

Micellar Catalysis on 1,10-Phenanthroline Promoted Chromic Acid Oxidation of Dimethyl Sulfoxide to Dimethyl Sulfone in Aqueous Media at Room Temperature

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Abstract

The monomeric species of Cr(VI) was found to be kinetically active in the absence of 1,10-phenanthroline (phen) under pseudo-first order conditions, whereas in the 1,10-phenanthroline promoted path, the Cr(VI)-phenanthroline complex undergoes a nucleophilic attack by dimethyl sulfoxide (DMSO) to form a ternary complex which subsequently undergoes a redox decomposition leading to dimethyl sulfone and Cr(III)-phenanthroline complex. A detailed study was done to investigate the effect of cationic surfactant N-cetylpyridinium chloride (CPC), anionic surfactant sodium dodecyl sulphate (SDS) and neutral surfactant (TX-100) on the phen promoted chromic acid oxidation of DMSO in aqueous media at 30°C. The aggregation and morphology of the micelles formed by the surfactants were studied by optical microscope and Transmission Electron Microscope (TEM). 1,10-phenanthroline in association with SDS micelle exhibited almost 70-fold rate enhancements compared to the uncatalyzed reaction path.

Keywords: Dimethyl sulfoxide; Cr(VI); 1,10-Phenanthroline; Sodium dodecyl sulphate; TX-100

Introduction

Surfactants are a surface active agent that shows characteristic behaviors at surfaces and interfaces [1-3]. The driving force for their adsorption at an interface is to lower the interfacial tension (i.e. interfacial free energy per unit area). The fundamental property of surfactant of reducing the interfacial tension is responsible for its use as emulsifier, detergent, foaming agent, wetting agent and so on [4-15]. Surfactant molecules consist of at least two parts, one of them is soluble to a specific fluid (lyophilic part) and the other is insoluble (lyophobic part). The terms are hydrophilic part and hydrophobic part respectively when water is used as the solvent. The concentration at which micelle formation starts is known as critical micelle concentration (CMC) which is an important feature of a surface active agent. Molecular structures of the surfactant, temperature, polarity of the medium are some of the factors on which CMC depends. In polar solvents, above CMC, the surfactant molecules spread their hydrophilic part in the polar medium and their hydrophobic ends being repelled, tend to associate generating similar environment. This type of micelle is generally called normal micelle. The fact is opposite in nonpolar solvent where the hydrophobic tail group is remaining out in the nonpolar medium and hydrophilic head group remains far from the non-polar medium. This type of micelle formation is known as reverse micellization. According to the charges on the hydrophilic head group surface active agents are divided in four categories (i) cationic (ii) anionic (iii) nonionic (iv) zwitterionic. The oxidation of various organic compounds by Cr(VI) was found to be more pronounced in the presence of micellar catalyst and promoters. Micellar catalysis plays an important role in many organic reactions [16,17]. Oxidation is a fundamental reaction in organic synthesis and will possibly play an important role in the development of value-added chemicals from biomass. We used dimethyl sulphoxide (DMSO) as an organic substrate which is oxidized to dimethyl sulfone by the powerful oxidant Cr(VI) consequent to the reduction of non-toxic Cr(III). Chromium has both beneficial and detrimental properties. The two oxidation states of chromium are naturally occurring; one is trivalent chromium and another is hexavalent chromium. The behavior of chromium species depends strongly on their oxidation states: Cr(III) is essential for human nutrients, whereas most hexavalent compounds are toxic, several of which even cause lung cancer. From the standpoint of carcinogenic effect of hexavalent chromium Cr(VI), the kinetic aspects of interaction of Cr(VI) with the different biologically relevant reducing agents have become very significant in recent days to both biochemists and inorganic chemists. Hexavalent chromium used as a strong oxidant in various organic synthesis [18]. But the rate of oxidation of dimethyl sulfoxide with Cr(VI) is very slow. Surfactant micelles and promoters are used to speed up the oxidation of DMSO by chromic acid. DMSO contains two methyl group along with S=O group. Previously, we investigated the mechanistic aspects of Cr(VI) oxidation of dimethyl sulfoxide (DMSO) in aqueous acidic media in the presence and absence of picolinic acid promoter [19,20]. In fact, Cr(VI) can oxidize DMSO slowly without any catalyst only under drastic conditions. The present paper describes the mechanistic aspects of oxidation of DMSO by Cr(VI) in the presence of phenanthroline in different types of micellar media. The major role of micellar media is to organize different chemical reactions as multifunctional nanoreactors. To achieve the target, several kinetic measurements were performed during the oxidation of DMSO. Micellar medium as a nano-reactor in combination with different promoting agents is a very efficient for rapid oxidation of DMSO. The N-hetero-aromatic nitrogen bases are generally used as chelating agents and found to act as an effective oxidation promoters. Different compounds such as picolinic acid, bipyridine, 1,10-phenanthroline, EDTA are used as promoters for Cr(VI) oxidation of organic substrates [1,2,16]. Our present work will be found out the preferable micellar medium that

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catalyses the oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) with 1,10-phenanthroline (phen) as promoter. In this study we have selected three different type of surfactants: cationic (cetyl pyridinium choloride, CPC), anionic (sodium dodecylsulfate, SDS), nonionic (octylphenol-polyoxyethylene ether, TX-100). The present paper describes the detailed micellar effect on the title reaction to provide a better insight to the reaction mechanism.

Experimental

Materials and reagents

All chemicals were commercially available and used directly as received from the manufacturer. DMSO (SRL, AR), $K_2Cr_2O_7$ (BDH, AR), H_2SO_4 (BDH, AR), 1,10-phenanthroline (AR, Merck), sodium dodecyl sulfate (AR, SRL, India), N-cetylpyridinium chloride (AR, SRL, India), Triton X-100 (AR, SRL) and all other necessary chemicals used in highest purity available commercially. Solutions were prepared by using doubly-distilled water.

Procedure and kinetic measurements

Solutions of the oxidant and reaction mixtures containing known quantities of the substrate (i.e. DMSO), and promoter (phen) are prepared under the pseudo-first-kinetic conditions (DMSO)>>(Cr(VI)) $_{T}$ and (phen)>>(Cr(VI))_T. Acid and other necessary chemicals were separately thermostated (\pm 0.1°C). The reaction was started by mixing requisite amount of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the decay of Cr(VI) at 450 nm wave length at different time intervals with the UV-VIS (UV-VIS-NIR-3600 (SHIMADZU)) spectrophotometer. Quartz cuvettes of path length 1 cm were used. The pseudo-first-order rate constants (k_{obs}, s^{-1}) were calculated from the slope of plots of $ln(A_{450})$ versus time (t) which were linear. No interference was observed due to other species at 450 nm. The scanned spectra, spectrum after completion of the reaction and other spectra were recorded with a UV-VIS spectrophotometer. Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was investigated and the rate of decomposition in this path was kinetically negligible.

Product analysis and stoichiometry

DMSO is quantitatively oxidized to sulfone under the kinetic condition (DMS)>>(Cr(VI))_T and Cr(VI) is finally reduced to a Cr(III)-phrn complex. Completion of the reaction was indicated by the disappearance of Cr(VI) color. A reaction mixture (under the kinetic conditions) containing the substrate and chromic acid was allowed to stand overnight, neutralised with sodium carbonate, and extracted with ether. The solvent was removed after drying (anhydrous Na₂SO₄) and a solid was obtained. Its m.p. (109°C) corresponds to the mp of dimethyl sulfone (Me₂SO₂) (literature reported M.P.=107-109°C) [19]. The (Cr(VI)):(DMSO) ratio was also estimated. The unreacted DMSO was estimated by Ce(IV). The stoichiometry conforms to

$$2HCrO_4^++3Me_2S=O+8H^+ \xrightarrow{Pheanthroline} 2Cr(III)+3Me_2SO_2+5H_2O$$

Results and Discussions

Dependence on (Cr(VI))_T

Under the experimental conditions $(DMSO)>>(phen)_T>>(Cr(VI))_T$, both in the presence and the absence of phen, the rate of disappearance of Cr(VI) shows a first-order dependence on $(Cr(VI))_T$. This first-order dependence on Cr(VI) is also maintained in the presence of surfactants [20].

Dependence on (phen)_T

The pseudo-first order rate constants (k_{obs} , s^{-1}) were determined from the slope of plots of $\ln(A_{450})$ against time (t) at wavelength 450 nm. The slope (Figure 1) obtained from the plots $\ln(A_{450})$ versus time (t) divided by the time(t=60 sec) using the equation: k_{obs} =slope/time (t) was equal to the pseudo-first order rate constants(k_{obs} , s^{-1}). Time t=60 sec or 1 min in the denominator of the equation has been divided as the total reaction was monitored for several minutes (Figure 1). When k_{obs} versus (phen)_T are plotted, it gives positive intercepts that measures the rate of the relatively slower uncatalyzed path. The pseudo-first order rate constant obtained in the absence of phen under the same conditions is nearly equal to the results measured from the intercept of the plot of k_{obs} versus (phen)_T (Figure 2). In the presence and absence of surfactants the observation is maintained. During the reaction, under the condition (phen)>>(Cr(VI))_T (phen) is reduced due to formation of inert Cr(III)-(phen) complex (Figure 2).

Spectroscopic analysis of the reaction

UV-VIS Spectra: The in vitro reduction of Cr(VI) to Cr(III) has been established by the help of UV VIS spectroscopy. The final color of the solution changes to pale blue ($\lambda_{max}{=}580$ nm, and $\lambda_{max}{=}415$ nm Figure 3) in unpromoted path while it turns into a pale violet (λ_{max} =553 nm) solution in phenanthroline mediated promotion. Two peaks are observed in unpromoted pathway due to the transition [21-23] from λ_{max} =580 nm for ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ and λ_{max} =415 nm for ${}^{4}A_{2g}(F)$ $\rightarrow {}^{4}T_{1\sigma}(F)$ of Cr(III) respectively. Interestingly, the spectra of the end solution in unpromoted path seems to be identical with that obtained from the aqueous solution of pure chromic sulphate but a different spectrum obtained in promoted pathway. It seems to contain Cr(III) promoter complex at the end solution in promoted pathway which has been established early [24,25]. A hypsochromic shift is associated for the transition ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ in promoted pathway compared to the final solutions of the unpromoted reaction pathway (Figure 3). The blue shift for the transition ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ indicates that the charge transfer band in the Cr(III) phen complex is due to the presence of strong electron donating atom (three nitrogen donor) in phen. A charge transfer band is associated with the band arising for the transition from ${}^{4}A_{2\sigma}(F) \rightarrow {}^{4}T_{1\sigma}(F)$ which is justified from the fact that a suitable charge transfer transition from the metal to ligand (MLCT) is possible and thus we observed the charge transfer band at lower energy visible range. The vacant π^* (antibonding) M.O. on ligand (phen) switches the electron-transfer from metal to ligand. Thus from the above results it reveals that, a charge transfer band at lower energy should be arising for the formation of a Cr(III) promoter complex at the end solution (Figure 3). A further study was done to investigate whether any reaction intermediate was formed at any time interval. The reaction solution with presence and absence of promoter and surfactant was scanned at a regular time interval in between 250-800 nm to follow the reaction progress. The observed spectrum show that there is a gradual decrease in concentration of Cr(VI) and subsequently appearance of Cr(III) with increase time in unpromoted reaction condition with no distinct isobestic point (Figure 4). From this spectrum (Figure 4), it can only be observed with course of time the rate of absorbance decreases indicating the concentration of Cr(VI) decreases with time. An isobestic point was observed at λ_{max} =527 nm for phen promoted reaction pathway (Figure 5). Isobestic point was shifted when a mixture of three micellar catalysts (CPC, SDS, TX-100) and promoter (phen) are introduced in the reaction solution (Figures 6-8). In this experimental condition the reaction solution was scanned and the observed spectrum gives a single isobestic point. Thus it follows

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Figure 1: Representative first-order plot to evaluate the pseudo-first-order rate constant (k_{obs}) for phenanthroline-promoted Cr(VI) oxidation of DMSO in aqueous solution at 30°C. (DMSO)_T=75 × 10⁻⁴ mol dm⁻¹, (Cr(VI))_T=5 × 10⁻⁴ mol dm⁻¹, (H₂SO₄)_T=0.5 mol dm⁻¹, (phen)_T=50 × 10⁻⁴ mol dm⁻¹.







Figure 3: Absorption spectra of (i) Unpromoted reaction mixture (after completion of reaction): $(DMSO)_{T}=75 \times 10^{4} \text{ mol } dm^{3}$, $(Cr(VI))_{T}=5 \times 10^{4} \text{ mol } dm^{3}$, $(H_{2}SO_{4})_{T}=0.5 \text{ mol } dm^{3}$ (The spectrum of the chromic sulfate is identical with this under the experimental condition). (ii) Promoted reaction mixture (after completion of reaction): $(DMSO)_{T}=75 \times 10^{4} \text{ mol } dm^{3}$, $(Cr(VI))_{T}=5 \times 10^{4} \text{ mol } dm^{3}$, $(H_{2}SO_{4})_{T}=0.5 \text{ mol } dm^{3}$, $(phen)=25 \times 10^{4} \text{ mol } dm^{3}$.



Figure 4: Scanned absorption spectra of the reaction mixture at regular time intervals (15 min). $(DMSO)_{T}=75 \times 10^{-4} \text{ mol dm}^{-3}$, $(Cr(VI))_{T}=5 \times 10^{-4} \text{ mol dm}^{-3}$, $(H_{2}SO_{4})_{T}=0.5 \text{ mol dm}^{-3}$.



Figure 5: Scanned absorption spectra of the reaction mixture at regular time intervals (3 min). $(DMSO)_{T}$ =75 × 10⁴ mol dm³, $(Cr(VI))_{T}$ =5 × 10⁴ mol dm³, $(H_{2}SO_{4})_{T}$ =0.5 mol dm³. (phen)_{T}=25 × 10⁴ mol dm³ Temp=30°C.



Figure 6: Scanned absorption spectra of the reaction mixture at regular time intervals (3 min). $(DMSO)_T = 75 \times 10^4 \text{ mol dm}^3$, $(Cr(VI))_T = 5 \times 10^4 \text{ mol dm}^3$, $(H_2SO_4)_T = 0.5 \text{ mol dm}^3$, $(phen)_T = 25 \times 10^4 \text{ mol dm}^3$ (SDS)_T = 2 × 10² mol dm³. $\lambda_{\text{sobestic}} = 525 \text{ nm}$. Temp=30°C.

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Figure 7: Scanned absorption spectra of the reaction mixture at regular time intervals (3 min). $(DMSO)_T = 75 \times 10^4 \text{ mol } dm^3$, $(Cr(VI))_T = 5 \times 10^4 \text{ mol } dm^3$, $(H_2SO_4)_T = 0.5 \text{ mol } dm^3$, $(TX-100)_T = 2 \times 10^{-2} \text{ mol } dm^3$, $(Phen)_T = 25 \times 10^4 \text{ mol } dm^3 \lambda_{\text{isobestic}} = 517 \text{ nm}$. Temp=30°C.



that there might be short lifetime intermediates Cr(IV) and Cr(V) [26] which can formed with the reduction from Cr(VI) to Cr(III) at very low concentrations and Cr(VI)-phen is the active oxidant in promoted oxidation pathway [23,25,27-31].

Mechanism of the reaction and rate law

From the spectroscopic analysis it clearly indicates that sulfone is the main oxidized product in the reaction. The mechanism of phen promoted chromic acid oxidation of DMSO has been shown in the Scheme 1 given below. The active oxidant Cr(VI)-phen complexes react (supported by Figure 9) with the substrate DMSO to form a ternary complex which undergoes redox decomposition in a rate-limiting step [25,32-34] giving rise to the product sulfone.

Effect of non-functional micellar catalyst on the reaction rate

Partitioning of reactant in promoted path: From the observed data, it is cleared that the rate of oxidation in phen promoted path is highest when it is catalyzed by SDS. The enhancement of rate arises from the preferential partitioning of the positively-charged Cr(VI)-phen (active oxidant, AO⁺) complex and neutral substrate (Scheme 1)

by electrostatic attraction in the micellar surface [35]. Acceleration of rate is also arises when combination of SDS and the hetero-aromatic nitrogen base (phen) is used (Figure 10a). The Cr(VI)-promoter complex for phen represented as AO⁺ (Scheme 1), a cationic complex, has been argued as the active oxidant in the promoted path. The most pronounced acceleration for the DMSO oxidation process is observed in the SDS catalyzed phen promoted path (Tables 1 and 2). The maximum rate enhancement arises from preferential partitioning of the positively-charged Cr(VI)-phen and neutral substrate (Scheme 1, Figure 10b) in the micellar surface. Because of the electrostatic attraction it can preferably distributed in the micellar pseudo-phase (Figure 10a) of the anionic surfactant SDS. Thus in presence of SDS micelle, the oxidation process can propagate in both the micellar pseudo-phase (where both the active oxidant and substrate are preferably concentrated) and aqueous phase to give the observed rate acceleration. A similar phenomenon of smaller rate acceleration has been noticed for combination of TX-100 micelles (Figure 10b) and phenanthroline used. Table 1 show that when phen is used as promoter in the micellar catalyzed path the rate of reaction is greater in SDS compared to TX-100 medium. This phenomenon is due to the larger size of the phen ring. The cationic micelle CPC retards the rate of reaction in presence of promoter also. The positive head groups of CPC micelle repel the positively charged active oxidant in the surface (Figure 10c). So the effective concentration of the reactant in the micellar region decreases and resulting retardation of the rate.

The substrate can make effective collision with the AO⁺ and enhancement of rate is produced in SDS. Such enhanced local concentration of reactants increases the observed rate of reaction to a remarkable extent. So the highest acceleration of rate in case of SDS catalyzed phen promoted path is explained by the easy entering of Cr(VI)-phen complex into the relatively hydrophobic core of SDS micelle compared to that of TX-100 micelle. SDS allows maximum number of Cr(VI)-phen compared to TX-100 micelles due to electrostatic and steric factor only. In this route the oxidation rate was almost 70 times enhanced compared to the ordinary uncatalyzed and unpromoted reaction path. So $t_{1/2}$ (half-life) for the reaction is minimum for SDS-phen combined reaction path (Tables 1 and 2). Considering all the above fact it can be concluded that SDS is the most suitable micellar catalyst for this conversion. The overall analysis of our experimental results compared to the literature works are presented in Table 3. From Table 1 it is shown that the rate is accelerated with increasing the concentration of hetero-aromatic nitrogen base promoter





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Figure 10: Schematic representation of partitioning of substrate and active oxidant (AO⁺=Cr(VI)-promoter complex) in (a) Anionic surfactant, (b) Neutral surfactant, and (c) Cationic surfactant.

Promoter (mol dm ⁻³)		Micellar catalyst (mol dm ⁻³)		10 ⁴ × <i>k</i> _{obs} (sec ⁻¹)	t _{1/2} (hrs)	
None		N	lone	0.125 ± 0.01 15.4		
1,10 - phenanthroline (phen)	0.0025 0.005 0.0075 0.01 0.0125	None		$\begin{array}{c} 0.33 \pm 0.03 \\ 0.833 \pm 0.02 \\ 1.33 \pm 0.01 \\ 1.5 \pm 0.04 \\ 1.8 \pm 0.02 \end{array}$	5.83 2.31 1.44 1.28 1.07	
1,10 - phenanthroline (phen)	0.0025 0.005 0.0075 0.01 0.0125	SDS	0.02	$2 \pm 0.01 4 \pm 0.03 5 \pm 0.02 7 \pm 0.01 9 \pm 0.02$	0.962 0.481 0.385 0.275 0.214	
1,10 - phenanthroline (phen)	0.0025 0.005 0.0075 0.01 0.0125	TX-100	0.02	$3.33 \pm 0.02 2.83 \pm 0.04 2.5 \pm 0.03 2.3 \pm 0.04 1.8 \pm 0.01$	0.57 0.68 0.77 0.83 1.06	
1,10 - phenanthroline (phen)	0.0025 0.005 0.0075 0.01	CPC	0.02	$\begin{array}{c} 0.5 \pm 0.01 \\ 0.67 \pm 0.02 \\ 1.0 \pm 0.02 \\ 0.86 \pm 0.03 \end{array}$	3.85 2.87 1.92 2.32	

 $(Cr(VI))_{\rm T}\text{=}5\times10^{\text{-}4}\,\text{mol}\;\text{dm}^{\text{-}3},\,(\text{H}_2\text{SO}_4)_{\rm T}\text{=}0.5\;\text{mol}\;\text{dm}^{\text{-}3},\,(\text{DMSO})_{\rm T}\text{=}75\times10^{\text{-}4}\;\text{mol}\;\text{dm}^{\text{-}3},\,\text{Temp=}30^{\circ}\text{C}$

Table 1: k_{obs} and half life of the reaction in presence and absence of promoter and non-functional micellar catalyst.

Promoter Micellar catalyst		k _{eff(promoter)(water)}	K _{eff(promoter)(surfactant)}	
1,10-phenanthroline	None	11	-	
1,10-phenanthroline	SDS	-	39	
1,10-phenanthroline	TX-100	-	19	

 $(Cr(VI))_{T}=5 \times 10^{4} \text{ mol dm}^{3}, (H_{2}SO_{4})_{T}=0.5 \text{ mol dm}^{3}, (DMSO)_{T}=75 \times 10^{4} \text{ mol dm}^{3}, (phenantholine)_{T}=100 \times 10^{4} \text{ mol dm}^{3}, (SDS)_{T}=2 \times 10^{4} \text{ mol dm}^{3}, Temp=30^{\circ}C$ **Table 2:** Kinetic parameters and some representative k_{eff} values for the Cr(VI) oxidation of DMSO in presence of promoter and micellar catalyst (surfactant) in aqueous acidic media.

Entry	Catalyst	Conditions	Reference	10 ⁴ k _{obs} (s ⁻¹) (rate constant)	Half life (t _{1/2}) (h)
1	(NaBrO ₃)-(NaHSO ₃)	(NaBrO ₃)=1 × 10 ⁻³ mol dm ⁻³ (NaHSO ₃)=2 × 10 ⁻³ mol dm ⁻³ Temp=30°C	[30]	1.96	0.982
2	DCSB in 1:1 water acid medium	(HClO ₄)=0.1 mol dm ⁻³ I=0.3 mol dm ⁻³ (DCSB)=1 × 10 ⁻³ mol dm ⁻³ Temp=30°C	[31]	1.9	1.01
3	Pd(II)	(IO ₄ ')=1 × 10 ⁴ mol dm ⁻³ (OH')=0.5 mol dm ⁻³ Pd(II)=1 × 10 ⁴ mol dm ⁻³ Temp=25°C	[32]	3.8	0.506
4	SDS (catalyst)+phen (promoter)	(phen)=0.0125 mol dm ⁻³ (SDS)=0.02 mol dm ⁻³	Curent work	9	0.214

Table 3: A comparative study of different catalysts used in DMSO to dimethyl sulfone conversion.

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phenanthroline. As a result of which the half life (t_{12}) value of the reaction decreases uniformly. SDS enhances the rate of DMSO oxidation (Figure 11) to a great extent compared to the micellar catalyst TX-100. On the other hand the rate is retarded in comparison to the uncatalyzed and unpromoted reaction when the micellar surface is cationic (CPC) (data not shown in Table 1). It was obtained that the combination of phenanthroline promoter and the CPC surfactant decreased the rate constant for the oxidation of DMSO by Cr(VI). In presence of anionic surfactant (SDS) the reaction undergoes completion just 38.52 minute under the kinetic experimental condition. Thus from the data in Table 1 it is shown that reaction is completed in least time and least half time (12.84 min) in presence of SDS at its highest concentration (125×10^{-4} mol dm⁻³) used. In case of neutral surfactant TX-100, with increasing phenanthroline concentration, the rate of entering large active oxidant (Cr(VI)-phen complex, AO⁺) in the micellar core decreases due to the steric effect resulting rate increment to a smaller extent (Figure 12). Here steric factor predominates over electrostatic interaction. When k_{obs} vs (phenanthroline)_T in presence of SDS is plotted the linear plot with positive intercept is obtained (Figure 11). The maximum rate enhancement observed in SDS catalyzed phenanthroline pathway with a rate constant of 9 \times 10⁻⁴ s⁻¹. The pseudo first order rate constants (k_{obs} , sec⁻¹) are determined from the slope of the plots of $-\ln(A_{450})$ versus time (A=absorbance of Cr(VI)) at wavelength 450 nm. The half-life values (t_{12}) are calculated from the data by the relation $t_{12} = \ln 2/k_{obs}$, where k_{obs} is pseudo first order rate constant.

Optical images of micelles

The optical micrographs are taken for mixtures three different surfactants CPC, SDS and TX-100 in 100× magnification in an optical microscope (LEICA DM 1000). The images (Figure 13) represent the evidence of micelle formation in aqueous medium. The formation of micelles in aqueous medium was clearly identified by the optical images found. They are observed in 10 µm scale in an optical microscope. Some of the micelles are attached to the inner walls of the empty vesicles as evident from the optical images.

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

The HR-TEM investigation was done at 20 kV acceleration voltages using lacey carbon coated Cu grid of 300 mess size in HR-TEM microscope (JEOL JEM 2100). Samples were prepared by placing sample mixture drops directly on the copper grids using a micropipette. The surfactants present in the aqueous medium were allowed to settle. TEM pictures (Figure 14) are presented which illustrate the multiple morphologies of the aggregates made from the different surfactants CPC, SDS and TX-100.

Conclusion

The active oxidant Cr(VI)-phen complex is responsible for oxidation of DMSO to sulfone in phen promoted aqueous micelle media. Though the cationic surfactant (CPC) retards the rate of oxidation, the rate is increased in presence of negative surfactant (SDS). Thus it is of growing interest to the chemist as not only an organic transformation is done in aqueous media but also the rate of transformation increases to a greater extent in aqueous micellar media (when the micelle is SDS). So the use of carcinogenic organic solvent may be reduced. Besides DMSO reduces Cr(VI) to Cr(III). Consequently, possibility of water pollution by carcinogenic Cr(VI) from industrial effluent can be reduced. In this study phen is used as promoter and CPC, SDS, TX-100 are used as micelle media. The oxidation product sulfone has been confirmed by















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its boiling point. Combination of SDS and phen accelerates the rate of DMSO oxidation by Cr(VI) up to 70-fold compared to the same reaction in the absence of surfactant.

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References

- Mandal J, Chowdhury KM, Paul KK, Saha B (2010) Kinetics and mechanism of 2, 2'-bipyridine-catalyzed chromium(VI) oxidation of propan-2-ol in the presence and absence of surfactants. J Coord Chem 63: 99-105.
- Chowdhury KM, Mandal J, Saha B (2009) Micellar catalysis of chromium(VI) oxidation of ethane-1,2-diol in the presence and absence of 2,2'-bipyridine in aqueous acid media. J Coord Chem 62: 1871-1878.
- Basu A, Ghosh SK, Saha R, Nandi R, Ghosh T, et al. (2011) Effect of some non functional surfactants and electrolytes on the hexavalent chromium reduction by glycerol: A mechanistic study. Tenside Surf Det 48: 453-458.
- Wadekar SD, Patil SV, Kale SB, Lali AM, Bhowmick DN, et al. (2011) Study of Glycerol Residue as a Carbon Source for Production of Rhamnolipids by Pseudomonas aeruginosa. Tenside Surf Det 48: 16-22.
- Nowicki J, Sokolowski A, Reska D (2011) Surface Activity and Adsorption Properties of New Perfluorinated Carbohydrate Surfactants. Tenside Surf Det 48 : 11-15.
- Fanun M, Glatter O (2011) SAXS Study on Azithromycin Loaded Nonionic Microemulsions. Tenside Surf Det 48 : 34-39.
- Ghosh S, Bhowmick DN, Pratap AP (2011) Application of Neem and Karanjia Oils as Natural Pesticide Microemulsion Systems. Tenside Surf Det 47: 369-375.
- Wadekar SD, Patil SV, Kale SB, Lali AM, Bhowmick DN, et al. (2010) Structural Elucidation and Surfactant Properties of Rhamnolipids Synthesized by Pseudomonas aeruginosa. Tenside Surf Det 48 : 286-292.
- Datla VM, Beck K, Shim E, Pourdeyhimi B (2010) Reverse Phase HPLC Analysis of Commercial Surfactants used as Melt Additives. Tenside Surf Det 47: 142-150.
- Kishore K, Upadhyaya SK (2010) Studies on Acoustic and Thermodynamic Behaviour of Terbium Laurate and Myristate in Mixed Organic Solvents. Tenside Surf Det 47: 184-189.
- Bajpai D, Tyagi VK (2010) Nonionic Surfactants: An Overview. Tenside Surf Det 47: 190-196.
- 12. Deb N, Bagchi S, Mukherjee AK (2010) Charge transfer complex formation between TX-100/CCl4 reverse micelle and a series of π -electron acceptors: determination of cmc and aggregation number. Mol Phys 108: 1505-1511.
- Nevidimov AV, Razumov VF (2009) Molecular dynamics simulations of AOT reverse micelles' self-assembly. Mol Phys 107: 2169-2180.
- Brodskaya EN, Mudzhikova GV (2006) Molecular dynamics simulation of AOT reverse micelles. Mol Phys 104: 3635-3643.
- Dubey N (2011) Thermodynamic and FT-IR Study of Micellization of Sodium Dodecylbenzene Sulfonate in Some Simple Alcohols. Chem Eng Commun 198: 1394-1404.
- Saha R, Ghosh A, Saha B (2011) Micellar catalysis on 1, 10-phenanthroline promoted hexavalent chromium oxidation of ethanol. J Coord Chem 64: 3729-3739.
- Sar P, Ghosh A, Malik S, Saha B (2015) Sodium dodecylsulphate-catalyzed hetero-aromatic nitrogen base-promoted chromium(VI) oxidation of 2-propenol to 2-propenal in aqueous media. Res Chem Intermed.
- 18. Sundaram S, Raghavan PS (2011) Chromium-VI Reagents: Synthetic Applications. Springer.
- Saha B, Islam M, Das AK (2005) Micellar effect on the catalytic co-oxidation of dimethyl sulfoxide and oxalic acid by chromium(VI) in aqueous acid media: A kinetic study. Prog React Kinet Mech 30: 145-156.
- Das AK, Mondal SK, Kar D, Das M (2001) Micellar Effect on the Reaction of Picolinic Acid Catalyzed Chromium(VI) Oxidation of Dimethyl Sulfoxide in Aqueous Acidic Media: A Kinetic Study. Int J Chem Kinet 33: 173-181.

- Ghosh SK, Saha R, Ghosh A, Mukherjee K, Saha B (2012) Micellar Catalysis on 1,10-Phenanthroline Promoted Chromic Acid Oxidation of Glycerol in Aqueous Media. Tenside Surf Det 49: 370-375.
- Meenakshisundaram SP, Gopalakrishnan M, Nagarajan S, Sarathi N (2007) Oxalic acid catalysed chromium (VI) oxidation of some 2-amino-4, 6-diarylpyrimidines. Catal Commun 8: 713-718.
- 23. Figgis BN (1966) Introduction to ligand fields, Wiley Eastern Limited, New Delhi, India. Pp. 222.
- Ud-Din K, Hartani K, Khan Z (2002) One-step three-electron oxidation of tartaric and glyoxylic acids by chromium(VI) in the absence and presence of manganese(II). Transition Met Chem 27: 617-624.
- Jorgensen CK (1964) Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press Ltd: Oxford/London. Pp. 290.
- Mandal J, Chowdhury KM, Paul KK, Saha B (2008) Kinetics and mechanism of 2,2'-bipyridyl promoted chromic acid oxidation of ethanol and propan-1-ol in aqueous micellar media. Open Catal J 1: 1-5.
- Khan Z, Masan S, Raju, Ud-Din K (2003) A mechanistic study of the ethylenediaminetetraacetic acid-, 2,2'-bipyridyl-, and manganese(II)-assisted one-step two- and three-electron oxidation of lactic acid by chromium(VI) Transition Met Chem 28: 881-887.
- Meenakshisundaram S, Markkandan R (2004) 1,10-Phenanthroline catalysis of the chromium(VI) oxidation of alcohols: a kinetic and mechanistic study Trans Met Chem 29: 136-143.
- Viroopakshappa J, Jagannadham V (2002) Kinetics and mechanism of oxidation of dimethyl sulphoxide by sodium bromate-sodium bisulphite reagent in aqueous medium. Proc Indian Acad Sci (Chem Sci) 114: 149-154.
- Gowda BT, Jayalakshmi KL, Jyothi K (2003) Kinetics and Mechanism of Oxidation of DimethylSulphoxide by Mono- and Di-Substituted N,N-Dichlorobenzenesulphonamides in Aqueous Acetic Acid. Z Naturforsch 58b: 787-794.
- Koli BI, Nandibewoor ST (2009) Kinetics and mechanism of palladium(II) catalysed oxidation of dimethyl sulfoxide by alkaline periodate. Indian J Chem 48A: 958-963.
- 32. Ghosh A, Saha R, Mukherjee K, Ghosh SK, Saha B, et al. (2013) Suitable combination of promoter and micellar catalyst for kilo fold rate acceleration on benzaldehyde to benzoic acid conversion in aqueous media at room temperature: a kinetic approach. Spectrochim Acta A Mol Biomol Spectrosc 109: 55-67.
- 33. Mukherjee K, Saha R, Ghosh A, Ghosh SK, Saha B, et al. (2013) Combination of best promoter and catalyst for hypervalent chromium oxidation of L-sorbose to lactone of C₅ aldonic acid in aqueous media at room temperature. J Mol Liq 179: 1-6.
- 34. Mukherjee K, Saha R, Ghosh A, Ghosh SK, Saha B, et al. (2013) Efficient combination of promoter and catalyst for chromic acid oxidation of propan-2-ol to acetone in aqueous acid media at room temperature. Spectrochim Acta A Mol Biomol Spectrosc 101: 294-305.
- 35. Ghosh A, Saha R, Mukhejee K, Ghosh SK, Bhattacharyya SS, et al. (2013) Selection of suitable combination of nonfunctional micellar catalyst and heteroaromatic nitrogen base as promoter for chromic acid oxidation of ethanol to acetaldehyde in aqueous medium at room temperature. Int J Chem Kinet 45: 175-186.