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1. Introduction

Saffron is the dried stigma of a flower scientifically known as "*Crocus sativus* Linn", a plant with four principal bioactive components, namely, crocin, crocetin, picrocrocin and safranal.¹ Other components are carbohydrates, mineral, mucilage, vitamin (riboflavin, thiamine), anthocyanin, carotene, lycopene and zeaxanthin.² The bioactive metabolites, such as crocin, picrocrocin and safranal, are responsible for the colour, taste and flavour of saffron, respectively. Crocins (red colored water soluble carotenoids), glycosides of crocetin are the main biologically active metabolites of saffron.³ The extraction, separation and purification process of these metabolites from saffron has been investigated and discussed comprehensively.^{4,5}

Surfactants (surface active agents) are unique class of chemical compounds that are omnipresent in modern society with a wide range of fascinating applications.⁶ Sugar-based surfactants are a type of amphiphilic materials having sugar moieties in their chemical structure. The name of sugar-based surfactants indicates that their hydrophilic part is a carbohydrate, generally mono or oligosaccharide. The incorporation of such natural saccharide into the amphiphile structure produced interesting physicochemical and biological functionality. In addition to the biodegradability, nontoxicity and

Biocompatible natural sugar-based surfactant assisted oxidation of citric acid by MnO_4^- in absence and presence of SDS⁺

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Crocin, a natural carotenoid with antioxidant properties, was used in the present investigation as a surfactant in the citric acid– MnO_4^- redox system for the first time. A conventional UV-Visible spectroscopic technique was used to determine the reaction rate with and without crocin. The reaction follows first-order kinetics with respect to [citric acid] under pseudo-first conditions. Crocin was found to catalyze the redox reaction, which was rationalized in terms of the solubilization and/or incorporation of reactants into the crocin aggregates. The micellar catalysis was explained using Menger–Portony pseudo-phase model modified by Bunton *et al.* The various parameters associated with the micellar catalysis and activation parameters were determined and discussed. Sodium dodecyl sulphate (SDS) inhibits citric acid oxidation. A mixture of non-ionic and anionic surfactant (crocin + SDS) also shows the inhibitory effect rather than catalytic effect. In the mix micellization, the SDS characters and electrostatic repulsion, dominate over the solubilization of reactants in to the Stern layer. On the basis of the observed results, probable mechanisms and reaction sites were proposed.

biocompatibility, sugar-based surfactants have a variety of potential applications.7 Surfactants based on natural resources have attracted considerable interest rather than petrochemical precursors because of the global demand for biocompatible materials. The excellent biodegradable nature of sugar-based surfactants has gained much attention as they are derived from renewable sources and are dermatological compatible.8,9 Sugar-based surfactants are a comparatively new class of surfactants with their increased use owing to their precious properties and nontoxic effects. These surfactants may occur in nature and can be synthesised chemically.10,11 The micelle concentrations (cmc) for nonionic sugar-based surfactants have the same order of magnitude as generally shown by conventional non ionic surfactants.12 The aggregation behaviour of sugar based surfactants is dependent on the hydrophobic chain length and the head-group structure. It has been found that if the hydrophilic head group is smaller and the hydrophobic part is larger than the cmc can be reduced.13 Different types of anionic, cationic, and nonionic sugar-based surfactants have been reported.14-16 Alkyl polyglucosides are sugar based surfactants that have attracted considerable attention^{17,18} owing to their non-toxic nature to the environment¹⁹ and remarkable physical properties such as low surface tension.20 Naess et al.21 reported the surface and aggregation properties of carotenoid crocin, a naturally occurring bolaform non-ionic surfactant by UV-Vis spectroscopy and surface tension studies. Khan et al. recently examined the self aggregation behaviour of crocin (natural sugar based bolaamphiphile) and its micellization with the cationic surfactant and cetyltrimethylammonium bromide



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(CTAB) and anionic sodium dodecyl sulfate (SDS) surfactant.²² The permanganate oxidation process is eco-friendly and it is one of the most versatile and vigorous oxidants used for the oxidation of organic and inorganic compounds in acidic and micellar media.²³⁻²⁵ Manganese(vII) is reduced to Mn(II) during the oxidation processes *via* many manganese species having different oxidation states such as Mn(vI), Mn(v), Mn(IV) and Mn(III). The appearance of these intermediate oxidation states depends on various reaction conditions, types of substrate and their stability. The importance of a sugar-based surfactant and sodium dodecyl sulfate (SDS) in the micellar catalysis of citric acid–MnO₄⁻ reaction system was investigated. In the present investigation, we examine the usefulness of antioxidant crocin as a sugar-based surfactant in citric acid oxidation by permanganate.

2. Experimental and methods

2.1. Materials

Citric acid (99%, BDH), potassium permanganate (99%, BDH), sodiumdodecyl sulphate (98%, Fluka), crocin (99%, Sigma Aldrich) were used as received. Double distilled deionized water (conductivity of $(1-2) \times 10^{-6}$ ohm⁻¹ cm⁻¹), previously subjected to deionization, followed by distillation in alkaline KMnO₄, was used as a solvent for the preparation of stock solutions. A solution of KMnO₄ was standardized with sodium thiosulphate and stored in an amber glass bottle.

2.2. Kinetic procedure

To determine the reaction rates, a series of kinetic runs were performed under different experimental conditions (crocin + MnO₄⁻, citric acid + MnO₄⁻, crocin + citric acid + MnO₄⁻, crocin + citric acid + SDS + MnO_4^- , and citric acid + SDS + MnO_4^-) at a fixed temperature. In a typical experiment, all required reactants solutions except MnO₄⁻ were taken in a separate three neck reaction vessel fitted with a double walled condenser to arrest evaporation and kept in a water bath at the desired temperature to attain equilibrium for each kinetic run. Both reactants were thermostated separately at the desired temperature before mixing. The required solution of MnO₄⁻ was added to the reaction vessel. The zero time was taken when half of the MnO₄⁻ solution had been added. The reaction volume was always 50 cm³. The progress of the reaction was followed by measuring the absorbance of the remaining MnO₄⁻ at definite time intervals at 525 nm (λ_{max} for MnO₄⁻) on a UV-Visible spectrophotometer (UV-260 Shimadzu, with 1 cm quartz cuvette). Pseudo-first-order conditions ([citric acid] \geq [MnO₄⁻]) were used to determine the rate constants (k_{obs} , s⁻¹). Duplicate runs obtained results that were reproducible to within $\pm 5\%$. To see the formation of water-soluble colloidal MnO₂ as an intermediate, some kinetic experiments were also conducted at 410 nm (permanganate has negligible absorbance at this wavelength). The pH of the reaction mixture was also measured at the end of each kinetic experiment and the pH drift during the course of the reaction was very small (within 0.03 unit). The pseudo-first-order rate constants were calculated from the

slopes of the tangents to the plots of log(absorbance) *versus* time with a fixed-time method for all kinetic experiments.^{25,26} The values of the average linear regression coefficient, $\gamma \geq 0.998$, were obtained for each kinetic run.

2.3. Products identification and stoichiometry

For identification of the oxidation products of citric acid, $[MnO_4^{-}] = 5.0 \times 10^{-3} \text{ mol } dm^{-3} \text{ was added in an aqueous}$ solution of [citric acid] = 5.0×10^{-2} mol dm⁻³ at room temperature. The formation of CO2 was estimated quantitatively. The evolved carbon dioxide was flushed out by passing a continuous current of pure N_2 gas (free from O_2 and CO_2), absorbed in standard Ba(OH)₂ solution and then titrated with a standard HCl solution.27 On the other hand, a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl was added to the reaction mixtures. The formation of yellow residue suggests that reaction product has a carbonyl group. The precipitate was filtered and washed with ethanol. The same method was repeated with known [3-oxopentanedioic acid]. The FT-IR spectra were obtained and identified as the 2,4-dinitrophenylhydrazone of 3-oxopentanedioic acid. The oxidation product of crocin was confirmed as follows: a solution of $[MnO_4^{-}] = (5.0 \times 10^{-3} \text{ mol } dm^{-3})$ was added to an aqueous solution of $[\text{crocin}] = 5.0 \times 10^{-3} \text{ mol dm}^3$. After completion of the reaction, a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl was added to the reaction mixture and was left overnight in a refrigerator. The yellow precipitate was filtered, washed and dried. The -CHO group was identified by the infrared spectrum of the yellow precipitate, which showed carbonyl stretching at 1725 cm^{-1} . It is well known that one –OH group of primary alcohol oxidizes to one -CHO. It was further observed that the aldehyde does not undergo oxidation with MnO₄⁻ under the present kinetic conditions because the spot test for carboxylic acid was negative.

3. Results and discussion

3.1. General considerations

Crocin, a diester of disaccharide gentiobiose and the dicarboxylic acid crocetin, is a natural sugar-based, highly unsaturated bola form bio surfactant, responsible for the color of saffron, and forms an orange color in water (Fig. 1). The oxidation kinetics of carbohydrates-MnO₄⁻ redox systems have been the subject of various investigations. In general, mineral acids were used as a source of [H⁺].²⁸⁻³⁰ Before attempting to discuss the role of crocin as a surfactant to the oxidation of citric acid by MnO₄⁻, it is necessary to discuss the stability of the crocin with MnO₄⁻ (oxidant). Tondre and his co-workers suggested avoiding the use of even buffer solutions to maintain the pH of micellar solutions because the control of pH and ionic strength is not as straightforward in micellar solutions as in ordinary solvents.31 We did not use any mineral acid to control the pH of the working solutions.31 The pH was found to be constant with increasing [crocin] (ESI Table T1[†]). To gain insight into the stability of crocin, a series of kinetic experiments were carried with different [crocin] (varying from 0.0 to



Fig. 1 Most active constituents of samon (crocus sativus Linn).

 $20.0 \times 10^{-4} \text{ mol dm}^{-3}$) at a fixed [MnO₄⁻] = $6.6 \times 10^{-4} \text{ mol dm}^{-3}$, and temperature = $20 \,^{\circ}\text{C}$ (ESI Table T1†). The observed results are depicted graphically in Fig. 2 as a k_{obs} -[crocin] profile. The crocin oxidation rates were found to increase with



Fig. 2 Plot of [crocin] versus k_{obs} . Reaction conditions: [MnO₄⁻] = 6.6 $\times 10^{-4}$ mol dm⁻³, temperature = 20 °C.

increasing [crocin]. The plot of log k_{obs} versus log[crocin] is linear with slope = 0.99, indicating a first-order dependence with [crocin] under our experimental conditions. The reducing nature of crocin might be due to the presence of gentiobiose sugar moieties (two units of p-glucose joined with β 1–6 linkage). One polar head group of gentiobiose residue has one primary –OH and 6 secondary –OH groups. It is well known that the oxidation of secondary –OH is not possible under normal reaction conditions.³² Thus, only primary –OH of gentiobiose is responsible for the reduction of MnO₄⁻ (Scheme 1).

In Scheme 1, the reaction proceeds through the formation of a complex between the gentiobiose unit of crocin and MnO_4^- . In the next step of this reaction, which is the rate determining step, the complex under goes one-step two electrons oxidation–reduction mechanism leading to the formation of Mn(v) (HMnO₃) and the oxidation product of the gentiobiose unit, *i.e.*, corresponding aldehyde.

3.2. Citric acid- MnO_4^- with crocin

To establish the role of [citric acid] and $[MnO_4^{-1}]$, a series of kinetic experiments were performed for different $[MnO_4^{-1}]$ (3.3 to 6.6×10^{-4} mol dm⁻³) at constant [citric acid] = 16.6×10^{-3} mol dm⁻³ and for different [citric acid] (from 0.0 to 20.0×10^{-3} mol dm⁻³) at fixed $[MnO_4^{-1}] = 6.6 \times 10^{-4}$ mol dm⁻³ (ESI Table T2†). The pseudo-first-order rate constants are also depicted





Scheme 1 Oxidation of crocin by MnO_4^- .

graphically (Fig. 3). The effect of [citric acid] indicates that the first-order kinetics at low citric acid concentrations shifts to higher-order at higher concentrations. To gain insight into the role of crocin (bola-form surfactant) on the oxidation kinetics of the citric acid– MnO_4^- redox system, the effects of [crocin]



Fig. 3 Plot of [citric acid] *versus* k_{obs} . Reaction conditions: [MnO₄⁻] = 6.6×10^{-4} mol dm⁻³, temperature = 20 °C.

Table 1 Values of the cmc and other parameters for the crocinassisted oxidation of citric acid by MnO_4^{-a}

Reaction conditions	10^4 cmc (mol dm ⁻³)	Parameters	Values
Crocin only Crocin + MnO_4^- Crocin + citric acid SDS only SDS + MnO_4^- SDS + citric acid	8.4 7.9 8.2 80.3 80.1 80.3	$10^4 k_w$ $10^2 k_w$ K_c K_s $10^3 k_m$	12.9 s ⁻¹ 8.0 mol ⁻¹ dm ³ s ⁻¹ 50 mol ⁻¹ dm ³ 45 mol ⁻¹ dm ³ 9.2 s ⁻¹

Activation parameters

$$\begin{split} E_{a} &= 32 \ (18) \ \text{kJ mol}^{-1} \\ \Delta H^{\#} &= 35 \ (21) \ \text{kJ mol}^{-1} \\ \Delta S^{\#} &= -87 \ (-130) \ \text{J K}^{-1} \ \text{mol}^{-1} \\ \Delta G^{\#} &= 61 \ (56) \ \text{kJ mol}^{-1} \end{split}$$

^{*a*} Reaction Conditions: $[MnO_4^{-}] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, [citric acid] = 16.6 × 10⁻³ mol dm⁻³, and temperature = 25 °C. For the crocin catalysed reaction, the activation parameters are given in the parenthesis.

(varying from 0.0 to $20.0 \times 10^{-4} \text{ mol dm}^{-3}$) in the presence of fixed [citric acid] = $16.6 \times 10^{-4} \text{ mol dm}^{-3}$, and [citric acid] (varying from 0.0 to $20.0 \times 10^{-4} \text{ mol dm}^{-3}$) at constant [crocin]

Table 2 Values of pH at different [citric acid], [crocin] and [SDS]

10 ³ [SDS]	10 ³ [citric acid]	10 ⁴ [crocin]	
$(\text{mol } \text{dm}^{-3})$	$(\text{mol } \text{dm}^{-3})$	$(\text{mol } \text{dm}^{-3})$	рН
		- 0	
0.0	0.0	5.0	6./
0.0	3.3	0.0	3.2
6.0	0.0	0.0	2.9
6.0	3.3	0.0	3.3
6.0	5.5	0.0	3.4
6.0	10.0	0.0	3.3
6.0	16.6	0.0	3.4
6.0	16.6	5.0	3.3
6.0	16.6	10.0	3.4
6.0	16.6	15.0	3.2
6.0	16.6	17.5	3.2
4.0	16.6	5.0	3.4
8.0	16.6	5.0	3.4
10.0	16.6	5.0	3.4
15.0	16.6	5.0	3.3
20.0	16.6	5.0	3.4

= 5.0×10^{-4} mol dm⁻³, respectively, studied at [MnO₄⁻] = 6.6×10^{-4} mol dm⁻³ and temperature = 20 °C (Table 2). The observed results are summarized in Fig. 4 and 5. An inspection of Fig. 4 indicates that the plot has an intercept on the *y*-axis, which might be due to the modest self oxidation of crocin by MnO₄⁻ (Fig. 2). The rate constants increase rapidly with [crocin]. The increase in k_{obs} was observed even at [crocin] < cmc (= 8.2×10^{-4} mol dm⁻³).²¹ This fact is usually interpreted as the reactants inducing micelle formation (surfactant molecules start aggregating below cmc). The catalysis observed under the experimental conditions is in agreement with similar bimolecular reactions in the presence of a surface active agent.^{33,34} It is further probable that crocin molecules display a certain catalytic effect, which may be rationalized in terms of increasing concentrations of the reactants (citric acid and MnO₄⁻) in the



Fig. 4 Plot of [citric acid] versus k_{obs} . Reaction conditions: $[MnO_4^-] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, $[crocin] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 20 °C.



Fig. 5 Plot of [crocin] versus k_{obs} . Reaction conditions: $[MnO_4^-] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, [citric acid] = $16.6 \times 10^{-3} \text{ mol dm}^{-3}$, temperature = 20 °C.

micellar pseudo phases through solubilization, incorporation, and/or association with hydrophobic interactions. The mechanism to the oxidation of citric acid by MnO_4^- is presented in Scheme 2.

In Scheme 2, eqn (1) is a one-step two electrons transfer oxidation–reduction mechanism (rate determining step), which leads to the formation of Mn(v) and 3-oxopentanedioic acid. Mn(v) is unstable, and is immediately converted to the stable form of Mn, *i.e.*, MnO_2 (eqn (2)). Water soluble colloidal MnO_2 , generally, formed as an intermediate in the MnO_4^- redox reactions.²⁴ Finally, colloidal MnO_2 reacts with another molecule of citric acid and formed Mn(i) as the reduction product of MnO_4^- .

3.3. Probable role of crocin

Crocin is a bola-form non-ionic sugar based bio surfactant. The rate enhancement of citric acid from 20.0×10^{-4} to 60.0×10^{-4} s⁻¹ with increasing [crocin] from 4.0×10^{-4} to 20.0×10^{-4} mol dm⁻³ (*ca.* 60 folds) clearly suggests that crocin aggregates, micelles, solubilize the reactants into its small volume. It was

$\begin{array}{c} \mathrm{CH}_{2}\mathrm{COOH}\\ \mathrm{HO-C-COOH}\\ \mathrm{CH}_{2}\mathrm{COOH} \end{array} + \mathrm{MnO}_{4}^{-} \end{array}$	k, rds	$\begin{array}{c} \mathrm{CH}_{2}\mathrm{COOH} \\ \mathrm{C=O} \\ \mathrm{CH}_{2}\mathrm{COOH} \end{array} + \mathrm{CO}_{2} + \mathrm{H}_{2}\mathrm{MnO}_{4}^{-} \end{array}$	(1)
$2H_2MnO_4^- + H^+$	Fast	$HMnO_4^- + MnO_2 + 2H_2O$	(2)
$\begin{array}{c} CH_2COOH\\ HO-C-COOH\\ CH_2COOH \end{array} + MnO_2 \end{array}$	Fast	$\begin{array}{c} CH_2COOH \\ C=O \\ CH_2COOH \end{array} + CO_2 + H_2MnO_2 \\ CH_2COOH \end{array}$	(3)
$3HMnO_4^- + H^+$	Fast	$2MnO_4^- + MnO_2 + 2H_2O$	(4)
$-\frac{d[MnO_4^-]}{dt} = k[MnO_4^-][citric a]$	ucid]		
or			
$k_{aba} = k[citric acid]$			

Scheme 2 Oxidation of citric acid by MnO₄⁻.

observed that the reaction rate increases with [crocin] (Fig. 3), which clearly demonstrate the crocin catalytic effect not only above but even below the cmc (i.e., micellar as well as premicellar catalyses are observed).35,36 It is well known that surfactant aggregates, micelles, change the reaction rates by incorporating the reactants into the micellar pseudo-phases. Various factors, such as the nature of the reactants, nature of micelles, and interactions (hydrophobic, electrostatic, hydrogen bonding, and van der Walls forces) are involved in the solubilization processes.37 Micelles are a porous cluster with a rough surface, deep-water-filled cavities, and water-rich surfaces, and do not provide a uniform reaction medium.³⁸ The water activity in the Stern layer in no different compared to the bulk medium. Micellar surfaces are water rich and the polarities of micellewater are lower than those of bulk water. Citric acid is water soluble. In the present case, the incorporation of citric acid and MnO₄⁻ into the micellar palisade- and Stern-layer of crocin micelles cannot be ruled out. The Stern-layer surface area of crocin aggregates is higher due to the presence of two polar gentiobiose sugar moieties at the head groups.²¹ As a result, the chances of MnO₄⁻ and citric acid solubilization in the reaction site, *i.e.*, Stern-layer, increases.^{39,40} Therefore, the surface area of the reactants decreases, which in turn increases the reaction rates. It is not possible to precisely locate the exact site for the micelle-mediated reactions, but at least, localization of the reactants can be considered. A possible understanding (although highly schematic) could be that as shown in Scheme 3.

3.4. Analysis of crocin catalyzed kinetic data

The catalytic behavior of crocin on the present study can be explain in terms of the pseudo phase model of micelles proposed by Menger and Portony⁴¹ and modified by Bunton *et al.* (Scheme 4).³⁴⁻³⁶

$$k_{\rm obs} = \frac{k_{\rm w}[\text{citric acid}] + (K_{\rm s}k_{\rm m} - k_{\rm w})M_{\rm C}^{\rm S}[{\rm D_n}]}{1 + K_{\rm s}[{\rm D_n}]}$$
(5)

where k_w and k_m are the second-order rate constant (first-order rate constant/[(citric acid)_w]) and second-order rate constant (first-order rate constant), respectively, in aqueous and micellar pseudo phases. $M_C^S =$ mole ratio of citric acid bound to the micellar head group ($M_C^S = [(citric acid)_m]/[D_n]$). To evaluate the value of M_C^S , the following equilibrium is considered.



Scheme 3 Schematic model showing the probable reaction site for sugar-based surfactant mediated oxidation reaction for citric acid-MnO₄⁻ redox system.



Scheme 4 Schematic of a micellar catalyzed reaction according to the pseudo-phase model, where K_s , K_c , k_w , k_m and $[D_n]$ have their usual significance. According to eqn (5) the following rate-law was derived for the bimolecular reaction (both the reactants are considered to be incorporated in the micellar phase) and Bunton considered the total volume of the micelles as a separate phase.

$$(\text{citric acid})_{w} + D_{n} \xrightarrow{K_{c}} (\text{citric acid})_{m}$$
 (6)

$$k_{\rm obs} = \frac{\left[({\rm citric \ acid})_{\rm m} \right]}{\left[({\rm citric \ acid})_{\rm w} \right] \left(D_{\rm n} - \left[({\rm citric \ acid})_{\rm m} \right] \right)}$$
(7)

Using eqn (8) and (9), a quadratic eqn (10) can be obtained, which is solved for [(citric acid)_m], with the help of a computer programme (where $K_c =$ an adjustable parameter).⁴²

$$(\text{citric acid})_{w} + D_{n} \xleftarrow{K_{c}} (\text{citric acid})_{m}$$
 (8)

$$K_{\rm c} = \frac{\left[\left(\text{citric acid}\right)_{\rm m}\right]}{\left[\left(\text{citric acid}\right)_{\rm w}\right]\left(D_{\rm n} - \left[\left(\text{citric acid}\right)_{\rm m}\right]\right)}$$
(9)

$$K_{c}[(\text{citric acid})_{m}]^{2} - (1 + K_{c}[D_{n}] + K_{c}[\text{citric acid}]_{T})[(\text{citric acid})_{m}] + K_{c}[D_{n}][(\text{citric acid})_{T}] = 0$$
(10)

For the calculation, the cmc values of crocin were calculated using the surface tension method under different experimental conditions (Table 1). A nonlinear least-square technique was used to determine K_c for which the value of Σd_i^2 turned out to be a minimum and was taken as the best value of K_c (Table 1).

3.5. Citric acid- MnO_4^- with SDS and crocin + SDS

It has been established that SDS surfactant is unstable with permanganate in an acidic solution of perchloric acid. The firstorder kinetics with respect to [SDS] at low concentrations shifted to second-order at higher concentrations. The -O-SO₃⁻ group was responsible for the oxidative degradation of SDS by MnO₄^{-.43} Therefore, the SDS stability is a crucial problem for the kinetic experiments that we address first. In the first set of experiments, a solution of SDS (5.0 $\rm cm^3,~0.01~mol~dm^{-3})$ was added to a solution of MnO_4^{-} (5.0 cm³, 0.001 mol dm⁻³) and the spectra of MnO₄⁻ were obtained at different time intervals. Interestingly, the absorbance of the reaction mixture remains constant for ca. 2 h, indicating that SDS is not oxidized and/or decomposed with MnO₄⁻ under our experimental conditions. The shape and position of the MnO₄⁻ spectra also does not alter in the presence of SDS. Thus, we may confidently state that SDS and MnO₄⁻ do not have any type of interactions due to electrostatic repulsion.

In the second set of experiments, a series of kinetic experiments were performed in the presence of [SDS] (from 1.3×10^{-3}



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Fig. 6 Plot of [SDS] versus k_{obs} . Reaction conditions: $[MnO_4^-] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, [citric acid] = $16.6 \times 10^{-3} \text{ mol dm}^{-3}$, temperature 20 °C.

to $66.6 \times 10^{-3} \text{ mol dm}^{-3}$) at a constant $[\text{MnO}_4^{-1}] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, [citric acid] = $16.6 \times 10^{-4} \text{ mol dm}^{-3}$, and temperature 20 °C. Interestingly, the reaction rate first increases (from 12.9×10^{-4} to $22.1 \times 10^{-4} \text{ s}^{-1}$) at lower [SDS] = $3.3 \times 10^{-3} \text{ mol dm}^{-3}$ and then decreases with increasing [SDS]. At higher [SDS] $\ge 16.6 \times 10^{-3} \text{ mol dm}^{-3}$, the SDS has no significant impact on the reaction rate (remain constant). Fig. 6 clearly indicates that the overall reaction rate decreases with increasing [SDS], which might be due to the electrostatic repulsion between the negative head group of SDS ($-OSO_3^{-1}$) and MnO_4^{-1} . Such type of repulsion can not be ruled completely with $-OSO_3^{-1}$ and lone-pairs of citric acid -OH and -COOH groups. Surprisingly, the crocin behaviour has been changed entirely from catalysis (Fig. 6) to inhibition (Fig. 7) in the presence of SDS.



Fig. 7 Plot of [SDS] versus $k_{\rm obs}$ in presence of crocin. Reaction conditions: $[MnO_4^-] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$, [citric acid] = $16.6 \times 10^{-3} \text{ mol dm}^{-3}$, [crocin] = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = $20 \,^{\circ}\text{C}$.

It is well known that pH shifts by about plus and/or minus two units are expected at the surface of CTAB and/or SDS micelles with respect to the bulk pH.44-46 However, a series of experiments were also performed to see any change in the macroscopic pH of the working solution in presence of different [SDS], [citric acid], and/or [crocin]. The pH was found nearly constant with increasing [SDS], [crocin], and [citric acid] (weak acid; $pK_1 = 3.13$, $pK_2 = 4.76$ and $pK_3 = 6.39$). The observed values of pH are given in Table 2. This is not surprising because ionic micelles show a marked difference in the effective local pH to exist at its micellar surface over that in the bulk aqueous solvent. The SDS aggregates concentrate hydrogen ions into the Stern layer so that there is extensive build up of the non ionic species of citric acid. On the other hand, crocin is a neutral nonionic species, which does not influence the pH of the working solutions.

Mahapatro et al. and Hasan and Rocek in their pioneering study proposed a one step three-electron oxidation mechanism for α-hydroxy acids and suggested that the oxidation of alcohols is accelerated by the presence of a carboxyl group (despite the electronegative character of this group, which should reduce the activity of the alcoholic group towards oxidation).47,48 In a reaction mixture containing MnO_4^- + crocin + citric acid, there is competition between crocin and citric acid to react with MnO_4^- first. The rate constants were found to be $1.0 \times 10^{-4} \text{ s}^{-1}$, $12.9\times10^{-4}~\text{s}^{-1}$ and $21.2\times10^{-4}~\text{s}^{-1}$ for crocin (5.0 $\times10^{-4}$ mol dm $^{-3}$), citric acid (16.6 \times 10 $^{-3}$ mol dm $^{-3}$), and crocin + citric acid $(5.0 \times 10^{-4} \text{ mol } \text{dm}^{-3} + 16.6 \times 10^{-4} \text{ mol } \text{dm}^{-3}$; ESI Tables T1 and T2[†]), at $[MnO_4^-] = 6.6 \times 10^{-4} \text{ mol dm}^{-3}$. The citric acid oxidation rate is 13 times higher than crocin, which might be due to the presence of -COOH at the α -carbon (-OH group carbon atom).⁴⁷ Higher oxidation rate (ca. $21.2 \times 10^{-4} \text{ s}^{-1}$ in presence of crocin) would be associated with the catalytic effects of crocin aggregates. The reduction potential of citric acid is higher than the reducing sugar (gentiobiose residue of crocin). Upon the addition of any MnO₄⁻ in a reaction mixture containing citric acid and crocin, citric acid was first oxidized, because it had a higher reducing potential. However, crocin oxidation cannot be ruled out completely but its oxidation alters the aggregation behaviour of crocin.

3.6. Activation parameters

To evaluate the activation parameters, k_{obs} was obtained by conducting kinetic experiments at different temperatures (from 25 to 40 °C) with and without surfactant(s) (ESI Fig. S1 and S2†). The activation energy (E_a), enthalpy of activation ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$), obtained from the Arrhenius and Eyring equations, are summarized in Table 1. Comparing the values with those calculated in an aqueous medium for the same reaction, we find that the presence of a sugar-based surfactant, crocin aggregates lowers the E_a , which clearly suggest that crocin aggregates (micelles) concentrate and/or solubilize the reactants within its small volume through hydrophobic and hydrogen bonding interactions, which in turn decreases the surface area of the reactants. As a result, the reaction rates increases with [crocin] and thus the citric acid MnO_4^- is catalysed by the nonionic micelles of sugar based bola crocin surfactant. This lowering occurs not only through the solubilization of both reactants (citric acid and MnO_4^-) into the polar region of aggregates, *i.e.*, Stern-layer, but also through stabilization of the transition state (Scheme 2: eqn (1)).³⁴ Thus, Arrhenius and Eyring equations are applicable to the micellar media, and the sensitivity of the micelle structure to temperature is kinetically unimportant.

4. Conclusions

In this study, we demonstrate the use of sugar-based crocin as a surfactant in the redox kinetics of citric acid by MnO₄⁻. Crocin is unstable in the presence of MnO₄⁻. Its reaction rate is negligible compared to citric acid. In the presence of crocin, the citric acid oxidation rate increases from $12.9 \times 10^{-4} \text{ s}^{-1}$ to 62.9 \times 10⁻⁴ s⁻¹ (nearly 60 fold). The catalytic behaviour has been explained in terms of the incorporation and/or solubilization of reactants into the micellar aggregates through hydrogen bonding. SDS has an inhibitory effect on citric acid oxidation, which might be due to the electrostatic repulsion between the negative head group of SDS and the reactants. The presence of two surfactants (anionic SDS + non-ionic crocin) also inhibits the reaction rate. During the whole processes, electrostatic forces play a more important role compared to hydrogen bonding. The activation energy increases and decreases with SDS and crocin, respectively.

References

- 1 S. Kianbakht and R. Hajiaghaee, J. Med. Plants Res., 2011, 10, 82–89.
- 2 M. S. Moghaddasi, J. Med. Plants Res., 2010, 4, 427-430.
- 3 M. J. Heravi, H. Parastar and H. E. Najafabadi, *J. Chromatogr. A*, 2009, **1216**, 6088–6097.
- 4 M. Zougagah, A. Rios and M. Valcarcel, *Anal. Chim. Acta*, 2006, **578**, 117–121.
- 5 L. Cullere, F. S. Juan and J. Cacho, *Food Chem.*, 2011, **127**, 1866–1871.
- 6 L. L. Schramm, E. N. Stasiukb and D. G. Marangonic, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem., 2003, 99, 3-48.
- 7 U. Komorek and K. A. Wilk, *J. Colloid Interface Sci.*, 2004, 271, 206–211.
- 8 K. Holmberg, Curr. Opin. Colloid Interface Sci., 2001, 6, 148– 159.
- 9 X. Zeng, Z. Lu and Y. Liu, J. Surfactants Deterg., 2013, 16, 131– 137.
- 10 N. Neta, J. D. Santos, S. D. Sancho, S. Rodrigues, L. R. Goncalves, L. R. Rodrigues and J. A. Teixeira, *Food Hydrocolloids*, 2012, 27, 324–331.
- 11 Z. Jin, S. L. Liang, X. Q. Zhang, S. Y. Han, C. Q. Ren, Y. Lin and S. P. Zheng, *Biotechnol. Bioprocess Eng.*, 2013, **18**, 365– 374.
- 12 G. Garofalakis, B. S. Murray and D. B. Sarney, J. Colloid Interface Sci., 2000, 229, 391–398.
- 13 C. Blecker, S. Piccicuto, G. Lognay, C. Deroanne, M. Marlier and M. Paquot, *J. Colloid Interface Sci.*, 2002, **247**, 424–428.

- 14 R. C. Bzaito and O. A. E. Seoud, *Langmuir*, 2002, **18**, 4362–4366.
- 15 K. Zielińska, K. A. Wilk and A. Jezierski, J. Colloid Interface Sci., 2008, **321**, 408–417.
- 16 E. Soussan, A. P. Banu and S. Consola, *ChemPhysChem*, 2005, 6, 2492–2494.
- 17 I. Johansson, C. Strandberg, B. Karlsson, G. Karlsson and K. Prog, *Colloid Polym. Sci.*, 2000, **116**, 26–32.
- 18 C. Stubenrauch, Curr. Opin. Colloid Interface Sci., 2001, 6, 160–170.
- 19 P. Schöberl, W. Guhl, N. Scholz and K. Taeger, *Tenside, Surfactants, Deterg.*, 1998, 35, 279–285.
- 20 T. Yoshimura, K. Ishihara and K. Esumi, *Langmuir*, 2005, **21**, 10409–10415.
- 21 S. N. Naess, A. Elgsaeter, B. J. Foss, B. Li, H.-R. Sliwka, V. Partali, T. Melo and K. R. Naqvi, *Helv. Chim. Acta*, 2006, 89, 45–53.
- 22 Z. Khan, M. A. Malik, S. A. AL-Thabaiti, O. Bashir and T. A. Khan, *Dyes Pigm.*, 2016, **131**, 168–176.
- 23 R. M. Hassan, S. A. El-Gaiar and A. M. El-Samman, *Collect. Czech. Chem. Commun.*, 1993, **58**, 538–546.
- 24 M. A. Malik, S. A. Al-Thabiti and Z. Khan, *Colloids Surf., A*, 2009, **377**, 9–14.
- 25 R. A. Sheikh, F. M. Al-Nowaiser, M. A. Malik, A. O. Al-Youbi and Z. Khan, *Colloids Surf.*, *A*, 2010, **366**, 129–134.
- 26 S. A. Al-Thabaiti, Z. Khan, S. Hussain and O. Bashir, J. Mol. Liq., 2015, 207, 200–205.
- 27 Z. Khan, T. Singh, J. I. Hussain, S. A. Al-Thabaiti, E. H. El-Mossalamy and A. Y. Obaid, *Colloids Surf.*, B, 2013, 102, 578–584.
- 28 S. M. Z. Andrabi, M. A. Malik and Z. Khan, *Colloids Surf., A*, 2007, **299**, 58–64.
- 29 J. F. Perez-Benito, J. Colloid Interface Sci., 2002, 248, 130-135.

- 30 L. F. Sala, S. R. Signorella, M. Rizotto, M. I. Frascaroli and F. Gandolfo, *Can. J. Chem.*, 1992, **70**, 2046–2052.
- 31 R. Cierpiszewski, M. Hebrant, J. Szymanowski and C. Tondre, J. Chem. Soc., Faraday Trans., 1996, 92, 249–255.
- 32 J. March, Advanced organic chemistry: reactions, mechanisms, and structure, John Wiley & Sons, New York, 1985, ISBN 0-471-85472-7.
- 33 G. Cerichelli, G. Mancini, L. Luchetti, G. Savelli and C. A. Bunton, *Langmuir*, 1994, 10, 3982–3987.
- 34 C. A. Bunton, Adv. Colloid Interface Sci., 2006, 123, 333-343.
- 35 C. A. Bunton, F. Nome, F. H. Quina and L. S. Romsted, *Acc. Chem. Res.*, 1991, **24**, 357–364.
- 36 C. A. Bunton, J. Mol. Liq., 1997, 72, 231-249.
- 37 S. Tascioglu, Tetrahedron, 1996, 52, 11113-11152.
- 38 M. N. Khan, J. Chem. Soc., Perkin Trans. 2, 1990, 445-457.
- 39 M. Niyaz Khan, Int. J. Chem. Kinet., 1991, 23, 567-578.
- 40 N. S. M. Yusof and M. N. Khan, *Adv. Colloid Interface Sci.*, 2013, **193–194**, 12–23.
- 41 F. M. Menger and C. E. Portony, *J. Am. Chem. Soc.*, 1967, **89**, 4698–4703.
- 42 Kabir-ud-Din, J. K. J. Salem, S. Kumar and Z. Khan, J. Colloid Interface Sci., 1999, 215, 9–15.
- 43 Raju and Z. Khan, Bull. Chem. Soc. Jpn., 2005, 78, 1218–1222.
- 44 C. Tondre and M. Hebrant, J. Mol. Liq., 1997, 72, 279-294.
- 45 R. Bacaloglu and C. A. Bunton, J. Phys. Chem., 1989, 93, 1497–1502.
- 46 C. Tondre and M. Boumezioud, *J. Phys. Chem.*, 1989, **93**, 846–854.
- 47 S. N. Mahapatro, M. Krumpolc and J. Rocek, *J. Am. Chem. Soc.*, 1980, **102**, 3799–3806.
- 48 F. Hasan and J. Rocek, J. Am. Chem. Soc., 1975, 97, 1444-1450.