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Combination of Sodium Dodecylsulfate and 2,2′-Bipyridine for Hundred Fold Rate Enhancement of Chromium(VI) Oxidation of Malonic Acid at Room Temperature: A Greener Approach

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Abstract Chromic acid oxidation of malonic acid in aqueous media has been investigated spectrophotometrically at 303 K. The product glyoxylic acid has been characterized by ^{13}C-NMR and FTIR spectroscopy. Three representative *N*-heteroaromatic nitrogen base promoters, 2-picolinic acid, 2,2′-bipyridine (bpy) and 1,10-phenanthroline, in combination with the anionic surfactant sodium dodecylsulfate (SDS) enhanced the rate of the oxidation reaction compared to the unpromoted reaction. 2,2′-Bipyridine produced the maximum rate enhancement of the three promoters used. The mechanism of the reaction has been proposed with the help of kinetic results and spectroscopic studies. The observed net enhancement of rate effects has been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants. The SDS and bpy combination is suitable for malonic acid oxidation.

Keywords Oxidation · Chromium(VI) · Surfactant · Green chemistry

1 Introduction

The development of greener reaction methods is an important goal in all areas of chemistry. Oxidation is key reaction in organic synthesis and will likely play a significant role in the development of value added chemicals from biomass, which is a very much targeted area of scientists worldwide [1]. Among numerous oxidants chromium(VI) has frequently

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been employed as an oxidant in both preparative and analytical chemistry, where chromic acid [2–8], aqueous dichromate [9], chromyl chloride [10], chromyl acetate [11] and ditertiary butyl chromate [12] are important chromium(VI) compounds used in the oxidation of a wide variety of organic and inorganic substrates in solution. Kinetic studies of interaction of Cr(VI) with the organic acids appear to be important and thus have been intensively investigated. The kinetic aspects of malonic acid oxidation by several higher valent metal ions including Cr(VI) have been studied by different workers under different conditions [13–15]. However in our experiment we investigated this reaction using greener approaches than previously.

Oxidation of malonic acid [H_2ma] is of great importance both from the chemical and the biological point of view. The oxidized product glyoxylic acid (GA) is an important organic compound which is clear from its great interest in research. Its use in the pharmaceuticals and the agrochemical industry [16], dye and plastic industries, cosmetics, electronics, food industry, etc. make it an important bulk chemical. Its condensation product with phenol is used as the precursor to the drug amoxillin. Glyoxylic acid is also an important fine chemical raw material in water treatment and pesticide synthesis. Odorants in the food industry such as vanillin and ethyl vanillin are synthesised from glyoxylic acid.

Various oxidants, including pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), and imidazolium dichromate (IDC) have been reported as selective oxidizing agents for the oxidation of a variety of organic compounds in several organic solvents like CH_2Cl_2, CH_3COCH_3, and $(CH_3)_2$ [17]. All these solvents have been treated as "non-environmental friendly" due to their serious and hazardous effects on human skin, respiratory system, eye and also on the nervous system. The development of alternative solvents is a subject of intense investigation. Here, water can be shown to be a superior solvent. Thus oxidation in aqueous acidic media is a much greener method [18]. This reaction is very attractive as the catalyst and the surfactant are recyclable and the overall kinetics are much faster and smarter.

Organic reactions in aqueous surfactant media is a challenging research field, as surfactants may form different types of aggregates (micelles, vesicle etc.), which cause rate acceleration or retardation. Micelles have been the subject of intensive investigation for years. Micelle formation and the dependence of micelle stability on environmental factors such as temperature, additives and catalyzing functions is an important physicochemical issue, needed for both basic understanding and application prospects. Due to similarities between enzyme catalyzed and micelle catalyzed reactions, micellar catalysis has received significant attention. The similarities between enzymatic reactions and catalysis or inhibition by micelles, include shape and size, polar surfaces, and hydrophobic cores. The micelles provide different microenvironments for different parts of the reactant [19].

Surfactants are classified on the basis of the nature of the hydrophilic group and micelles that are formed through a self assembly process which represents a tiny template/nanoreactor which is generally used for preparing nano-structured materials of desired sizes and shapes with required functionalities and attributes. Nanoreactors have been designed using the concept of micelles [20]. Micelles are formed using surfactants that are usually organic compounds that are amphiphilic, meaning they contain a hydrophobic tail as well as a hydrophilic head [21]. Using miceller nanoreactors/microemulsions, various experiments have been reported. The used micellar catalysts can some times be easily recycled in the reaction. Micelles and other types of surfactant aggregates are effective catalysts for a wide range of organic reactions [22–24]. It has been already reported that reaction rates are affected by solubilization of reactants, changes in

local concentrations due to compartmentalization of reaction media, and changes in medium properties [25].

In the present work, complete preliminary investigations on the effect of micellar media on the oxidation reaction and several kinetics measurements were performed. Product identification was by different spectroscopic studies. This work was intended to determine the reaction rate constant, micellar effect, and the localization of substrate in the micelle. Dynamic light scattering (DLS) and transmission electron microscope (TEM) images were used to determine shape, size, and morphology of micelles indicating the micellar aggregate. The total oxidation procedure has been performed in an environmental friendly aqueous micellar medium rather than hazardous organic solvents.

2 Experimental

2.1 Materials and Reagents

All chemicals were of analytical reagent (AR) grade. Malonic acid (99.0 %, SRL, India), $K_2Cr_2O_7$ (99.9 %, BDH), H_2SO_4 (98 %, Merck), picolinic acid (99 %, Sigma Aldrich), 2,2′-bipyridine (99 %, Spectrochem, India), 1,10-phenanthroline (99.5 %, Merck), sodium dodecyl sulfate (SRL, India), D_2O (Sigma Aldrich) and doubly distilled water was used for the preparation of required solutions. All other used chemicals were purchased in their available commercially highest purity state.

2.2 Instrumentation

A Sartorius BSA224S-CW balance was used for weighing the samples. The solutions were prepared using a digital ultrasonic cleaner CD 4820 sonicator and a Z206A, Hermle Labortechnik GmbH, was used for centrifugation. UV–Vis spectra were recorded on a UV-1601PC (SHIMADZU), spectrometer equipped with a temperature controller (TCC SHI-MADZU). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Ascend 500 MHz spectrometer at room temperature. DLS studies were investigated with a Malvern Zetasizer Nano ZS-90 instrument and TEM images were taken in a JEOL JEM 2100 instrument. IR Prestige-21 (SHIMADZU) for FTIR having resolution 4 cm^{-1} and range 400–4000 cm^{-1}, infra red is the light source and % transmittance is the measurement mode.
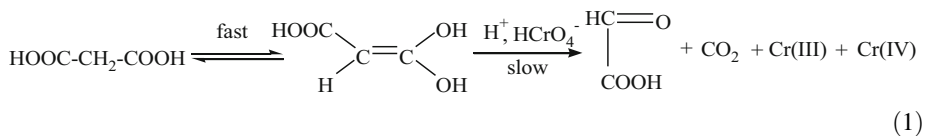
2.3 Procedure and Kinetics Measurements

Solutions of the oxidant and reaction mixtures containing known quantities of the substrate (malonic acid), promoter (picolinic acid, 2,2′-bipyridine, or 1,10-phenanthroline) under the kinetics conditions [malonic acid]$_T \gg$ [Cr(VI)]$_T$ and [promoter]$_T \gg$ [Cr(VI)]$_T$, have been used to monitor the progress of the reaction. The reactions were run under pseudo-first-order conditions by using an excess of malonic acid over Cr(VI). Reactant solutions were previously thermostated and transferred into 1 cm path length cell immediately after mixing. Experiments have been performed using 0.5 (mol·dm^{-3}) H_2SO_4 at 30 °C [26]. The pseudo-first-order rate constants were calculated from the slopes of the plot of log$_{10}$ [Cr(VI)]$_T$ versus time (t), which were linear for at least three half lives. The scanned spectra and the spectrum after completion of the reaction were recorded with a UV–Vis spectrophotometer. Under our experimental conditions, the possibility of decomposition of

the surfactants by Cr(VI) was investigated. The rate of decomposition was kinetically negligible.

2.4 Product Analysis and Stoichiometry

Malonic acid is oxidized to the corresponding glyoxylic acid, detected by spot tests using the reagent solution prepared by dissolving 4 g of urea and 0.2 g of stannous chloride in 10 mL 40 % sulfuric acid under the heating condition [27]. One drop of the final solution containing the oxidized product of malonic acid has been treated with about 15 drops of the reagent solution in a hard glass test tube and heated for a prolonged time. Then, the color of the resultant solutions appeared red, which indicates the formation of glyoxylic acid. The same observation was made using an authentic sample of glyoxylic acid. The reaction mixtures have been concentrated and acidified by adding HCl so that the concentration of the latter remained at ~ 2.0 mol·dm^{-3}. A solution of 2,4-dinitrophenylhydrazine was added to the reaction mixture and then the mixture has been left overnight at refrigerator temperature. The yellow–orange solid, which settled at the bottom of the vessel, was collected after decanting the liquid. This residue was washed with ice-cold water and then air-dried. The FTIR spectral analysis of this product indicated the product to be an aldehyde form of the substrate (Fig. 1) [28]. The reaction stiochiometry has been ascertained by equilibrating the reaction mixture containing an excess of chromium(VI) over malonic acid (in varying ratio), [malonic acid] $\ll$ [Cr(VI)] at 50 °C. Estimation of residual chromium(VI) in different reactions shows that one mole of malonic acid consumes two moles of Cr(VI) as shown in Eq. 1:

$$\text{HOOC-CH}_2\text{-COOH} \xrightleftharpoons{\text{fast}} \underset{H}{\overset{HOOC}{>}}C=C\underset{OH}{\overset{OH}{<}} \xrightarrow[\text{slow}]{H^+, HCrO_4^-} \underset{COOH}{\overset{HC=O}{|}} + CO_2 + Cr(III) + Cr(IV)$$

(1)

The product has been confirmed by IR spectra of the 2,4-DNP derivative of malonic acid. IR spectral analysis of the 2,4-DNP derivative of malonic acid shows the C=N stretch at 1618 cm^{-1} and a broad band around 3421 cm^{-1} corresponding to the N–H symmetric stretching.

2.5 ^{13}C-NMR Spectrum

The product has been also identified by taking the ^{13}C-NMR spectrum of the isolated product in D$_2$O solvent. There are two different types of carbon environments from ^{13}C-NMR analysis as the chemical shift values has been obtained as 163 ppm for carboxyl carbon and 185 ppm for carbonyl carbon (Fig. 2).

2.6 Test for Free Radical

The addition of acrylonitrile solution (40 %, V/V) to the reaction mixture under the protection of nitrogen gas has been carried out gently. Considerable white deposits were found, indicating that the reaction system can initiate polymerization of acrylonitrile
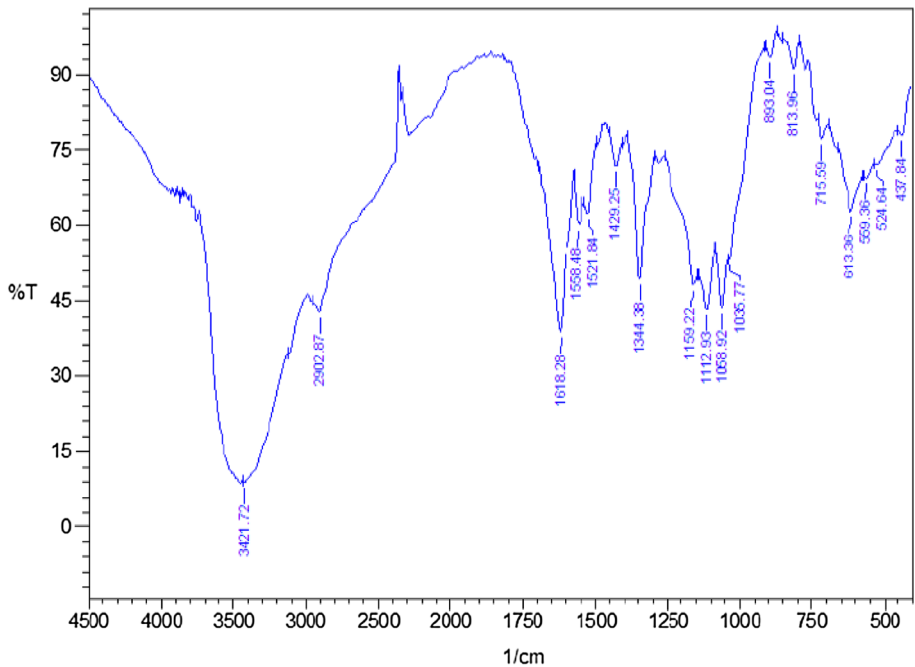
Fig. 1 FTIR spectrum of the 2,4-DNP derivative of product

[29, 30]. The appearance of precipitate proves the generation of free radicals in the reaction.

2.7 Measurements of Critical Micelle Concentration (CMC) Values of SDS

The critical micelle concentration (CMC) values of the SDS in the presence and absence of malonic acid have been obtained from conductometry. Experiments have been made under different conditions, i.e., solvent being water and water + malonic acid (2.0×10^{-3} mol·dm^{-3}), and the respective CMC values are 8.2 [31–33] and 8 mmol·dm^{-3} (Fig. 3a, b).
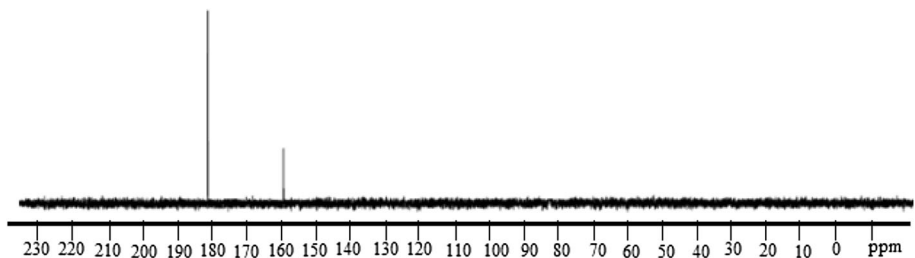
Fig. 2 The ^{13}C-NMR spectrum of oxidized product in D$_2$O solvent

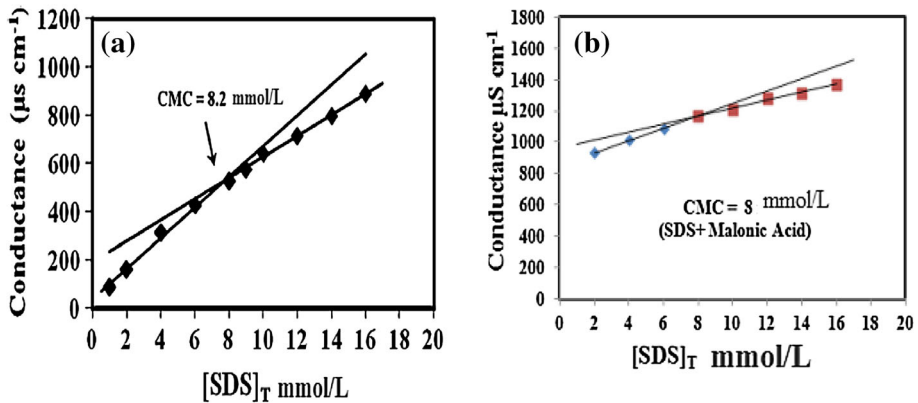**Fig. 3** Conductance versus [SDS] plot at 30 °C. **a** in water, **b** in malonic acid ([Cr(VI)] = 1.0×10^{-4} mol·dm^{-3}, [malonic acid] = 1.0×10^{-3} mol·dm^{-3}; [H$_2$SO$_4$] = 0.5 mol·dm^{-3}), $\mu = 2.0 \times 10^{-3}$ mol·dm^{-3}

3 Result and Discussion

All the kinetic measurements have been carried out at 30 °C. The reaction rate increases linearly with an increase of propanedioic acid concentration, showing that the reaction is first order. The rate of oxidation increases linearly with an increase in the acidity of the solution [34]. The pseudo-first-order rate constants (k_{obs}, s^{-1}) have been determined from the slopes of plots of ln(A_{450}) against time (t). This observed dependence of absorbance on time is more or less similar with butanal oxidation by Cr(VI) [27]. The $t_{1/2}$ values have been directly calculated (see Table 1) by using relation $t_{1/2} = \ln 2/k_{obs}$ (Fig. 4).

The data in Table 1 shows better k_{obs} for the SDS micelle catalyzed reaction than for the corresponding uncatalyzed reaction. This observation is also true for the promoted path compared to the unpromoted path. It was observed that the reactions of organic compounds were significantly improved in aqueous micellar solutions of ionic surfactants.

Table 1 Pseudo-first-order rate constant (k_{obs}) and half life of the reaction with and without promoter and non-functional micellar catalyst

$10^4 \times$ [Promoter] (mol·dm^{-3})		$10^4 \times$ [Micellar catalyst] (mol·dm^{-3})		$10^4 \times k_{obs}$ (s^{-1})	$t_{1/2}$ (h)
Water		–		4.32 ± 0.03	44.56
PA	150	None		9.496 ± 0.04	20.27
bipy	125	None		6.41 ± 0.07	30.03
phen	75	None		5.44 ± 0.01	35.38
–		SDS	400	8.667 ± 0.04	22.21
PA	150	SDS	400	151 ± 0.04	1.27
bipy	125	SDS	400	2730 ± 0.03	0.0705
phen	75	SDS	400	550 ± 0.03	0.35

[Cr(VI)]$_T$ = 5×10^{-4} mol·dm^{-3}, [H$_2$SO$_4$] = 0.5 mol·dm^{-3}, [malonic acid]$_T$ = 75×10^{-3} mol·dm^{-3}, [bpy]$_T$ = 0.0125 mol·dm^{-3}, [phen]$_T$ = 0.0075 mol·dm^{-3}, temperature = 30 °C
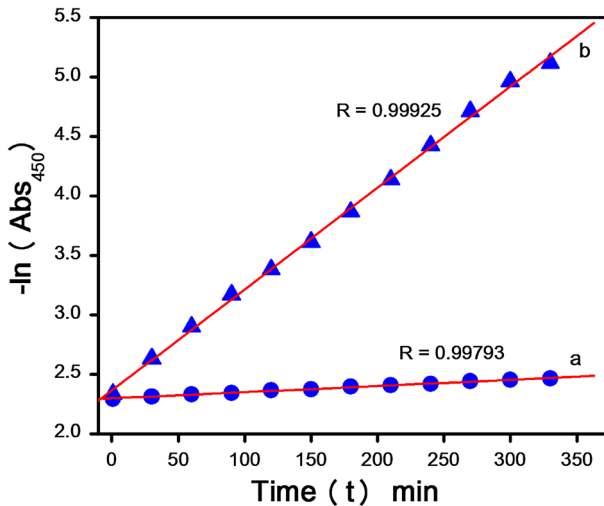
Fig. 4 Representative first order plot for Cr(VI) oxidation of malonic acid in (a) uncatalyzed and (b) catalyzed paths at 30 °C. $[Cr(VI)]_T = 5 \times 10^{-4}$ mol·dm^{-3}, $[H_2SO_4]_T = 0.5$ mol·dm^{-3}, [malonic acid]$_T = 75 \times 10^{-3}$ mol·dm^{-3}, (a) $[SDS]_T = 0$ mol·dm^{-3}; (b) $[PA]_T = 150 \times 10^{-2}$ mol·dm^{-3}, $[SDS]_T = 4 \times 10^{-2}$ mol·dm^{-3}

3.1 Kinetic Study

The absorbance maximum at 450 nm reflects the electronic transitions of the chromium(VI) species. The color of Cr(VI) species in aqueous medium is due to the LMCT bands. In this work, malonic acid is oxidized to glyoxylic acid by Cr(VI) species in aqueous acidic medium. Due to the excess of malonic acid present, as compared to chromium(VI), it is expected that the chromium(VI) ion will be totally reduced to Cr(III) (green solution) at the end of reaction. Indeed, solutions of Cr(VI) salts are yellow in the presence of acid, whereas solutions of Cr(III) salts are green [6, 35]. The progress of the oxidation of malonic acid with chromium(VI) in the presence and absence of SDS (Fig. 5a–c) was indicated by significant changes in the electronic spectrum at certain time intervals (3 min).

3.2 Influence of Promoter

The promoters are used as chelating agents and they are found to be similar in reactivity as they contain one or two hetero atoms, i.e., nitrogen in the aromatic ring. Naturally, they are strong bases and act as an effective oxidation catalyst. The rate of the reaction increase with introduction of heteroaromatic nitrogen base promoters such as picolinic acid (PA), 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen).

3.3 Influence of SDS on Reaction Rate

Specific hydrogen ion catalyzed hydrolyses are generally accelerated by anionic micelles, e.g., of sodium dodecyl sulfate, n-C$_{12}$H$_{25}$OSO$_3$–Na$^+$, SDS, which was used in much of this early work, and rates increased as the substrate and H$^+$ became micellar bound and then
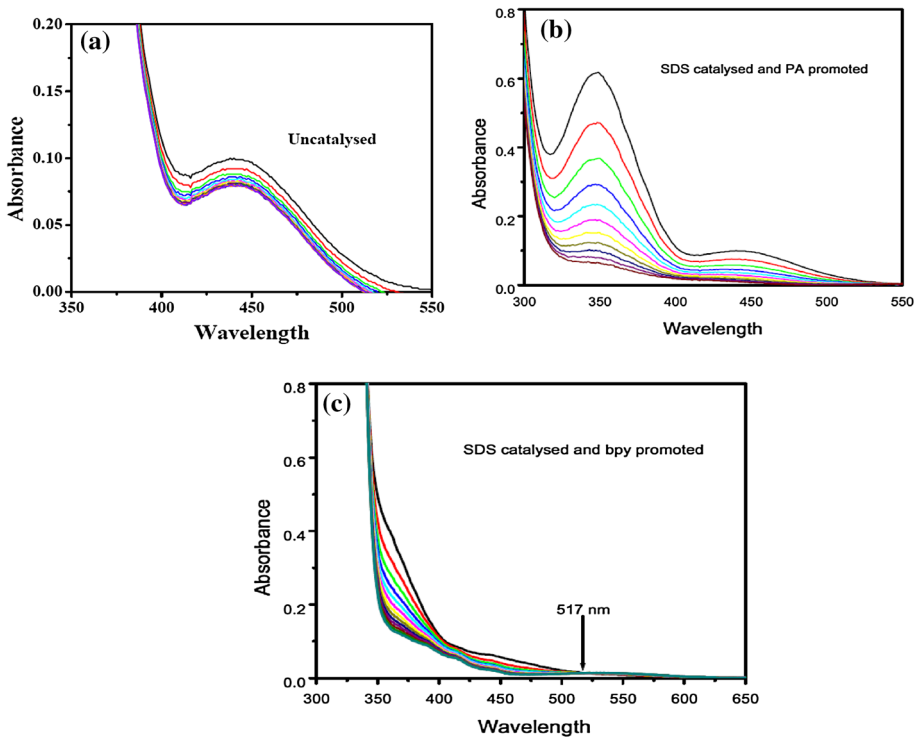
Fig. 5 Scanned absorption spectra of the promoted reaction mixture in micellar medium at regular time intervals (3 min) at 30 °C. [Malonic acid]$_T$ = 75 × 10^{-4} mol·dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol·dm^{-3}, [H$_2$SO$_4$]$_T$ = 0.5 mol·dm^{-3}, **a** [PA] = 0 mol·dm^{-3}, [SDS]$_T$ = 0 mol·dm^{-3}, **b** [SDS]$_T$ = 4 × 10^{-2} mol·dm^{-3}, [PA]$_T$ = 150 × 10^{-2} mol·dm^{-3}, **c** [SDS]$_T$ = 4 × 10^{-2} mol·dm^{-3}, [bpy]$_T$ = 125 × 10^{-4} mol·dm^{-3}; $\lambda_{isosbestic}$ = 517 nm

went through maxima due to competition between H$^+$ and Na$^+$. SDS is actually a mixture of sodium alkyl sulfates with sodium dodecyl sulfate being the predominant one. Also, the solutions usually contain 0.5 % or more sodium sulfate. SDS makes a micro heterogeneous environment and catalyses the reaction in which the reaction preferentially occurs at the micelle. Solute and surfactant monomers transfer between water and micelles much faster than the thermal reactions but not faster than rapid photochemical or radical reactions. FTIR spectra (Fig. 6) are useful in examining micelle–ion structures, and sharp signals indicate rapid reagent transfer and show that the monomers have free movement in spherical micelles but are less free in large rod-like micelles [36].

The Stern region represents an interfacial zone between the hydrocarbon core and bulk water. In line with this division in zones, in the pseudo-phase formalism, micelles and bulk water are considered to be different reaction regions, exerting different reaction medium effects. As such, taking into account the clear differences between the micellar core and the Stern region, these zones themselves can also be considered as two distinct pseudo-phases inside the micelles. Remarkable success in enhancing reaction rates has been achieved by applying micelles as catalysts (introducing catalytic moieties in micelle forming SDS surfactant). In micelle-assisted catalysis, micelles solubilize the reactants and the catalyst, placing them in close proximity inside the small volume of the micellar pseudophase [37].
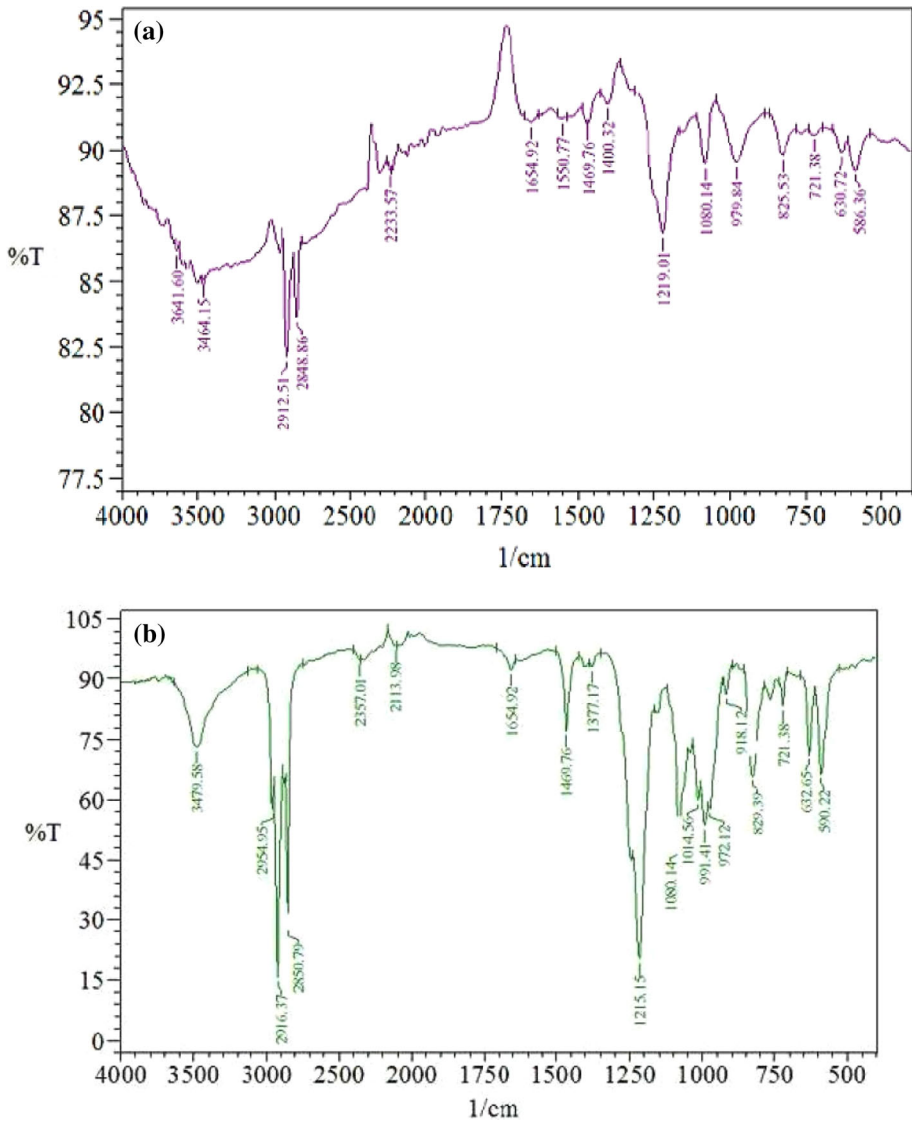
Fig. 6 Infrared spectra of **a** aqueous SDS and **b** its solution with 1.0×10^{-3} mol·dm^{-3} malonic acid

The positive catalytic effect of SDS indicates the incorporation/association of the reactants into or at the surface of the anionic SDS micelles. In this case for SDS, there is a strong electrostatic attraction between the anionic head group ($-OSO_3^-$) and the positively charged reactive Cr(VI) species. Thus, an increase in the effective concentration of Cr(VI) within a small volume of nanometer sized SDS micelles takes place. In addition, the partitioning of malonic acid in the micellar pseudophase cannot be ruled out because the Stern layer is water rich (the water activity in the aqueous phase and in the micellar pseudophase is similar.

(a)

(b)
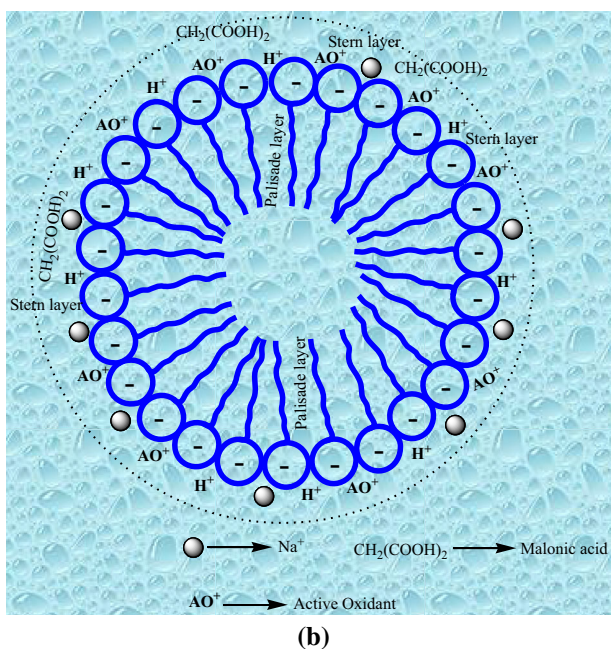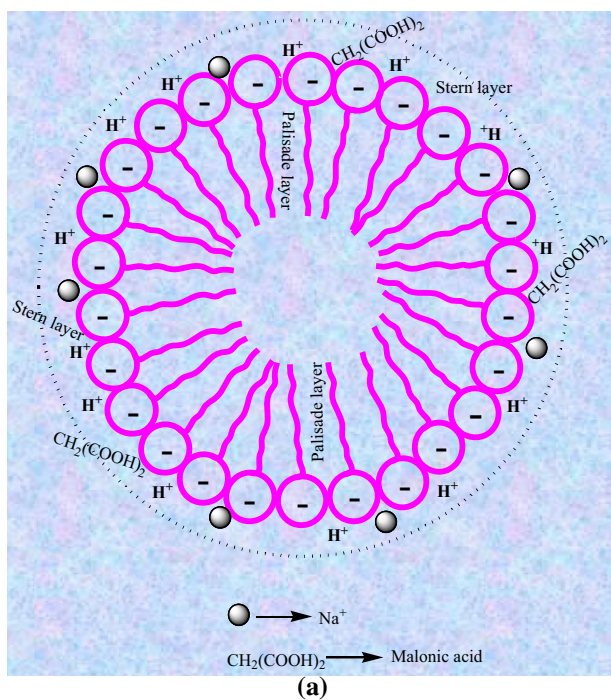
Scheme 1 Schematic model showing probable reaction site for the SDS micellar mediated oxidation reaction between: **a** malonic acid and proton; **b** substrate and active oxidant [$AO^+ = Cr(VI)$–promoter complex]

Now the Cr(VI)–promoter complex forms a positively charged association complex with malonic acid, so they can accumulate in the Stern layer of SDS micelles (Scheme 1a, b). This increases the effective concentrations of the reactants as well as increases the collision probability giving rise to a higher reaction rate [38, 39]. Interaction of SDS molecules with substrate malonic acid results in increasing the reaction rate or changing the yield of reaction and sometimes these surfactant molecules act as reactants [40]. The role of the surfactant in this case is to facilitate substrate solubilization and its close contact with the catalyst. In fact, interactions between substrate dissolved within micelles and water soluble charged metal catalysts are possible by employing surfactants with complementary charge with respect to the catalyst, thus favoring [36] the interaction between the two reaction partners in the Stern layer of the micelles (Scheme 1).

3.4 Partitioning of Reactants in Micellar Environment

The Cr(VI)–promoter complexes for PA, bipy, and phen represented as AO^+, a cationic complex, have been argued as the active oxidants in the promoted path. The most prominent acceleration for the malonic acid oxidation process is observed in the SDS catalyzed bipy promoted path (Table 1). The maximum rate enhancement arises from preferential partitioning of the positively charged [Cr(VI)–bpy] and neutral substrate in the micellar surface. Acceleration of the rate is also observed when combinations of SDS and any of the three hetero-aromatic nitrogen bases (PA, bipy and phen) are used (Table 1). Because of the electrostatic attraction, it can be distributed in the micellar pseudo-phase of the anionic surfactant. In the presence of SDS micelles, the oxidation process can reach both the micellar pseudo-phase (where both the active oxidant and substrate are preferentially concentrated) and aqueous phase to give the observed rate acceleration [41–43]. The active oxidants Cr(VI)–PA, Cr(VI)–bipy and Cr(VI)–phen complexes react with malonic acid to form a ternary complex that undergoes redox decomposition in a rate limiting step [44], giving rise to the product.

4 Interaction of Substrate (MA) with SDS Micelles

4.1 FTIR Study

The interaction between malonic acid and the surfactant was characterized by FTIR. The bands at 3464, 2912, 1467, 1221, 1078 and 867 cm^{-1} correspond (Fig. 6a) to water O–H stretching vibration, C–H stretching and bending, S=O stretching vibration of SO_4 from the SDS molecule and C–H stretching, respectively. The asymmetric and symmetric CH_2 stretching vibrational frequencies (v_{as} (CH_2) and $v_{sym}(CH_2)$) are observed at 2912 and 2848 cm^{-1}, respectively. As observed in Fig. 6a, $v_{as}(SO_2)$ is located at 1219 cm^{-1}.

The observation of an intense band in 1219 cm^{-1} (Fig. 6b), the same as that in Fig. 6a, may be an indication of strong head-to-head lateral interaction. An important aspect of the SO_2 symmetric vibrational feature is its observation at 1080 cm^{-1} due to the $v_{sym}(SO_2)$ mode being shifted. The explanation for this shift is the loss of interaction between the head group and counter ions [45]. Figure 6a, b depicts the FTIR spectra of SDS and SDS-capped malonic acid. From Fig. 6a it is to be noted that the symmetric and asymmetric –CH_2 stretching vibrations of pure SDS lie at 2912 and 2848 cm^{-1} and remained (Fig. 6b) almost same in the presence of malonic acid within the experimental errors. Therefore, from FTIR results, it is clear that the peaks due to the SDS head group region are shifted

without any significant shift in the hydrocarbon tail region. These results confirm the stabilization of malonic acid by encapsulation and interaction of SDS in the head group region [46].
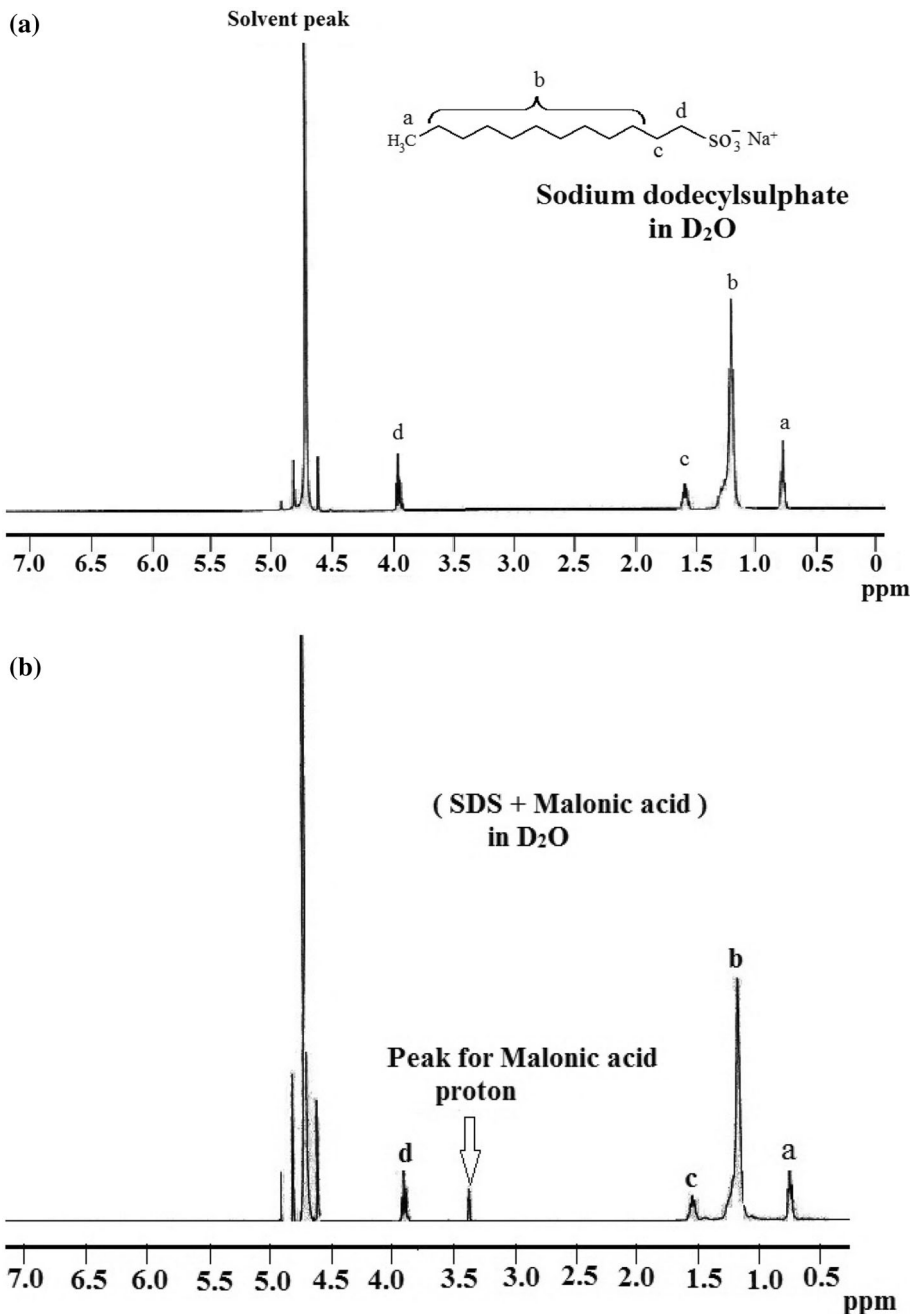

Fig. 7 The ^{1}H-NMR spectrum of SDS (**a**) and SDS + malonic acid (**b**) in D_2O

4.2 ^{1}H-NMR Study

Malonic acid interactions with SDS monomers were investigated by the analysis of chemical shifts in the SDS protons (Fig. 7). Addition of SDS surfactant above its CMC (2×10^{-2} mol·dm^{-3}), with malonic acid (75×10^{-4} mol·dm^{-3}), caused a distinct upfield shift. Notably the chemical shifts in the proton signals of SDS from normal micelles (Fig. 7a) and in the presence of malonic acid are distinctly different (Fig. 7b). This is an indication that the SDS micelle structures are modulated in the presence of malonic acid. On the other hand, the NMR measurement with malonic acid and SDS displayed broader proton peaks, with very little change in the chemical shifts of the dodecyl chains due to the hydrophobic–hydrophilic interaction (Table 2).

5 Interaction of Cr(VI) Species with SDS Micelles

5.1 DLS Study

It was found from the plot (Fig. 8) that, in the case of SDS, the size or diameter of micelles change when malonic acid is added to the micellar medium. The plot informs us about changes in micellar diameter when reactants are present in the reaction medium. This helps us to understand that an interaction occurs between substrate (malonic acid) and SDS with the "Stern layer" of the micelle. The overall charge of SDS micelles is anionic, therefore SDS interacts with the aggregates and substrate molecules reside in the "Stern layer" of the micelle. The size of SDS was 4.5 nm as found in the plot. Upon interaction of substrate (malonic acid) with the outer surface of the aggregates the diameter of the SDS micelle increases from 4.5 to 6.3 nm.

5.2 HRTEM Study

The HR-TEM investigation was done at 20 kV acceleration voltage using a lacy carbon coated Cu grid of 300 mess size in a HR-TEM microscope. Samples were prepared by placing the sample mixture drops directly on the copper grids using a micropipette. The reactants, including the surfactant, present in the aqueous mixture were allowed to settle. TEM pictures of SDS (Fig. 9a) are presented, which illustrate the multiple morphologies of the aggregates made from the surfactant SDS. Also, the micrograph suggests a relatively narrow size distribution of the micelle diameters, but a widely variable length. TEM images of blank SDS micelles and Cr(VI) + SDS micelles are taken Fig. 9a, b. From Fig. 9a it can be observed that SDS micelles are roughly spherical in aqueous acid media. Small holes are seen in the micellar surface when Cr(VI) is added to the SDS aqueous acidic medium. So we can say that incorporation of Cr(VI) takes place inside the micelle.

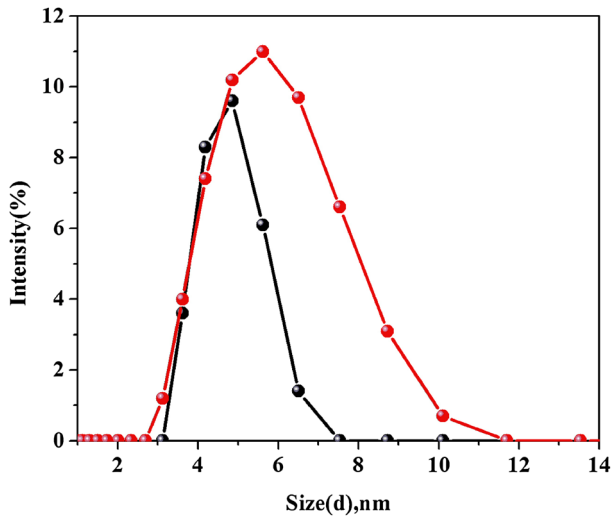| Table 2 Chemical shift values (ppm) for different protons of SDS	SDS	SDS + malonic acid
a-protons	0.763	0.754–0.721
b-protons	1.260	1.155
c-protons	1.545	1.538–1.520
d-protons	3.919	3.915–3.882

Fig. 8 Variation of particle size distribution of SDS micelles/vesicles determined by dynamic light scattering (DLS). The average particle sizes for only (*black sphere*) SDS is 4.5 nm and malonic acid incorporated (*red sphere*) SDS is 6.3 nm. [malonic acid] $= 5 \times 10^{-4}$ mol·dm^{-3}, [SDS] $= 2 \times 10^{-2}$ mol·dm^{-3} (Color figure online)
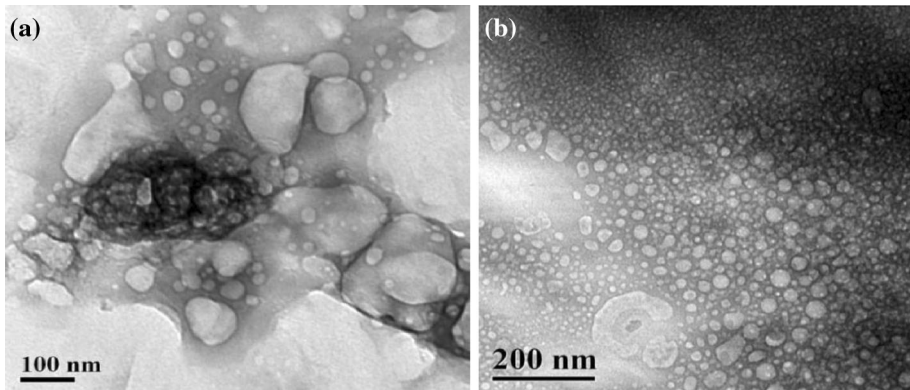

Fig. 9 TEM images of **a** SDS micelles and **b** SDS micelles and Cr(VI)

6 Reaction Mechanism

In the uncatalyzed path the proposed mechanism involves the formation of [Cr(VI)–S] (S = malonic acid) complex followed by a slow redox decomposition (Scheme 2) giving rise to a HC(COOH)$_2$ radical, which is rapidly oxidized by Cr(IV). Chromium(IV) forms by the reaction:

$$Cr(VI) + Cr(IV) \rightleftharpoons 2Cr(V), \quad K_a = 4.0 \times 10^{-4} \quad (Refs. 47, 48)$$
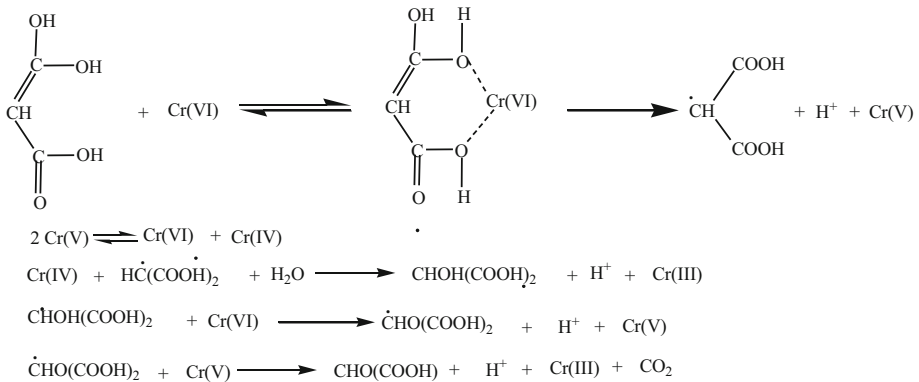
Scheme 2 Partial oxidation of malonic acid by Cr(VI)

Thus the formation of hydroxymalonic acid and its further partial oxidation to glyoxylic acid can be accounted for by the above reaction schemes.

7 Separation of Surfactant from the Reaction Mixture

The surfactant was separated out from the reaction mixture by simple chemical precipitation with the help of calcium hydroxide solution. The aqueous filtrate was obtained after the completion of reaction, and the product was neutralized by adding $Ca(OH)_2$ (15 mmol). When $Ca(OH)_2$ was added in small lots to the aqueous filtrate, the sodium dodecylsulfate was precipitated in the aqueous solution as calcium dodecylsulfate (CaDS) [36]. The precipitate of CaDS was then separated from the reaction vessel through filtration.

Table 3 A comparative result for oxidation of malonic acid using different oxidants and catalysts

Catalyst	Conditions	k_{obs} (s^{-1})	Reference
–	$[\text{Malonic acid}]_T = 5 \times 10^{-2}$ mol·dm^{-3} $[\text{Cr(VI)}] = 1.98 \times 10^{-3}$ mol·dm^{-3} $[\text{H}_2\text{SO}_4]_T = 1.0$ mol·dm^{-3} $I = 3.0$ mol·dm^{-3} 60 °C	0.96×10^{-4}	[13]
–	$[\text{Malonic acid}]_T = 0.05$ mol·dm^{-3} $[\text{Ce(IV)}] = [\text{H}_2\text{SO}_4]_T = 1.5$ mol·dm^{-3} 25 °C	6.0×10^{-3}	[14]
–	$[\text{Malonic acid}]_T = 4.0 \times 10^{-2}$ mol·dm^{-3} $[\text{Mn(III)}] = 5 \times 10^{-4}$ mol·dm^{-3} $[\text{H}_2\text{SO}_4]_T = 0.5$ mol·dm^{-3} 20 °C	60×10^{-3}	[15]
SDS = 0.04 mol·dm^{-3}, 2,2′-bipyridine = 0.0125 mol·dm^{-3}	$[\text{Malonic acid}]_T = 75 \times 10^{-4}$ mol·dm^{-3} $[\text{Cr(VI)}]_T = 5 \times 10^{-4}$ mol·dm^{-3} $[\text{SDS}]_T = 4 \times 10^{-2}$ mol·dm^{-3} 30 °C	2730×10^{-4}	Present work

In the Table 3 the result obtained for the rate constant for the SDS mediated chromic acid oxidation of malonic acid is higher, compared to other reported works.

8 Conclusions

The electron transfer kinetics oxidation of malonic acid to glyoxylic acid in aqueous micellar media rather than in a hazardous solvent have been studied because there is a growing and challenging preference that synthetic chemists carry out organic transformations using ''green'' aqueous solutions. In this context, the use of water as a solvent features many benefits: not only is water safe, but it can also potentially improve reactivities and selectivities of organic transformations, and thus simplify the work up procedures. Micelles act as nano-reactors and efficiently increase the effective local concentration of reactants inside its surface. The ^{1}H-NMR studies establish that the stern region of micellar reactor is the most probable location of reactants in this oxidation process. It is interesting to note that the rate of oxidation increased drastically when SDS was used as the micellar catalyst in combination with the bipy promoter at a particular concentration. The product was confirmed by a 2,4-DNP test, IR studies of the DNP derivative, and ^{13}C-NMR. DLS improves the size effect of the micelle. TEM images are helpful to predict the formation of compound micelles. In conclusion, the overall investigation of the present work is simple, cost effective and eco-friendly, as compared to previous research. Micellar catalysis by SDS in association with a bipy promoter increases the rate of reaction around 650 fold with no consumption of energy and time. Considering all the above facts, it is quite reasonable to select a combination of SDS and bipy as the most suitable for chromic acid oxidation of malonic acid to glyoxylic acid in aqueous media.

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