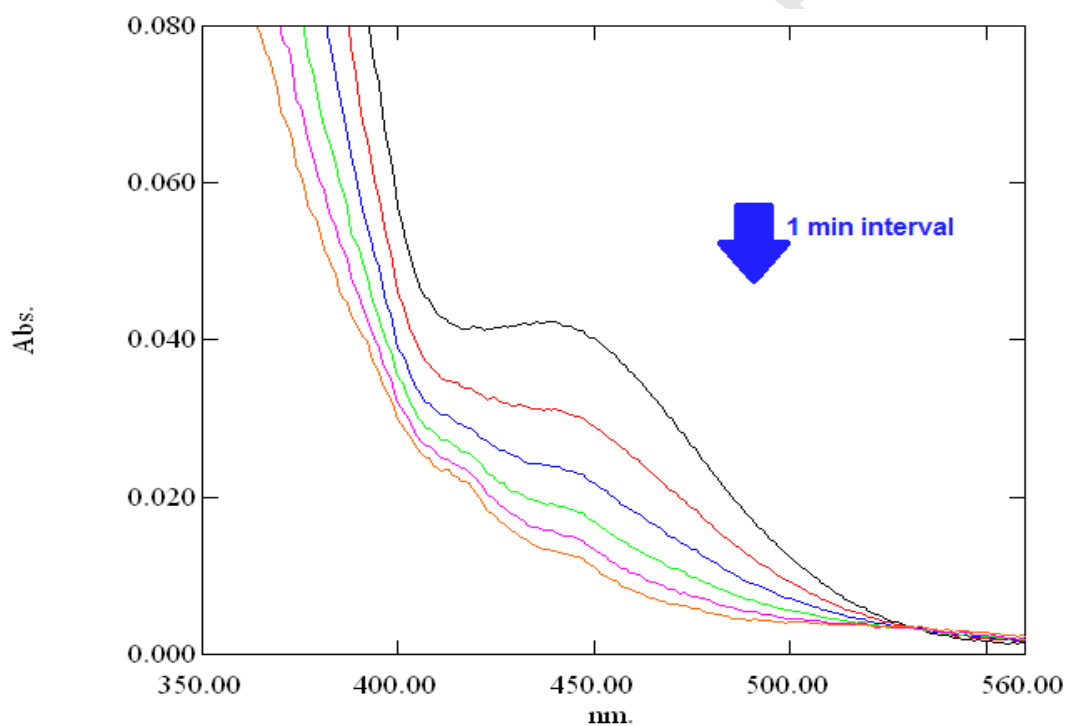


Fig. 1 Scanned absorption spectra of the reaction at regular time interval: $[\text{Octanal}]_{\text{T}} = 3.75 \times 10^{-3}$ (M), $[\text{Cr(VI)}]_{\text{T}} = 2.5 \times 10^{-4}$ (M), $[\text{H}_2\text{SO}_4]_{\text{T}} = 0.3$ (M), $[\text{SDS}]_{\text{T}} = 0.03$ (M), $[\text{Bpy}]_{\text{T}} = 1 \times 10^{-3}$ (M) Temperature = 25°C.

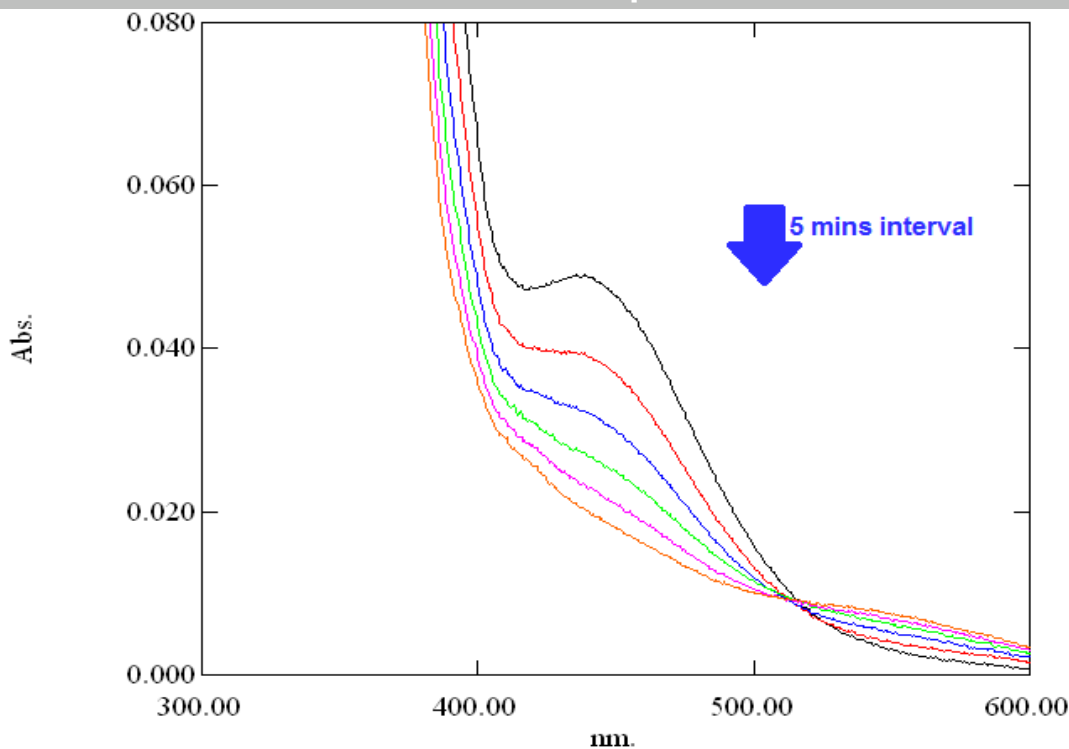


Fig. 2 Scanned absorption spectra of the reaction at regular time interval: $[\text{Octanal}]_T = 3.75 \times 10^{-3}$ (M), $[\text{Cr(VI)}]_T = 2.5 \times 10^{-4}$ (M), $[\text{H}_2\text{SO}_4]_T = 0.3$ (M), $[\text{TX-100}]_T = 0.02$ (M), $[\text{Phen}]_T = 5 \times 10^{-3}$ (M) Temperature = 25°C .

2.4. Separation of surfactants

Though surfactants help to solubilize organic substances in aqueous medium, they have own toxic effects to environment. [26-28] So, to drain out the surfactants in our experiments some steps have been taken chemically and thermally. When the reaction is over SDS has been precipitated as $\text{Ca}(\text{DS})_2$ by using CaCl_2 , CPC has been eliminated using KBr and TX-100 has been precipitated thermally and the precipitates were filtered off therefrom.[29]

3. Results and discussion

3.1. UV-Vis spectral analysis

The kinetics have been studied spectrophotometrically and absorption intensities of the reaction solutions have been used to calculate the pseudo 1st order rate constants (k_{obs}). Actually, the progress of reactions in micellar media shows a decrease in absorbances at $\lambda_{\text{max}} = 438\text{nm}$ at a regular time interval (Fig. 1, 2, S2a, S2b, S3a, S3b) and using this absorbances graphs of $-\ln(A_{438})$ with respect to **time(minute)** have been plotted in form of straight lines from which we get easily the slope of the straight lines i.e. k_{obs} . (Fig. 3) Then using the equation $t_{1/2} = 0.693/k_{\text{obs}}$ half-lives ($t_{1/2}$) of reactions have been calculated. All the experimentally obtained k_{obs} and $t_{1/2}$

have been mentioned below in a tabular form in details (Table 2). From the table, it can easily be seen that in presence of the promoters the reaction rates have geared up considerably. Some additional changes in the nature of spectrum in presence of those promoters seem to be caused by the formation of Cr(III)-promoter complex. Some significant UV-vis spectra have been produced having one isosbestic point each of them (Fig. 1, 2, S2a, S2b, S3a, S3b) which reveal that in the completion of this whole reaction, chromium seems not to be present in any intermediate oxidation states e.g. Cr(V) and Cr(IV). [30]

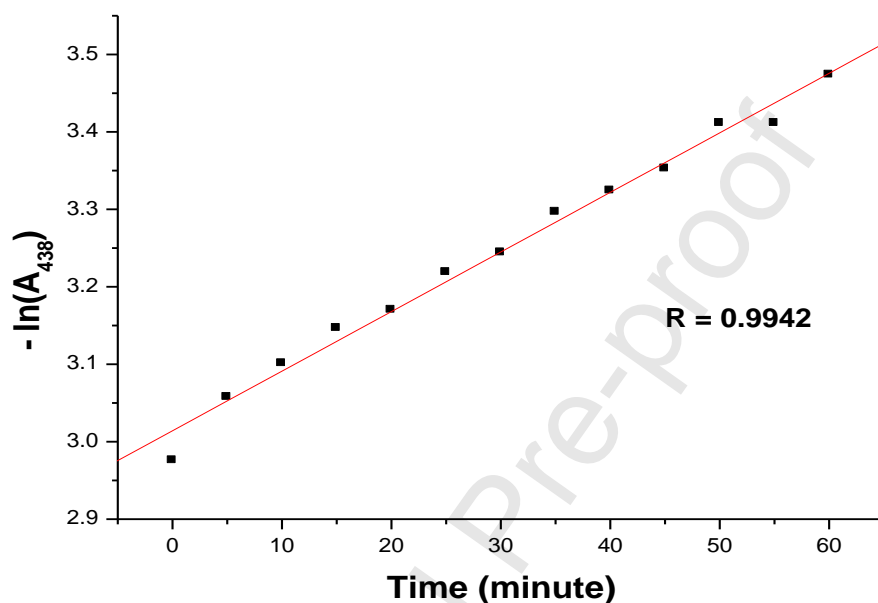


Fig. 3 Representative plot for SDS promoted oxidation path at 25°C for calculation of pseudo first order rate constant: A_{438} is the absorbance at 438 nm. $[\text{Octanal}]_T = 3.75 \times 10^{-3}(\text{M})$, $[\text{Cr(VI)}]_T = 2.5 \times 10^{-4}(\text{M})$, $[\text{SDS}]_T = 0.03(\text{M})$, $[\text{H}_2\text{SO}_4]_T = 0.3(\text{M})$, Temperature = 25°C.

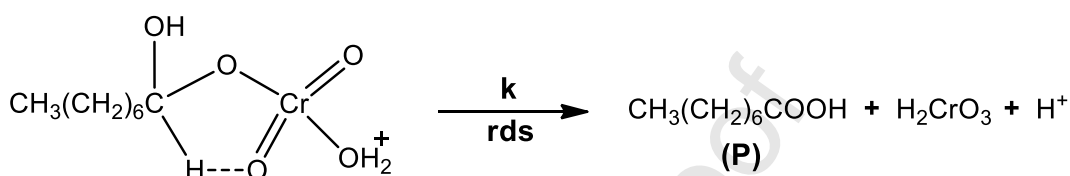
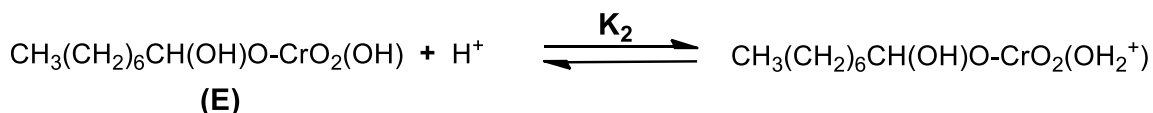
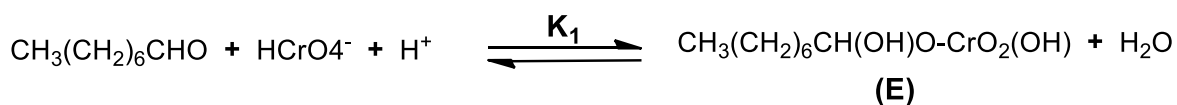
3.2. Mechanism of the reaction

In the present study reactions have been carried out in two different ways. Firstly, in unpromoted micellar media and secondly, in promoted micellar media. Both the cases have been explained in depth separately in this section.

3.2.1. Unpromoted micellar oxidation

In this experiment three different types of surfactants, i.e. cationic, anionic and neutral, have been used above their CMC which can solubilize very small amount hydrophobic octanal. CPC and TX-100 have been found to be more solubilizing in this experiment than SDS, may be due to having more hydrophobic parts in CPC and TX-100 than that of SDS. Oxidation of octanal in micellar media has been seen very much successful with some additional observations of catalysing power of SDS and TX-100. With increase in concentrations of SDS and TX-100, the

rate of present oxidation reaction increases gradually. Though in presence of CPC the oxidation rate is greater than that of SDS and TX-100, on increasing CPC concentration reaction rate decreases. (Table 2) (Fig. 4) A possible reason of these observations has been proposed mechanistically. (Scheme 1)



Scheme 1. Mechanistic pathway of oxidation of octanal by Cr(VI).

On dissolving potassium dichromate in acidic aqueous medium an anionic chromium species HCrO_4^- is generated though it gets protonated in acidic micellar media favouring the binding of H_2CrO_4 on the micellar surface at stern layer by hydrogen bonding and ion-dipole interaction. [29] Actually, an interaction does exist between the Cr(VI) species and micelles which is supported by the absorbance spectrum shown below displaying red shifted λ_{max} in case of mixtures of Cr(VI) and surfactants. (Fig. S4) The HCrO_4^- in acidic medium plays a vital role producing a neutral chromate ester (E) in reaction with octanal. The chromate ester (E) is the main intermediate of this oxidation reaction leading to the product (P) by acid catalysed decomposition.

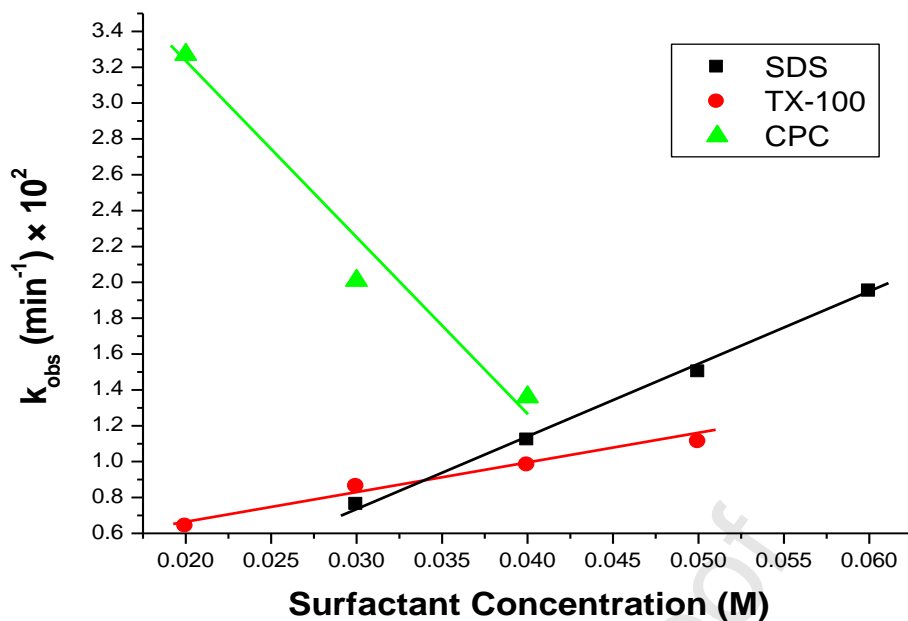


Fig. 4 Dependence of k_{obs} on $[micellar\ catalyst]_T$ for Cr(VI) oxidation of octanal (in absence of promoter) in aqueous H_2SO_4 media at $25^\circ C$. $[Octanal]_T = 3.75 \times 10^{-3}(M)$, $[Cr(VI)]_T = 2.5 \times 10^{-4}(M)$, $[H_2SO_4]_T = 0.3(M)$.

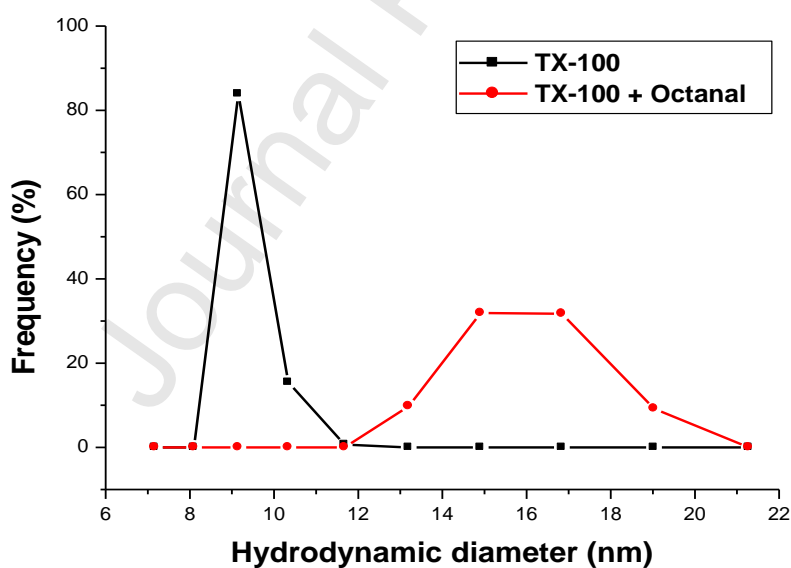


Fig. 5 Dynamic Light Scattering (DLS) study of micellar aggregates. The average hydrodynamic diameter for TX-100 is 9.2 nm and octanal incorporated TX-100 is 15.9 nm. $[Cr(VI)]_T = 2.5 \times 10^{-4}(M)$, $[TX-100]_T = 0.02(M)$ and $[Octanal]_T = 3.75 \times 10^{-3}(M)$.

Surfactants form a molecular aggregation, above their CMC, named micelle [4] in which Cr(VI) resides at the stern layer [9] and the hydrophobic substrate molecule resides in the core which has been proved by DLS experiment. DLS study of TX-100 and mixture of TX-100

with octanal shows that there is an increase in hydrodynamic radius of TX-100 (9.2 nm) in presence of octanal (15.9 nm) (Fig. 5) and this fact proves the octanal to be placed in the core of the micelles. So, up to formation of the chromate ester (**E**) in every micellar medium the oxidation rate seems not to be altering but the next step, acid catalysed decomposition of the said chromate ester, is anticipated to be the reason of this rate alteration. In fact, the charge of the peripheral surface of the micelles formed by respective surfactants is the main factor here. In case of SDS the anionic hydrophilic part, projecting outward at the surface of the micelle, facilitates the approach of positively charged H^+ toward the chromate ester (**E**) at the core of the micelle and favours the rds (rate determining step) enhancing **k**. Similarly, CPC being cationic surfactant forms positively charged micellar surface which inhibits the approach of H^+ to **E** lowering **k** value. So, a neutral surfactant TX-100 having no such coulombic interactions with the H^+ ion shows a rate variation consistently. (Fig. 6) After the disappearance of pale yellow colour of each micellar catalysed reaction solution the completion curves shows peaks at 581nm and 409 nm corresponding to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions respectively. (Fig. S5) [30]

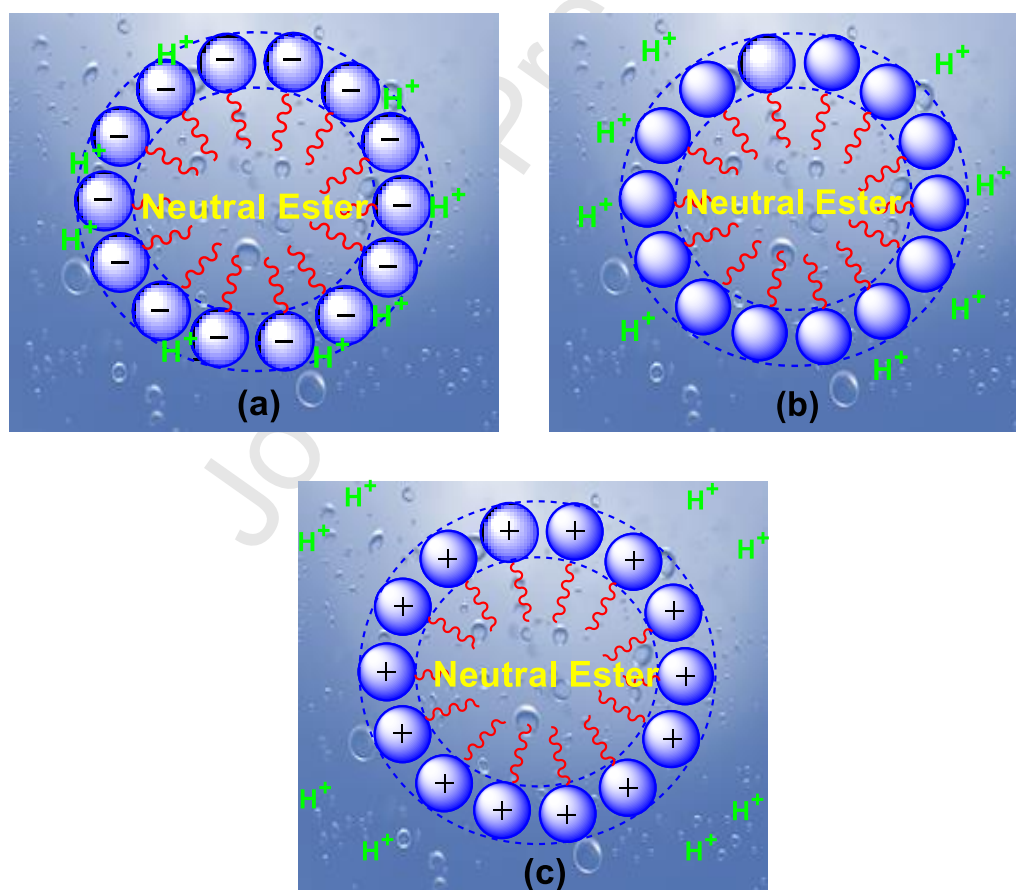


Fig. 6 Schematic representation of unpromoted micellar reactions. (a) SDS catalysed; (b) TX-100 catalysed; (c) CPC uncatalysed.

3.2.2. Promoted micellar oxidation

In the promoted path each of the hetero-aromatic bases shows additional enhancement of oxidation rate in SDS and TX-100 micellar media to a great extent. Among the three promoters 2, 2'- bipyridine has been found to be the strongest in SDS micellar medium and with increase in concentration of the promoters in the SDS and TX-100 micellar media the rates also increase consistently. (Table 2, 1S)

Table 2 k_{obs} and half-life ($t_{1/2}$) of the reaction in presence of micellar catalyts and promoters (Temperature = 25°C).

Micellar catalyst (M)		Promoters (M) $\times 10^3$		$k_{\text{obs}} (\text{min}^{-1}) \times 10^2$	Half-life [$t_{1/2}$](mins)
SDS	0.03	None		0.76	90.12
	0.04			1.12	61.87
	0.05			1.50	46.20
	0.06			1.95	35.60
TX-100	0.02	None		0.64	108.28
	0.03			0.86	80.58
	0.04			0.98	70.71
	0.05			1.11	62.43
CPC	0.02	None		3.27	21.16
	0.03			2.01	34.35
	0.04			1.36	50.96
SDS	0.03	Phen	1.25	0.90	77.00
			2.50	1.59	43.31
			3.75	2.19	31.64
			5.00	2.99	23.12
		PA	1.25	1.52	45.59
			2.50	3.11	22.29

			3.75	4.43	15.60
			5.00	5.34	12.98
		Bpy	0.25	3.55	19.52
			0.50	12.22	5.67
			0.75	21.67	3.19
			1.00	34.66	1.99
TX-100	0.02	Phen	1.25	1.72	40.29
			2.50	2.42	28.64
			3.75	3.40	20.38
			5.00	4.00	17.31
		PA	1.25	1.35	51.33
			2.50	1.50	46.20
			3.75	1.65	42.00
			5.00	1.77	39.15
		Bpy	1.25	1.23	56.34
			2.50	2.06	33.64
			3.75	3.04	22.79
			5.00	3.56	19.44
CPC	0.03	Phen	1.25	2.17	31.94
			2.50	2.64	26.25
			3.75	3.50	19.80
			5.00	4.31	16.07
		PA	1.25	3.89	17.81
			2.50	4.71	14.71

			3.75	5.77	12.01
			5.00	6.89	10.05
		Bpy	1.25	2.81	24.66
			2.50	3.46	20.02
			3.75	4.50	15.40
			5.00	5.70	12.16

In promoted micellar oxidation, the mechanism is proposed to be quite different with the formation of Cr(III)-promoter complexes by the hetero aromatic bases, as said before. Some different species (OX^+) plays the role of oxidant in place of HCrO_4^- . On addition of promoters (Phen, Bpy and PA) initially in the acidic reaction solution the Cr(VI) gets captured to form the oxidant species OX^+ which then oxidise the octanal to its corresponding product. (Scheme 1, 2 and 3) Interaction between Cr(VI) and those promoters has been confirmed by comparing the UV-Vis spectra of only Cr(VI) solution (aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$) with the mixtures of Cr(VI) and promoters. In the spectra Cr(VI) shows peaks near 440 nm and 350 nm whereas, in most cases of [Cr(VI) + promoters] absence of the peak at 350 nm is very common. (Fig. 7) In addition, NMR study and fluorometric measurements also proved previously the same interference of complex formation between Cr(VI) and promoters. [9]

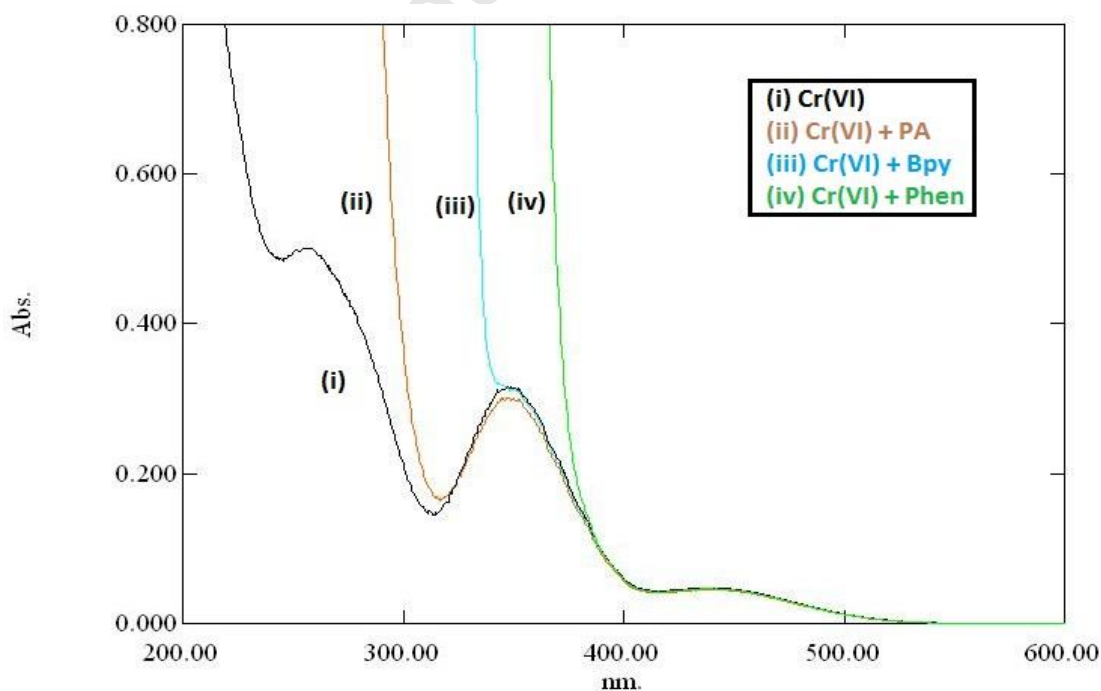


Fig. 7 Absorption spectrum of $[\text{Cr(VI)}]_{\text{T}} = 2.5 \times 10^{-4}(\text{M})$, $[\text{H}_2\text{SO}_4] = 0.3(\text{M})$, $[\text{PA}]_{\text{T}} = 0.025(\text{M})$, $[\text{Bpy}]_{\text{T}} = 0.025(\text{M})$; $[\text{Phen}]_{\text{T}} = 0.025(\text{M})$, Temperature = 25°C .

The promoted micellar reaction rates are controlled firstly, by the coulombic interaction between oxidant species (OX^+) with surface charge of the micelles and secondly, by the pi electron densities of the promoters. The oxidant species of both Phen and Bpy being di-positive can approach the anionic micellar surface of SDS more easily than the mono-positive oxidant species of PA. (Fig. S12a) So, $k_{\text{obs}}(\text{Bpy})$ is expected to be quite equal to $k_{\text{obs}}(\text{Phen})$ and $k_{\text{obs}}(\text{PA})$ is expected to be the lowest. SDS has no pi electrons so there is no question of pi-pi interaction with promoters but the coulombic repulsive interaction of pi electrons of those promoters with the anionic surface of the SDS micelle can never be ignored. PA in its oxidant species (OX^+) having least pi electron density among the other oxidant species undergoes less repulsive interaction to approach the substrate (octanal) in the core of the micelle whereas, Phen has the highest pi electron density and Bpy has the second highest pi electron density. So, on the basis of this pi electron repulsion with anionic micellar surface of SDS the rate order should be $k_{\text{obs}}(\text{PA}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen})$. But, due to the concomitant effect of present and previous reason the reaction rate order becomes $k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA}) > k_{\text{obs}}(\text{Phen})$ which fully supports our results. (Fig. 8) A very relevant and essential point is to be noticed here that Bpy is far better a promoter only in its 10 times lower concentration and the reaction just gets completed in a twinkling of an eye at slightly more concentration. (Table 2, 1S) In case of neutral TX-100 micellar surface there is no chance of coulombic interaction with oxidant species (OX^+) as before (like SDS) (Fig. S12b) but pi-pi interaction between the promoters in oxidant species and aromatic ring in neutral surfactant molecule controls the reaction rates making the rate order $k_{\text{obs}}(\text{Phen}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{PA})$. In case of CPC, due to bi-positive charge the oxidant species (OX^+) in Bpy experiences more coulombic repulsion than that of PA with mono-positive charge. So, PA is expected a better promoter than Bpy and the oxidant species of Phen also having di-positive charge and being bulkier than other two promoters experiences more steric hindrance making the rate order $k_{\text{obs}}(\text{PA}) > k_{\text{obs}}(\text{Bpy}) > k_{\text{obs}}(\text{Phen})$. (Fig. S12c, 8)

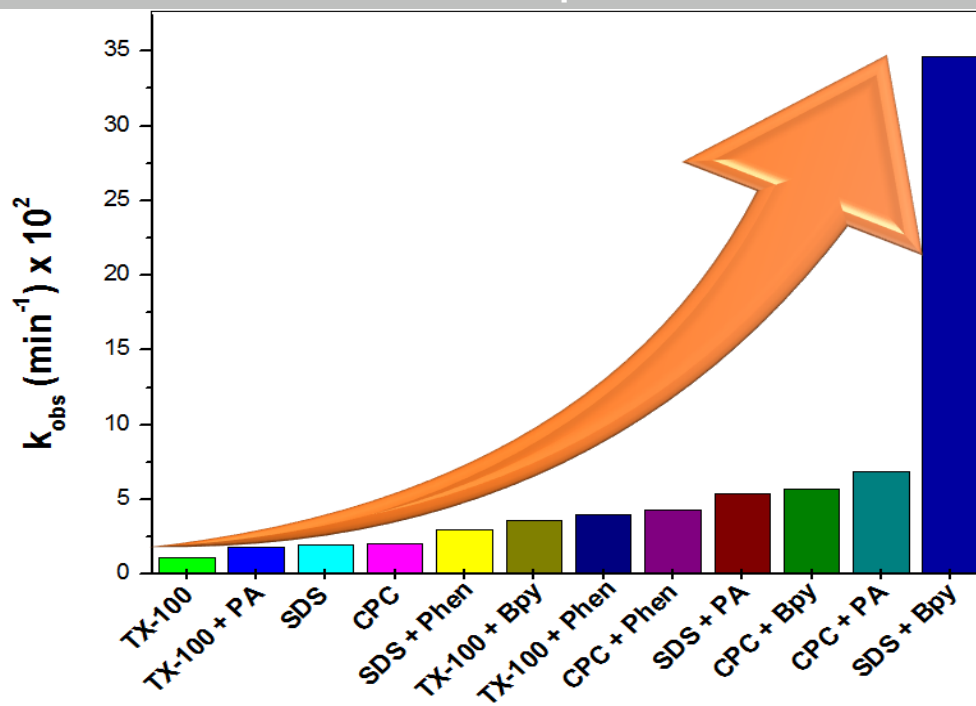
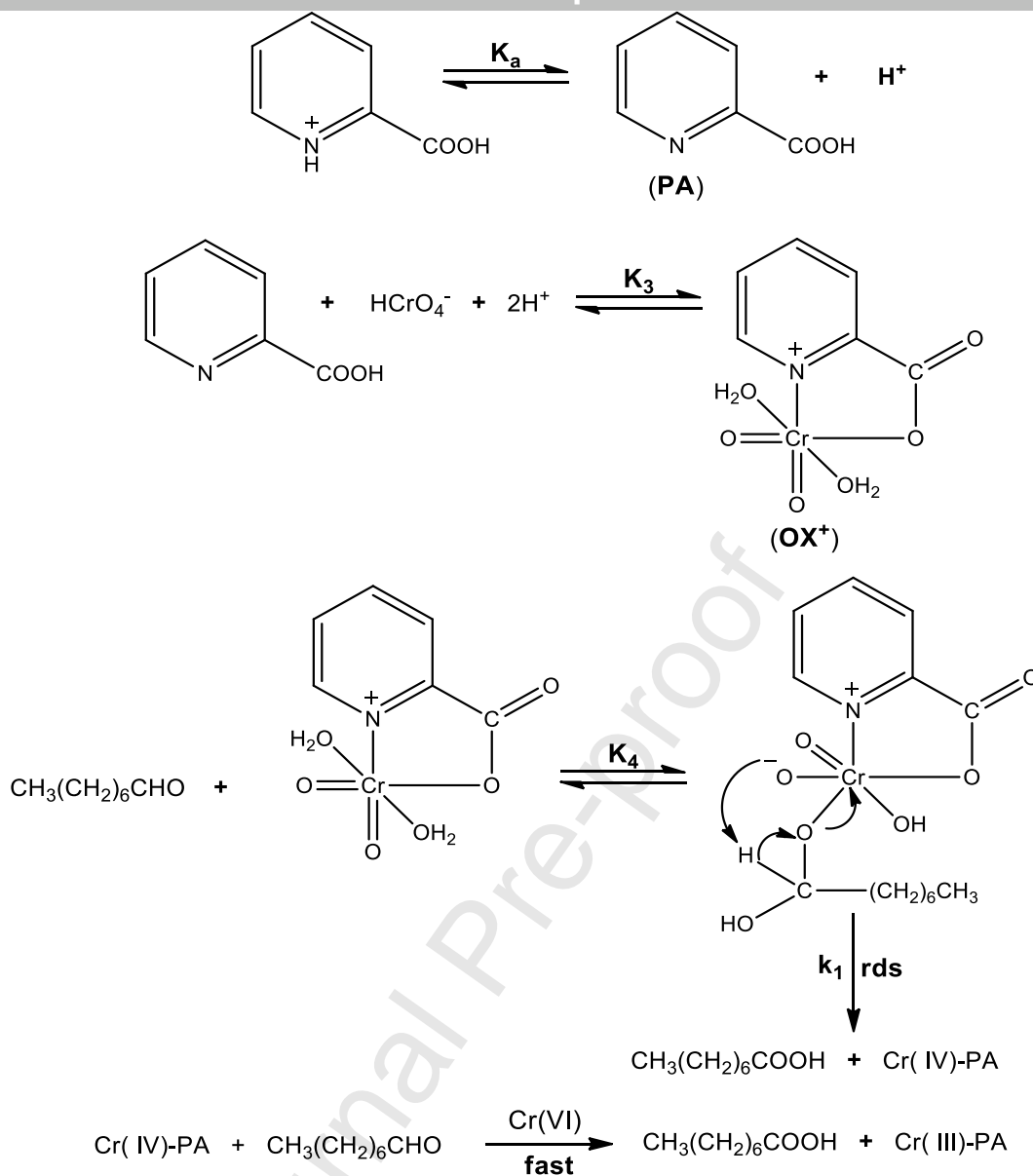


Fig. 8 Representative bar diagram of k_{obs} with maximum concentration of surfactants and promoters. $[\text{Octanal}]_{\text{T}} = 3.75 \times 10^{-3}(\text{M})$, $[\text{Cr(VI)}]_{\text{T}} = 2.5 \times 10^{-4}(\text{M})$, $[\text{H}_2\text{SO}_4] = 0.3(\text{M})$, Temperature = 25°C .



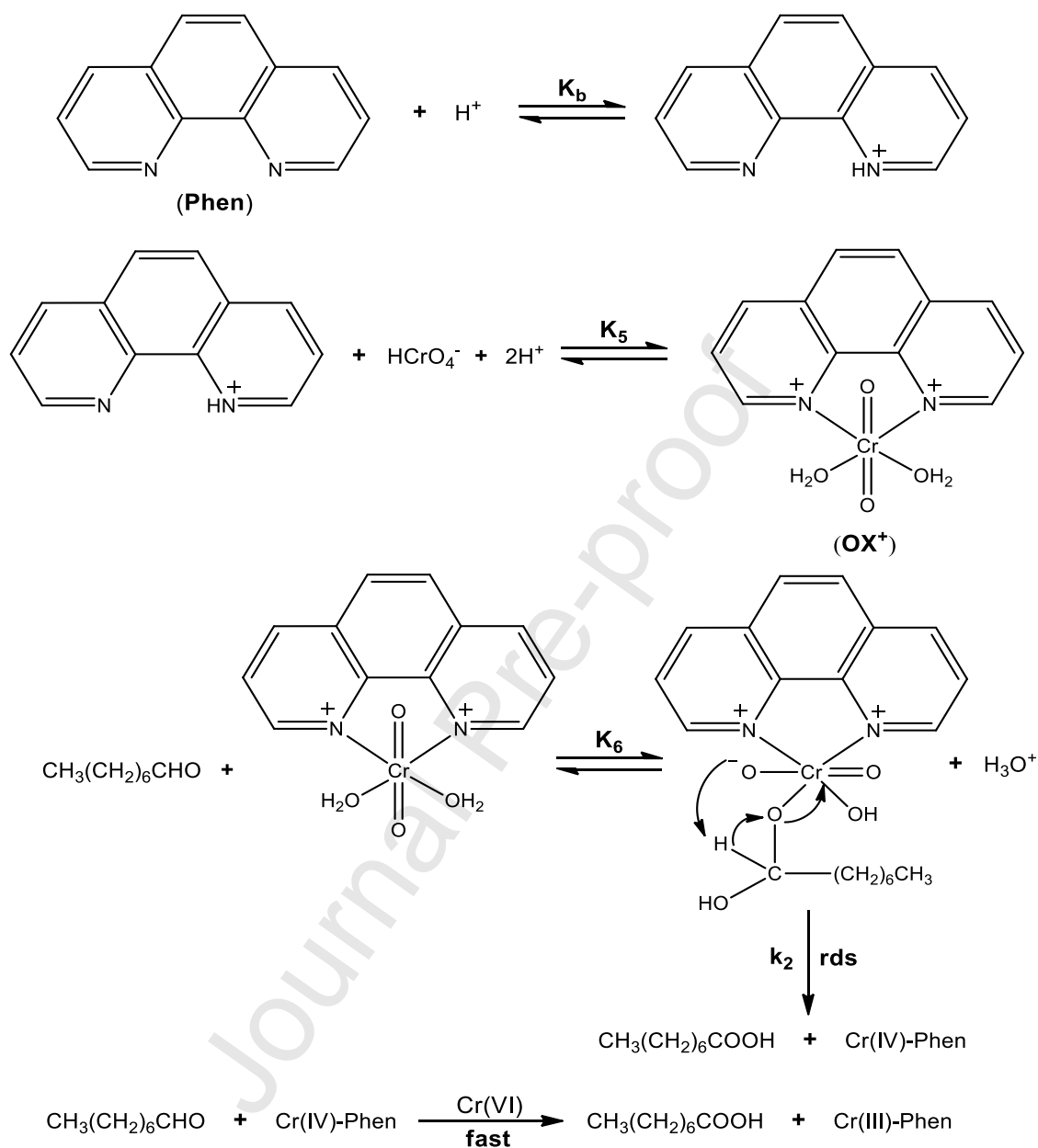
Scheme 2. Mechanistic pathway of oxidation of octanal by Cr(VI) in presence of PA promoter.

3.3. Interaction between octanal and surfactants

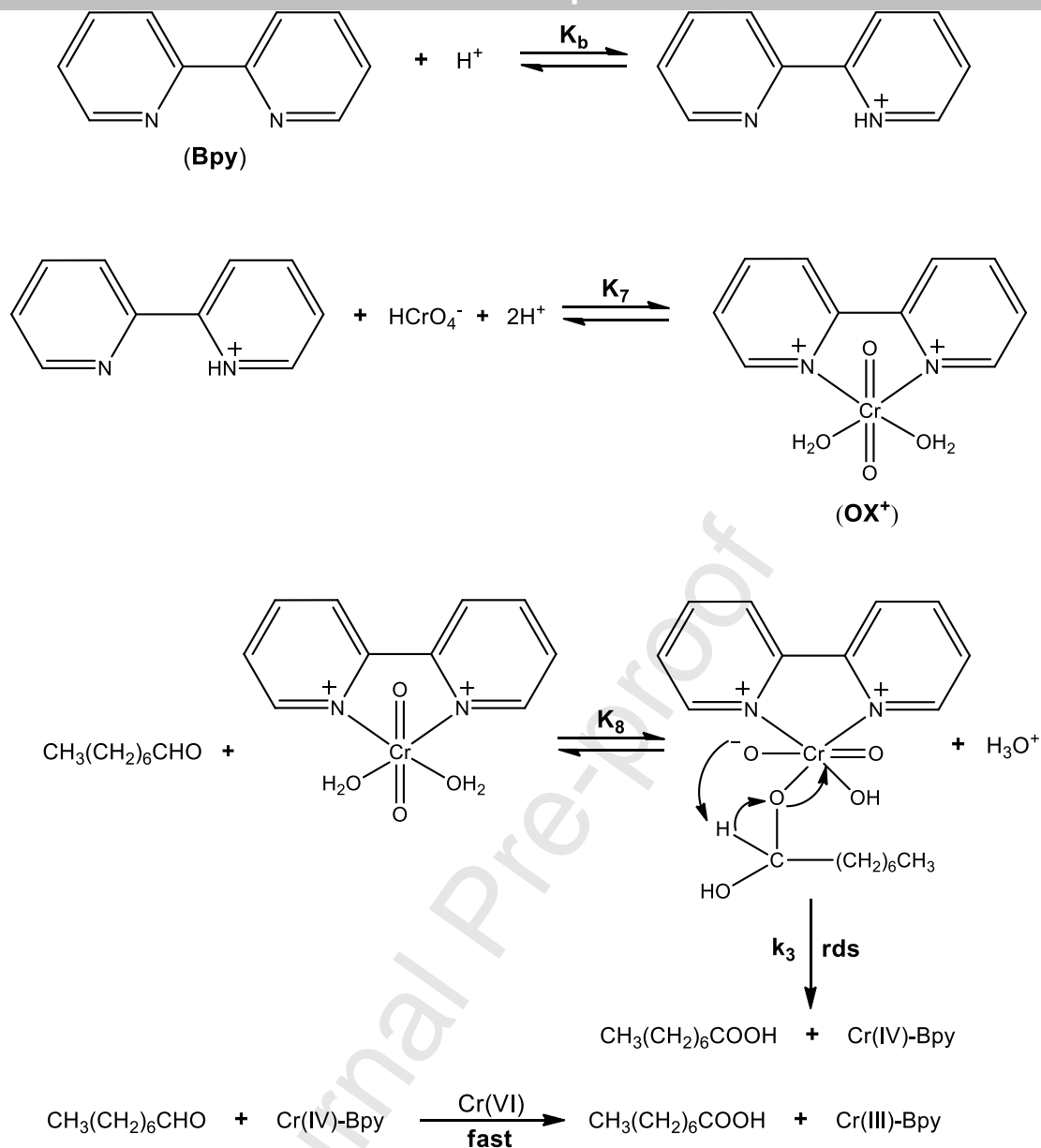
In the present experiment surfactants have a great role as a solubilising agent and catalyst in the oxidation of the fatty aldehyde (octanal) in aqueous medium. There are interactions among the surfactants and the substrate molecules, octanal. The fatty aldehyde has been predicted to be resided at the core of micelles formed by those surfactants and in support of the said interactions among the chemical species $^1\text{H-NMR}$ spectra of the individual surfactants and mixture of surfactants with octanal have been recorded (Fig. S6, S7, S8, S9, S10 and S11) and the chemical shift values (δ) have been produced here in tabular form. (Table 3, 4 and 5)

From the table it can be very clearly seen that in each and every cases there is a prominent up-field shift in δ (ppm) values. That means on mixing surfactants to the substrate molecule there must arise some induced type interactions among the hydrophobic tails of

surfactants (SDS, TX-100 and CPC) and $-\text{CHO}$ group in addition to the long chain hydrocarbon of octanal molecules which increase the electron densities around the protons of the hydrophobic tails showing up-field chemical shift (δ) in every cases.

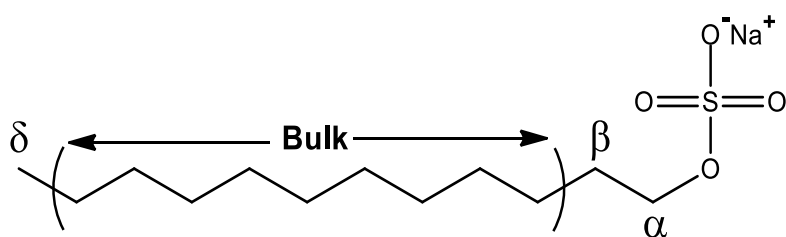


Scheme 3. Mechanistic pathway of oxidation of octanal by Cr(VI) in presence of Phen promoter.

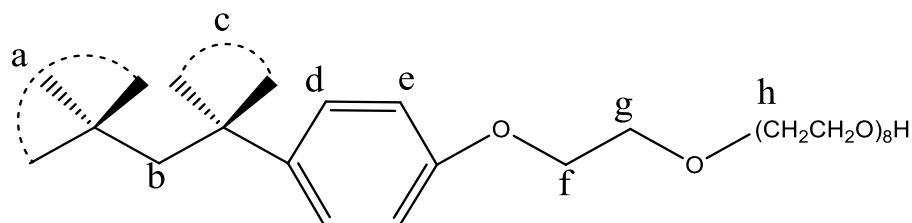


Scheme 4. Mechanistic pathway of oxidation of octanal by Cr(VI) in presence of Bpy promoter.

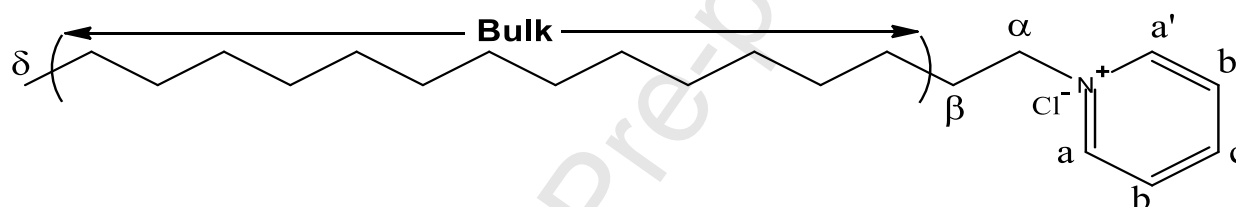
Table 3 Chemical shift (ppm) values of head group protons of SDS from $^1\text{H-NMR}$ spectrum.



	H_α	H_β	Bulk H's	H_δ
SDS	3.982	1.634	1.25	0.85
SDS + Octanal	3.861	1.486	1.149	0.739

Table 4 Chemical shift (ppm) values of head group protons of TX 100 from $^1\text{H-NMR}$ spectrum.

	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h
TX-100	0.711	1.66	1.287	7.189	6.821	4.031	3.746	3.638-3.719
TX-100 + Octanal	0.267	1.219	0.832	6.763	6.386	3.59	3.358	Up-field

Table 5 Chemical shift (ppm) values of head group protons of CPC from $^1\text{H-NMR}$ spectrum.

	H_α	H_β	$\text{H}_{a,a'}$	$\text{H}_{b,b'}$	H_c	Bulk H's	H_δ
CPC	4.699	1.98	8.976	8.114	8.585	1.10-1.29	0.703
CPC + Octanal	4.355	1.655	8.642	7.792	8.262	0.82-0.98	0.423

3.4. Calculation of activation parameters

Study of thermodynamic properties, basically enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger), is essential in kinetics measurement of any reaction. Here, in this experiment also ΔH^\ddagger and ΔS^\ddagger values have been calculated by (Table 6) determining \mathbf{k}_{obs} (\mathbf{k} in Eq. 1) of requisite reactions at three different temperatures (25°C, 35°C and 40°C) (Table 1, 2S) and using Eyring equation (Eq. 1). Actually, $-\ln(\mathbf{k}\mathbf{h}/\mathbf{k}_B\mathbf{T})$ vs $1/\mathbf{T}$ graphs have been plotted for each of the reactions which give straight line and from the slope we get ΔH^\ddagger and from the intercept we get ΔS^\ddagger . (Fig. 9) In this experiment, all the promoted micellar reactions show greater ΔH^\ddagger than that of the non-promoted micellar reactions which signifies the lower energy of the transition states in case of promoted reactions and therefore fast reactions. The combination of SDS and Bpy gives the lowest ΔH^\ddagger value because it has the highest reaction rate. The combinations showing

greater - ΔS^\ddagger values correspond to the more ordered transition states in comparison to the ground states of the reaction.

$$\ln(kh/k_B T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad \dots(\text{Eq. 1})$$

1)

(Where, k = observed rate constant, h = Planck's constant, k_B = Boltzmann constant, T = absolute temperature, R = universal gas constant)

Table 6 Representation of activation parameters.

Micellar catalyst (M)		Promoters (M) $\times 10^3$		ΔH^\ddagger (kJmol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
SDS	0.03	None		50.38	116.79
TX-100	0.02	None		59.00	89.21
CPC	0.02	None		32.76	163.68
SDS	0.03	Phen	2.5	38.59	144.53
		PA	2.5	26.93	183.49
		Bpy	0.25	22.38	191.38
TX-100	0.02	Phen	2.5	31.14	171.43
		PA	2.5	40.58	143.74
		Bpy	2.5	35.92	156.80
CPC	0.02	Phen	2.5	30.46	169.34
		PA	2.5	19.29	201.86
		Bpy	2.5	23.51	190.56

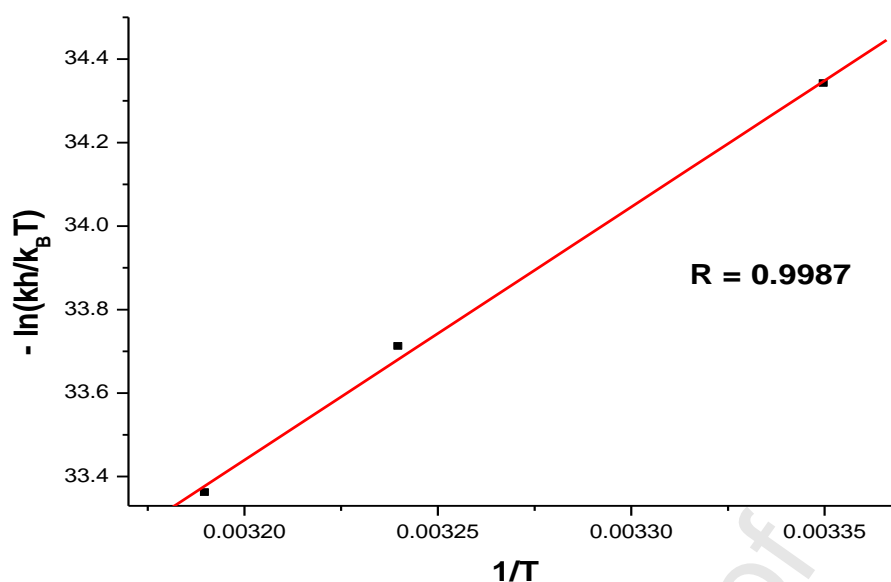


Fig. 9 Representative plot for evaluation of activation parameters. $[\text{Octanal}]_T = 3.75 \times 10^{-3}(\text{M})$, $[\text{Cr(VI)}]_T = 2.5 \times 10^{-4}(\text{M})$, $[\text{H}_2\text{SO}_4] = 0.3(\text{M})$, $[\text{SDS}]_T = 0.03(\text{M})$, temperature 25°C , 35°C , 40°C .

4. Conclusion

After the elongated discussion on the kinetics of our said reaction, there are no other alternatives other than saying that it is really a novel achievement of oxidising a fatty aldehyde with Cr(VI) in an aqueous medium with the help of amphiphilic property of surfactants and at the very moment catalysing the same reaction with the same amphiphilic species. The surface phenomena of those amphiphilic surfactants have truly a lot of contribution in attaining this novelty in this reaction. Many aromatic and aliphatic aldehydes were oxidised previously using higher valent metal oxidants in micellar medium but, no one is as exemplary as this one. [16, 32-35] It is also very factual that Bpy, among the used promoters, has shown the best performance in combination with SDS, the anionic surfactant, in our attempt. So, it will help researchers go ahead in the field of micellar catalysis and they can show the dare to untie the bunch of research works on fatty molecules in a hygienic way.

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Author Statement

The highlights of the manuscript (MOLLIQ_2020_1096_R1) have been amended with necessary corrections mentioning core findings of this experiment briefly according to the comment of the respected editor and reviewer. It is seemed that this manuscript needs no further revision to be published in The Journal of Molecular Liquids.

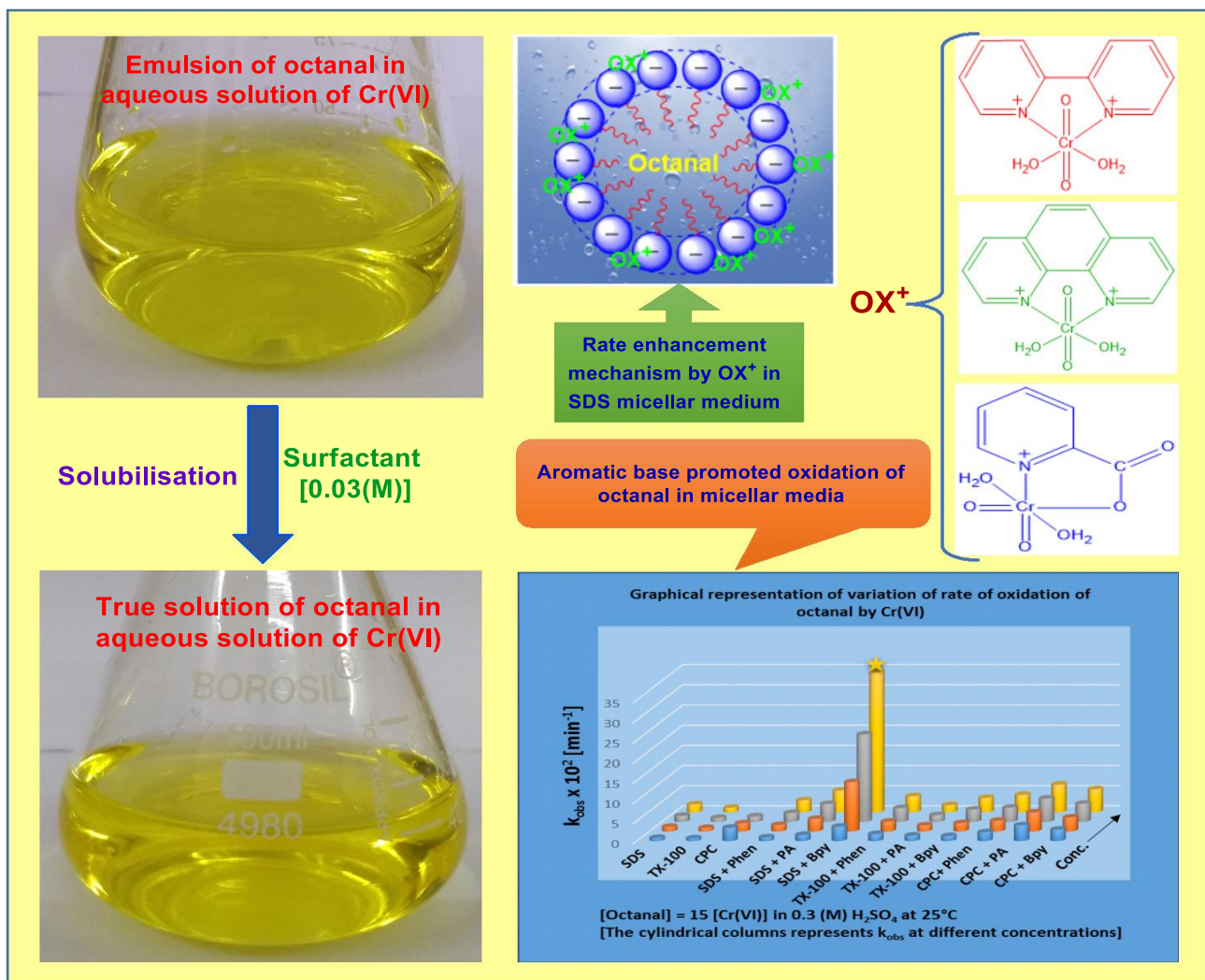
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Declaration of interest

No financial or others competing interests are known to the best the knowledge of the authors in performing this experimental work.

Journal Pre-proof

Graphical Abstract



Journal

Highlights

- Successful oxidation of long chain hydrophobic octanal in aqueous medium.
- Surfactants, above CMC, solubilize octanal and effectively catalyse its oxidation.
- Additional rate enhancement by using promoters Phen, PA and Bpy.
- The combination of SDS and Bpy shows maximum rate enhancement.
- UV, IR, NMR and DLS studies support the results.

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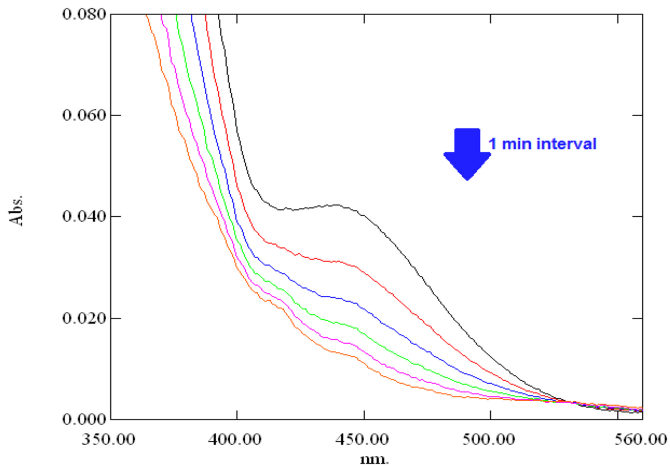


Figure 1

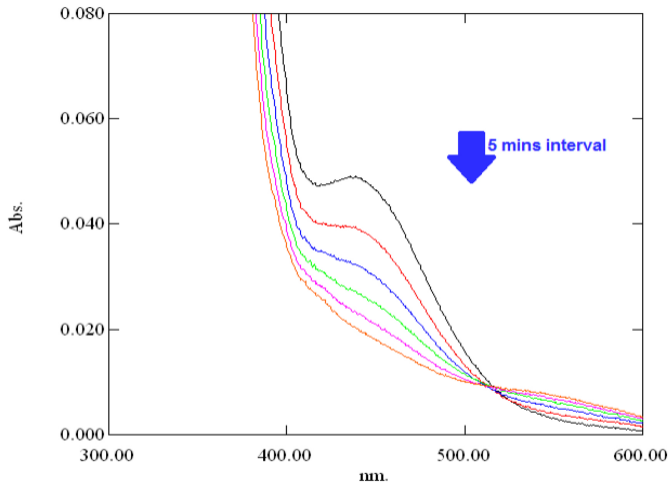


Figure 2

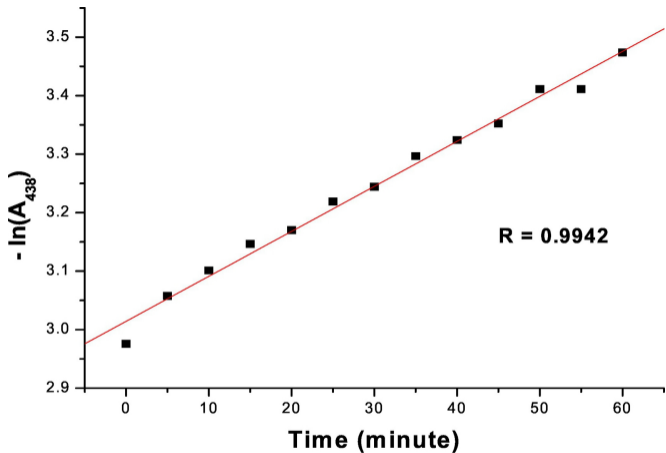


Figure 3

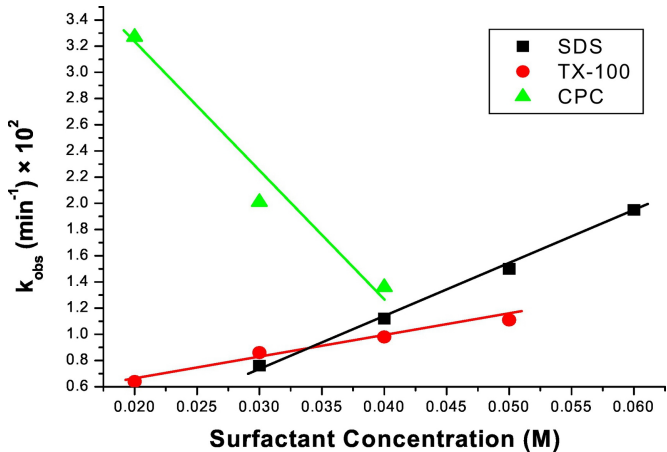


Figure 4

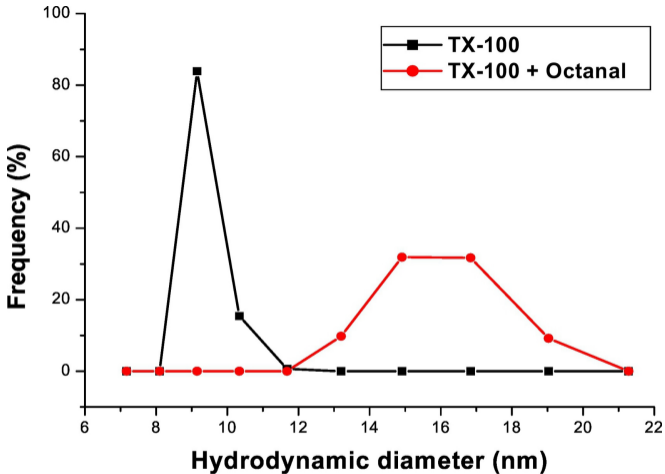


Figure 5

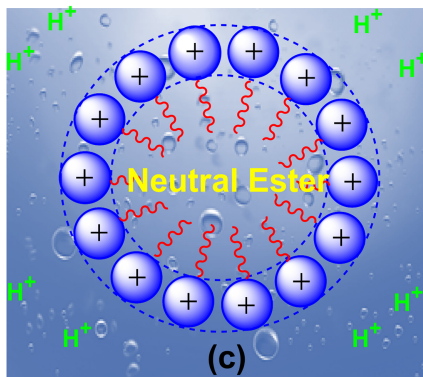
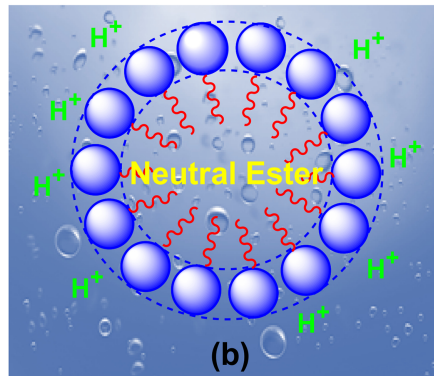
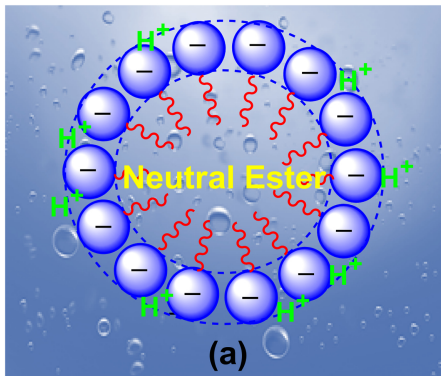


Figure 6

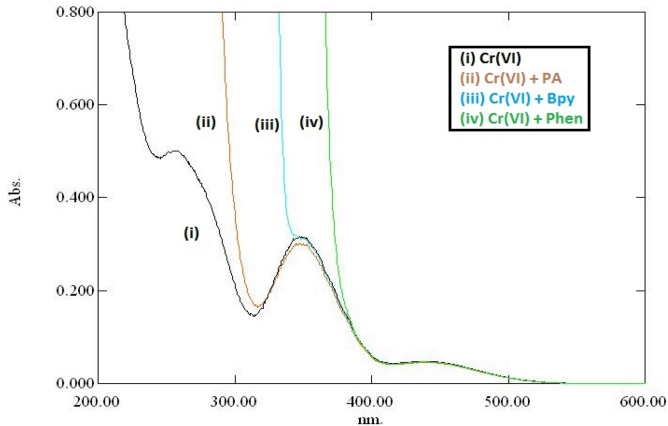


Figure 7

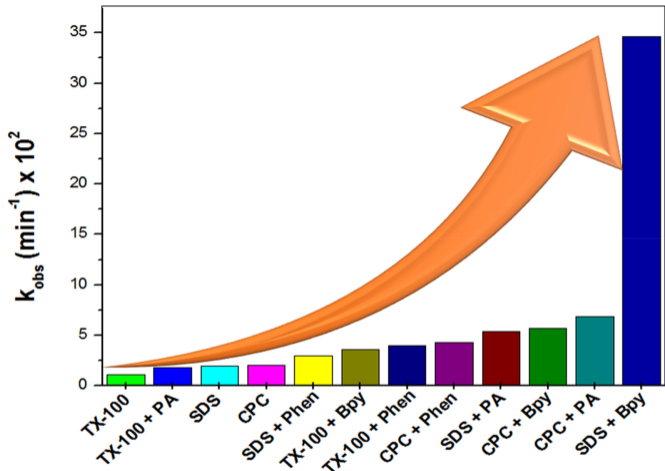


Figure 8

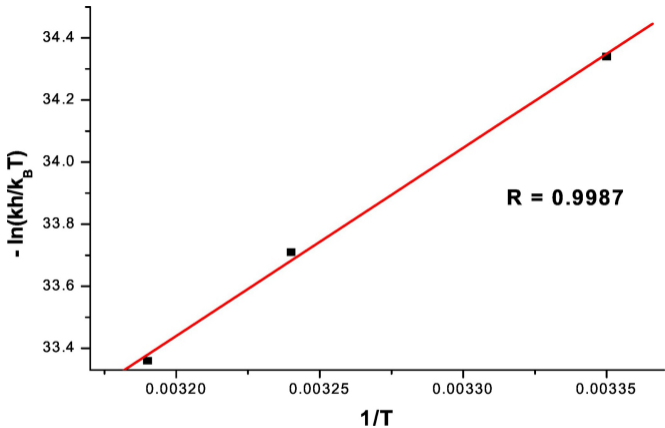


Figure 9