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ORIGINAL CONTRIBUTION

Kinetic study of oxidation of paracetamol by water-soluble colloidal MnO$_2$ in the presence of an anionic surfactant

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Md. Abu Bin Hasan Susan[3]

Abstract The kinetics of the oxidation of paracetamol [PCM] by water-soluble colloidal MnO$_2$ was investigated spectrophotometrically at 298 K in the absence and presence of an anionic surfactant, sodium dodecyl sulphate (SDS), in aqueous solution. The reaction was first order with respect to [MnO$_2$], [PCM] and [H$_2$SO$_4$]. The effects of [Mn(II)], [salt], dielectric constant and ionic strength of the medium on the kinetics of the reaction have also been examined. Micelles of SDS in aqueous solution accelerated the reaction rate, and partitioning of MnO$_2$ in favour of the micellar pseudophase was remarkable. The catalytic effect of SDS in aqueous solutions has been treated by well-defined mathematical (Tuncay), Menger and Portnoy, and Piszkiewicz models. The binding constant (7.59×10^{-2} mol^{-1} dm^3), dissociation constant (32.43), rate constant in the micellar phase (5.15×10^4 s^{-1}), cooperativity index (1.98) and various thermodynamic activation parameters have been evaluated, and on the basis of the observed kinetic data, possible reaction mechanism and rate law have been proposed.

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Introduction

Micellar catalysis has been an intriguing domain of research for the last few decades. There has been a surge of interest on catalysis of reactions by micelles of surfactants with a view to their widespread applications in chemical, industrial, pharmaceutical, environmental and biological fields. Surfactants are amphiphilic substances, and formation of micelles in aqueous solution is induced by the hydrophobic interaction among the hydrophobic moiety of the surface-active agent balanced by their hydration and electrostatic repulsive effects [1–5]. Hydrophobic substrates when dissolved in aqueous micellar solutions result in high localized concentration inside the core of the micelles and may interact with micellar aggregates (incorporated inside the core and/or bound on the surface of micelles) to enhance apparent reactivity, and as a consequence, the kinetics of a reaction may be significantly enhanced as compared to pure aqueous solution [3]. For ionic surfactants, micellization is favoured by the factors that cause reduction in the electrostatic repulsion among the hydrophilic moieties (i.e. micellar head groups) [6]. A thorough systematic study of coupled systems comprising electron transfer reaction and micelle formation process of surfactants might therefore distinctly help to understand the electron transport in enzymes [7]. Numerous studies have established beyond reasonable doubt the ability of micelles to alter the reaction rate, equilibrium and concentration of reactants within the interfacial region [8–11]. The notable attempts concern kinetic oxidation of various organic compounds like sugars [12–16], amino acid [17–21], ketones [22, 23] and drugs [24, 25] by various oxidants in the presence of micellar solutions. The oxidation of
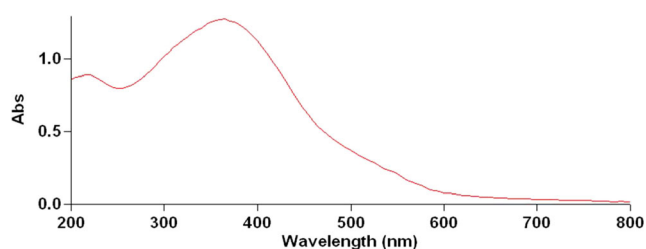
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Fig. 1 Absorption spectra of water-soluble colloidal MnO_2 (0.6×10^{-4} mol dm^{-3}) i.e. the reaction product of $KMnO_4$ (1.0×10^{-2} mol dm^{-3}) and $Na_2S_2O_3$ (1.0×10^{-2} mol dm^{-3})

paracetamol (PCM) as a substrate by colloidal MnO_2 in the micellar system also appears to be a suitable model reaction for unveiling the mechanism of micellar catalysis.

MnO_2 is the most effective and vital oxidizing agent and offers the potential for degrading various organic pollutants [26]. The existence of manganese(IV) in the aqueous solution in colloidal form and as negatively charged species has been reported in the literature [27–29], and the oxidizing ability has been found to be limited under ordinary conditions due to its insolubility [30]. In natural water, it exists as insoluble Mn(III) and Mn(IV) oxides and as soluble Mn(II) ions, which are thermodynamically stable in oxygenated solutions. Reactions between colloidal MnO_2 and an organic reductant can play an important role to convert MnO_2 into manganese by photo-oxidation [31, 32].

PCM, known as acetaminophen or (*N*-acetyl-4-aminophenol), is used in therapeutic purposes and is a frequently detected anthropogenic compound in pharmaceutical wastewater [33–36]. When the compound enters into the environment through anthropogenic sources, it causes harm to aquatic and terrestrial organisms [37]. Various techniques have therefore been reported for the degradation or transformation of PCM from the aqueous solutions which inter alia include advanced oxidation process using ozonation/H_2O_2/
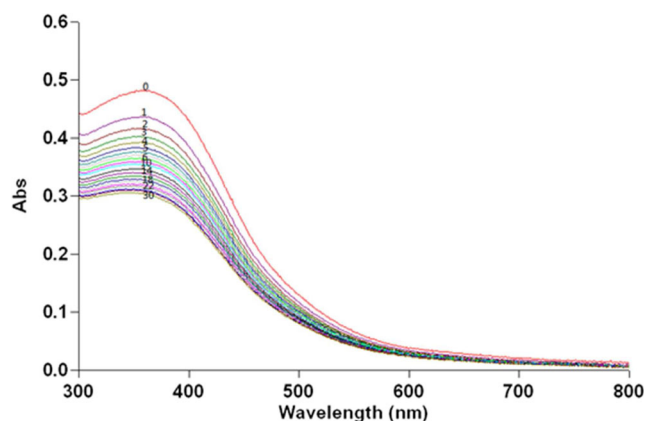

Fig. 2 UV-visible spectral changes during the oxidation of paracetamol by colloidal MnO_2 in the presence of anionic surfactant (SDS) in acidic medium at 298 K with time. (Conditions: [PCM] = 1.2×10^{-5} mol dm^{-3}, [MnO_2] = 0.6×10^{-4} mol dm^{-3}, [H_2SO_4] = 1.0×10^{-4} mol dm^{-3} and [SDS] = 8.0×10^{-3} mol dm^{-3}). The time interval during scan was 1 min
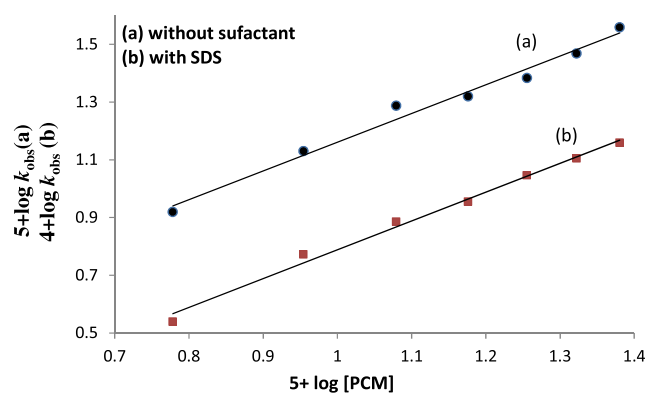

Fig. 3 Effect of [PCM] on k_{obs} for the oxidation of paracetamol by colloidal MnO_2 at 298 K. (Conditions: [MnO_2] = 1.2×10^{-4} mol dm^{-3}, [H_2SO_4] = 1.0×10^{-4} mol dm^{-3}, [SDS] = 8.0×10^{-3} mol dm^{-3} and [PCM] = (1) 0.6×10^{-3}, (2) 0.9×10^{-3}, (3) 1.2×10^{-3}, (4) 1.5×10^{-3}, (5) 1.8×10^{-3}, (6) 2.1×10^{-3} and (7) 2.4×10^{-3} mol dm^{-3})

UV [38], UV/Fe^{2+}/Cu^{2+} [39], UV/TiO_2 [40, 41], photodegradation [42, 43], TiO_2 and $CuO/TiO_2/Al_2O_3$ [44], Fe_3O_4 magnetic nanoparticles [45], photo-Fenton [46–49], solar/photo-Fenton processes [50] and kinetic degradation [51–56] etc. For instance, Kumar and Khan [56] studied the kinetics of the formation and decomposition of water-soluble colloidal MnO_2 spectrophotometrically in aqueous neutral media and reported the unusual stabilization of water-soluble colloidal MnO_2 during the oxidation of paracetamol by MnO_4^-. However, an efficient cost-effective universal method with a complete understanding of the mechanism of degradation of PCM in acidic as well as neutral media and in the presence of micelles still remains an elusive goal.

In the present investigation, we therefore aim at degrading PCM by water-soluble colloidal MnO_2 in the absence and presence of micellar solution of an anionic surfactant, sodium dodecyl sulphate (SDS), in aqueous acidic solution and comparing the reaction kinetics of the uncatalyzed reaction with those catalyzed by micellar solutions. We have focussed our attention in deducing an appropriate rate law with kinetic results to elucidate the reaction mechanism in the absence and presence of SDS in aqueous solution. Attempts have been made to identify the oxidation product of PCM and evaluate thermodynamic activation parameters and theoretically explain the results. The ultimate goal has been to unveil the mechanism of micellar catalysis of the title reaction for successful exploitation of the advent of the micellar systems for degradation of a commonly used drug in an efficient way under different conditions.

Experimental

Reagents

Potassium permanganate (E. Merck), sodium thiosulphate (E. Merck), paracetamol (S.D. Fine, India), sulphuric

acid (E. Merck), potassium nitrate (E. Merck), acetonitrile (E. Merck), manganese(II) chloride (E. Merck), sodium dodecyl sulphate (E. Merck), potassium chloride (CDH, India), potassium bromide (E. Merck) and sodium disulphate (E. Merck) were used as received without further purification. Solutions were prepared using triply distilled water.

Preparation and characterization of colloidal MnO$_2$

Water-soluble colloidal MnO$_2$ was prepared following the procedure reported by Perez-Benito et al. [57–59]. The dark pink-coloured solution of KMnO$_4$ (1.0×10^{-2} mol dm^{-3}) suddenly changed into transparent dark brown-coloured solution upon drop-wise addition of Na$_2$S$_2$O$_3$ (1.0×10^{-2} mol dm^{-3}) solution with proper stirring. Development of the brown colour solution is due to the formation of colloidal MnO$_2$ solution (0.6×10^{-4} mol dm^{-3}), which was confirmed by the absorption maximum, λ_{max}, of 375 nm (Fig. 1). The solution of colloidal MnO$_2$ was kept in the dark and stored for prolonged use. The addition of various inorganic salts in the solution of colloidal MnO$_2$ causes precipitation in the Mn(IV) form, which confirms the synthesis of colloidal MnO$_2$ [28, 29] according to the following reaction.

$$8MnO_4^-(aq) + 3S_2O_3^{2-} + 2H^+ \rightarrow 8MnO_2(aq) + 6SO_4^{2-} + H_2O \quad (1)$$
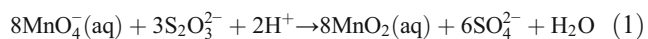
Kinetic measurements

In all the kinetic runs, the oxidation of PCM by colloidal MnO$_2$ was carried out under pseudo first-order conditions. PCM concentration was at least tenfold excess over the MnO$_2$ concentration. The requisite amounts of reactants (MnO$_2$ and H$_2$SO$_4$) were taken in the test tube, and the reaction was initiated on the addition of PCM in both the aqueous and micellar catalyzed media at 298 K. The absorbance of the decay of colloidal MnO$_2$ was recorded spectrophotometrically at the wavelength corresponding to absorption maximum
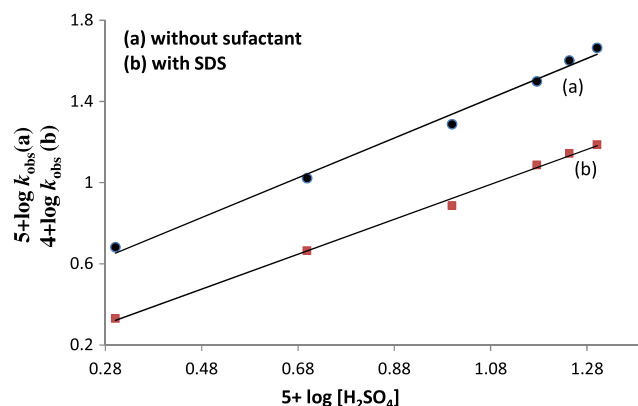

Fig. 4 Effect of [H$_2$SO$_4$] on k_{obs} for the oxidation of paracetamol by colloidal MnO$_2$ at 298 K. (Conditions: [MnO$_2$] = 1.2×10^{-4} mol dm^{-3}, [PCM] = 1.2×10^{-3} mol dm^{-3}, [SDS] = 8.0×10^{-3} mol dm^{-3} and [H$_2$SO$_4$] = (1) 0.2×10^{-4}, (2) 0.5×10^{-4}, (3) 1.0×10^{-4}, (4) 1.5×10^{-4}, (5) 1.75×10^{-4} and (6) 2.0×10^{-4} mol dm^{-3})

(λ_{max} = 375 nm) at various time intervals. All the kinetic runs were normally followed up to 80 % completion. The spectral changes during the course of the reaction in both the uncatalyzed and micelle (SDS)-catalyzed reactions are shown in Fig. 2 and Fig. S1. The pseudo first-order rate constants (k_{obs} or k_Ψ in s^{-1}) were evaluated from semilogarithmic plots of log(abs) versus time.

Stoichiometry and product analysis

Under the condition of [MnO$_2$] $\gg$ [PCM], various sets of experiments were performed with a different ratio of [MnO$_2$]/[PCM]. The mixture containing PCM, H$_2$SO$_4$ and MnO$_2$ were allowed to stand for 72 h at room temperature to ensure the completion of the reaction. Unreacted MnO$_2$ was estimated spectrophotometrically after the completion of the reaction. Unreacted MnO$_2$ was estimated spectrophotometrically after the completion of the reaction. The [MnO$_2$] in the residues estimated in each set demonstrated that 1 mol of PCM consumed 1 mol of MnO$_2$. The reaction with the stoichiometry may be given by

(2)
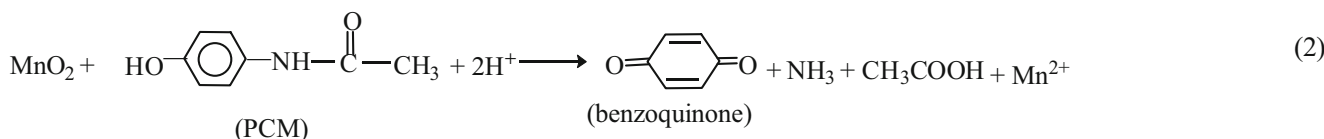
The products were separated out with ether after the completion of the kinetic experiments. The main oxidation product of PCM after evaporation of the ether layer was benzoquinone [60, 61], which was detected by spot test [62, 63]. The presence of ammonia in aqueous solution as an ammonium ion could also be detected [64, 65].

The products identified also support the projected reaction mechanism (vide infra).

For varying concentrations of SDS (from 1.0×10^{-3} to 8.0×10^{-3} mol dm^{-3}), 1.2×10^{-4} mol dm^{-3} of MnO$_2$ was reacted with [H$_2$SO$_4$] (1.0×10^{-4} mol dm^{-3}) and [PCM] (1.2×10^{-3} mol dm^{-3}). The absorption spectra of the mixture
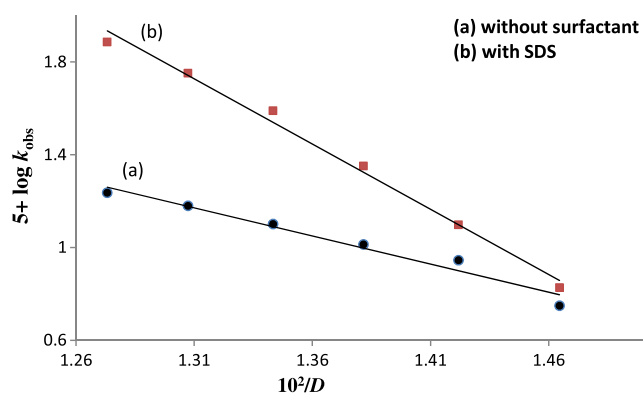
Fig. 5 Effect of dielectric constant on k_{obs} for the oxidation of paracetamol by colloidal MnO_2 at 298 K. (Conditions: $[MnO_2] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[PCM] = 1.2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0 \times 10^{-4}$ and $[SDS] = 8.0 \times 10^{-3}$ mol dm^{-3})

after completion of the reaction were checked. No noticeable change in the λ_{max} and absorption spectra (figure not shown) as a whole proves that the SDS is not degraded by PCM. SDS has also been not found to undergo degradation by MnO_2 as evident from no change in absorption spectra of MnO_2 in the presence of SDS at a wide range of concentrations.

Test for free radicals

The influence of free radicals on the title reaction was investigated. Acetonitrile was added in the reaction mixture in a certain amount and was allowed to stand for 24 h under inert atmosphere. Dilution of the mixture using methanol resulted in precipitation to indicate interruption by the free radicals in the reaction mechanism.

Results and discussion

Oxidation of PCM by colloidal MnO₂ in aqueous solution

The absorbance at 375 nm due to colloidal MnO_2 was found to decrease with time (Fig. 2) to indicate the decay of colloidal MnO_2 during the course of reaction with PCM in aqueous solution both in the absence and presence of surfactant to

Table 1 Thermodynamic parameters for activation energy in the absence and presence of SDS

Thermodynamic parameters	k_{obs} in aqueous medium (10^{-4} s^{-1})	k_{obs} in aqueous SDS solution (10^{-4} s^{-1})
Ea (kJ mol^{-1})	62.86	51.75
$\Delta H^{\#}$ (kJ mol^{-1})	60.38	49.29
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−105.07	−130.81
$\Delta G^{\#}$ (kJ mol^{-1})	29.07	10.29
logPz	7.30	5.96

[#] Change in enthalpy of activation

cause degradation of PCM. The kinetics of the reaction with systematic variation of different factors was investigated.

Effect of [MnO₂]

The kinetics of the reaction was investigated at various concentrations of MnO_2 (0.4×10^{-4}–1.8×10^{-4} mol dm^{-3}) at constant [PCM] (1.2×10^{-3} mol dm^{-3}) and $[H_2SO_4]$ (1.0×10^{-4} mol dm^{-3}) at 298 K both in the absence and presence of SDS, and order of the reaction with respect to $[MnO_2]$ was evaluated. Linearity of the semilogarithmic plots of log(abs) versus time indicates that the reaction is first order with respect to $[MnO_2]$ in both media. The values of the observed rate constant, k_{obs}, decreased as the initial $[MnO_2]$ increased (Table S1, Fig. S3). This may be attributed to the flocculation of colloidal MnO_2 particles [29, 30, 32]. This is in agreement with the observations by Kumar and Khan [56].
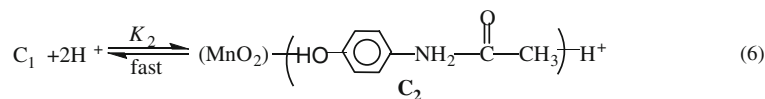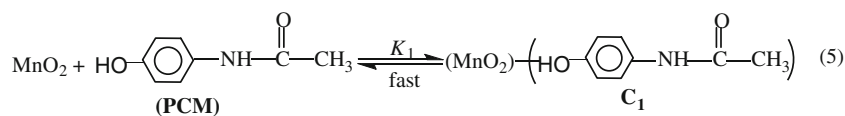
Effect of [PCM]

The concentration of the substrate, [PCM], was varied (0.6×10^{-3}–2.4×10^{-3} mol dm^{-3}) at a fixed concentration of all other reactants at 298 K, and the rate of the reaction was monitored. The reaction rate was found to increase linearly with increasing [PCM] in the absence of SDS (Table S1), and the reaction therefore followed the first-order kinetics with respect to PCM. For both in the absence and presence of SDS, the plot of log k_{obs} versus log [PCM] are straight lines with a slope of 0.995 ($R^2 = 0.982$) (Fig. 3) to substantiate the evaluation. This is in sharp contrast to the literature [56]. In the presence of SDS, the reaction was also observed to be first order with respect to [PCM], and the k_{obs} value increased (3.46×10^{-4}–14.43×10^{-4} s^{-1}) with increasing [PCM] in the range of 0.6×10^{-3} to 2.4×10^{-3} mol dm^{-3} (Fig. 3).

Effect of pH

Effect of pH on the kinetics of the title reaction has been investigated. The concentration of H_2SO_4 was varied in the range of 0.2×10^{-4} to 2.0×10^{-4} mol dm^{-3} to study the influence of pH on the rate constant at constant concentrations of MnO_2 and PCM at 298 K both in the absence and presence of SDS. The rate constant increased with increasing H_2SO_4 concentration i.e. decreasing pH, which agrees well with Kumar and Khan [56] (Table S1), and the order with respect to H_2SO_4 was found to be unity (Fig. 4).

The configuration of PCM is likely to change depending on the pH of the solution since an increase in the pH enhances the rate of the title reaction. PCM and MnO_2 react to form a complex, which reacts with the H$^+$ ions to form another complex which is positively charged and is involved in the rate determining step. The formation of the positively charged

Scheme 1 Reaction scheme for oxidation of paracetamol by water-soluble colloidal MnO_2 in the absence of SDS

$$MnO_2 + HO-\!\!\bigcirc\!\!-NH-\overset{O}{\underset{}{C}}-CH_3 \underset{fast}{\overset{K_1}{\rightleftharpoons}} (MnO_2)\!\!\left(HO-\!\!\bigcirc\!\!-NH-\overset{O}{\underset{}{C}}-CH_3\right) \quad (5)$$

$$\underset{C_1}{}$$

$$C_1 + 2H^+ \underset{fast}{\overset{K_2}{\rightleftharpoons}} (MnO_2)\!\!\left(HO-\!\!\bigcirc\!\!-NH_2-\overset{O}{\underset{}{C}}-CH_3\right)\!\!H^+ \quad (6)$$

$$\underset{C_2}{}$$

$$C_2 \xrightarrow[slow]{k} Products \quad (7)$$

complex relies on the pH of the system to result in enhancement in the rate of the reaction with decreasing pH.

The influence of pH on the catalysis by SDS may be explained similarly. SDS is an anionic surfactant, and the active ingredient is negatively charged. The counterion, Na^+, of SDS is diffused in the Stern layer of the micelles. When pH is increased, H^+ ions can be in close vicinity with the anion of the micellized SDS replacing less mobile Na^+ ions and may promote the formation of a complex in the system in the rate determining step to cause further enhancement of catalysis. The addition of H^+ ions therefore influences the catalysis by negatively charged SDS micelles.

Effect of ionic strength

The effect of ionic strength on the reaction rate was examined using Brønsted and Bjerrum theory [51, 52, 66] for reactions involving two charged species given by

$$\log k_1 = \log k_0 + 1.02 Z_A Z_B I^{1/2} \quad (3)$$

where Z_A and Z_B indicate the valencies of the ions A and B, I is ionic strength and k_1 and k_0 refer to the rate constants in the presence and absence of the added electrolyte, respectively. A positive slope means that Z_A and Z_B have similar signs in the reaction, and the rate of reaction increases with increasing ionic strength, and vice versa. In the present case, the observed
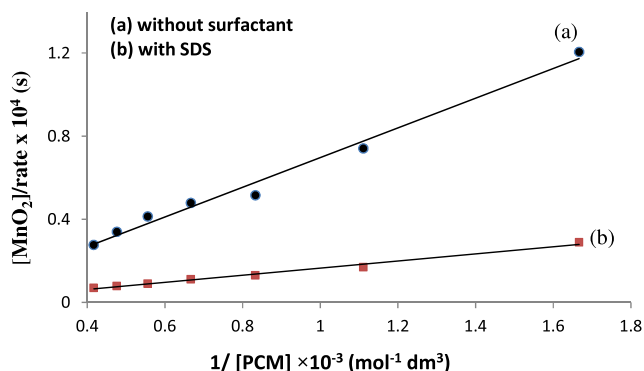
rate of the reaction did not show any appreciable change and the rate remained constant with change in concentration of KNO_3 (3.0×10^{-3}–9.0×10^{-3} mol dm^{-3}) in the aqueous system in the absence and presence of SDS. The ionic strength does not thereby change the kinetics of the reaction.

Effect of dielectric constant

Acetonitrile did not undergo any reaction with the oxidant under experimental conditions and could therefore be used as a solvent. To investigate the influence of dielectric constant on the kinetics of the reaction, different amount of acetonitrile was used in the reaction mixture keeping [PCM], [MnO_2] and [H_2SO_4] constant for all runs at 298 K in aqueous medium. The rate decreased for lowering the dielectric constant of the medium (Table S2). The effect is given by

$$\log k_1 = \log k_0' - \frac{Z_A Z_B e^2 N}{2.303(4\pi\varepsilon_o)d_{AB}RT} \times \frac{1}{D} \quad (4)$$

where Z_A and Z_B are the charges of reacting ions, d_{AB} is the size of the activated complex, k_0 refers to the rate constant in a medium of infinite dielectric constant, D is the dielectric constant and T is the absolute temperature. A negative slope of the plot of log k_1 versus $1/D$ (Fig. 5) is indicative of a possible interaction between negative ions and a dipole or between two dipoles, while a positive slope indicates an interaction between positive ions and dipoles [67, 68]. The rate of the

Fig. 6 Verification of rate law for 1/[PCM] on the oxidation of paracetamol by colloidal MnO_2 in the absence and presence of SDS at 298 K. (Conditions: [MnO_2] = 1.2×10^{-4} mol dm^{-3} and [H_2SO_4] = 1.0×10^{-4} mol dm^{-3})

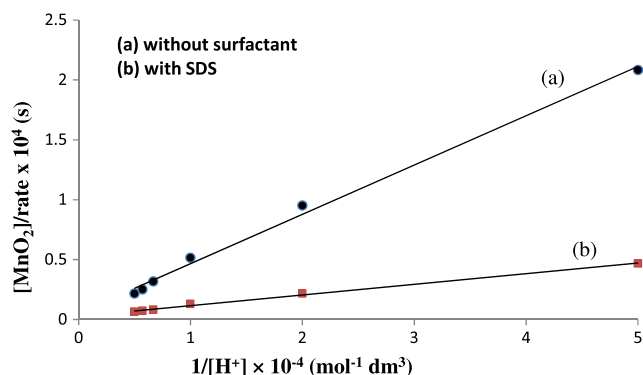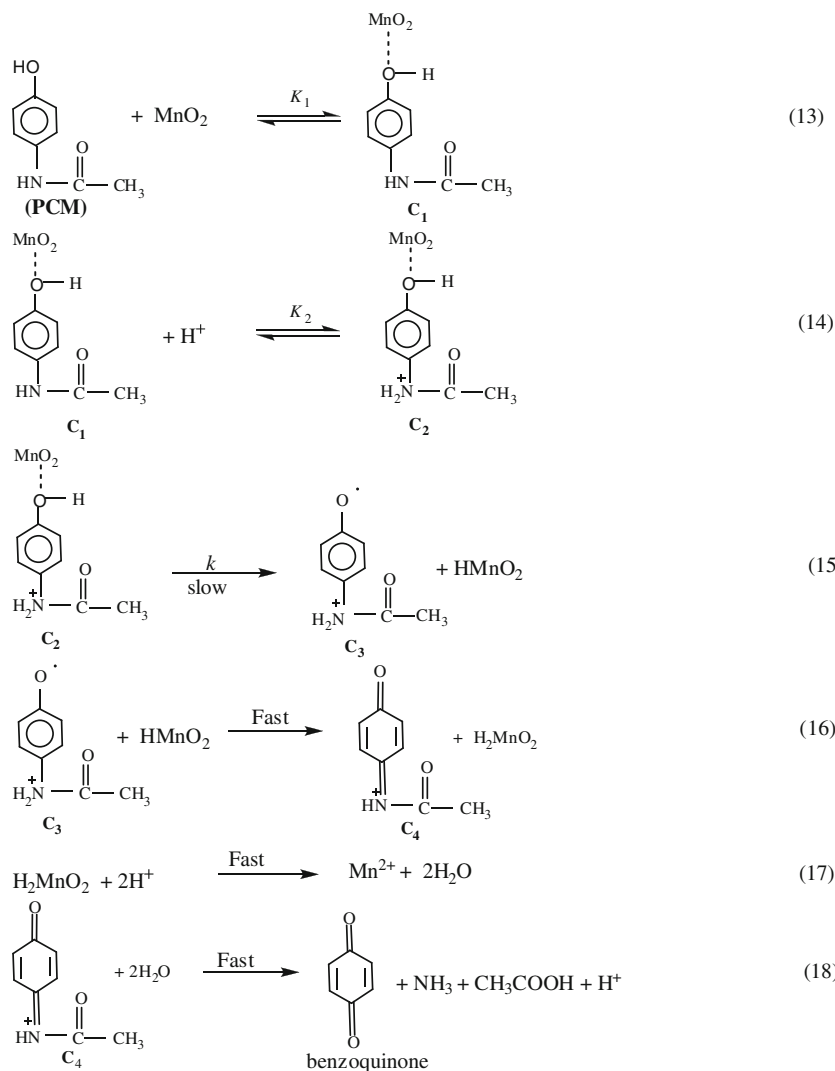**Fig. 7** Verification of rate law for 1/[H$^+$] of oxidation of paracetamol by colloidal MnO_2 in the absence and presence of SDS at 298 K. (Conditions: [PCM] = 1.2×10^{-3} mol dm^{-3} and [MnO_2] = 1.2×10^{-4} mol dm^{-3})

Scheme 2 Reaction mechanism for oxidation of paracetamol by water-soluble colloidal MnO_2 in the absence of SDS

$$C_1 \quad (13)$$

$$C_1 + H^+ \xrightleftharpoons{K_2} C_2 \quad (14)$$

$$C_2 \xrightarrow[\text{slow}]{k} C_3 + HMnO_2 \quad (15)$$

$$C_3 + HMnO_2 \xrightarrow{\text{Fast}} C_4 + H_2MnO_2 \quad (16)$$

$$H_2MnO_2 + 2H^+ \xrightarrow{\text{Fast}} Mn^{2+} + 2H_2O \quad (17)$$

$$C_4 + 2H_2O \xrightarrow{\text{Fast}} \text{benzoquinone} + NH_3 + CH_3COOH + H^+ \quad (18)$$

reaction decreased with decreasing dielectric constant of the medium both in the absence and presence of SDS (Table S2, Fig. 5).

The absorption spectra of the products did not exhibit any change due to change in the amount of acetonitrile. The absorption maximum (λ_{max}) also remained unchanged (figure not shown). Since the degradation products could be identified beyond reasonable doubt and also followed the stoichiometric ratio, possibility of a decrease in concentration of MnO_2 due to reaction with acetonitrile is unlikely. These are decisive of no reaction of acetonitrile with MnO_2.

Effect of [Mn(II)]

During the oxidation of PCM by colloidal MnO_2, the role of added Mn(II) was investigated. The concentration of Mn(II) ($MnCl_2$) was varied, and the reaction rate was found to decrease with increasing [Mn(II)] when other variables and

Scheme 3 Reaction mechanism for oxidation of paracetamol by water-soluble colloidal MnO_2 in the presence of SDS
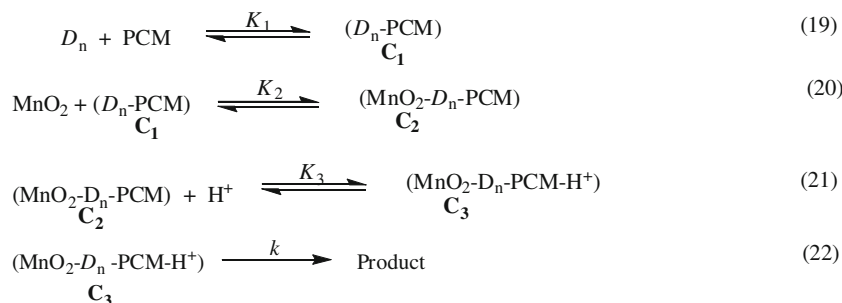
$$D_n + PCM \xrightleftharpoons{K_1} (D_n\text{-}PCM)\ C_1 \quad (19)$$

$$MnO_2 + (D_n\text{-}PCM)\ C_1 \xrightleftharpoons{K_2} (MnO_2\text{-}D_n\text{-}PCM)\ C_2 \quad (20)$$

$$(MnO_2\text{-}D_n\text{-}PCM)\ C_2 + H^+ \xrightleftharpoons{K_3} (MnO_2\text{-}D_n\text{-}PCM\text{-}H^+)\ C_3 \quad (21)$$

$$(MnO_2\text{-}D_n\text{-}PCM\text{-}H^+)\ C_3 \xrightarrow{k} \text{Product} \quad (22)$$

Table 2 Effect of [SDS] on the oxidation of paracetamol by colloidal MnO_2 at 298 K

[SDS] (10^{-3} mol dm^{-3})	k_{obs} (10^{-4} s^{-1})
0.0	0.19
1.0	0.25
2.0	0.34
3.0	0.42
4.0	0.49
5.0	0.56
6.0	0.65
7.0	0.72
8.0	0.77
9.0	0.76
10.0	0.77
12.0	0.75

Experimental conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, [MnO$_2$] = 1.2×10^{-4} mol dm^{-3}, [H$_2$SO$_4$] = 1.0×10^{-4} mol dm^{-3}

Fig. 8 Log k_Ψ versus log [SDS] for the oxidation of paracetamol by colloidal MnO_2 at 298 K. (Reaction conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, [MnO$_2$] = 1.2×10^{-4} mol dm^{-3} and [H$_2$SO$_4$] = 1.0×10^{-4} mol dm^{-3})

(k_{obs}) increased with increasing temperature from 293 to 308 K in both phases (Table S4). The activation parameters could be evaluated from the plot of log k_{obs} versus $1/T$ using Arrhenius equation (Table 1).
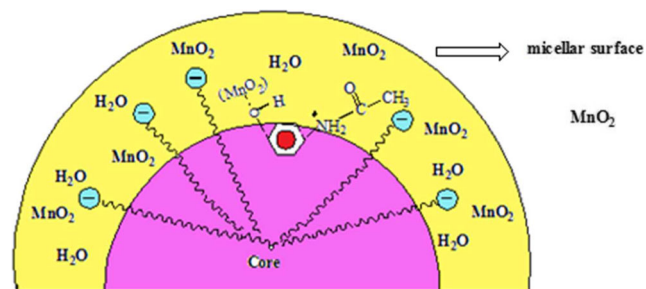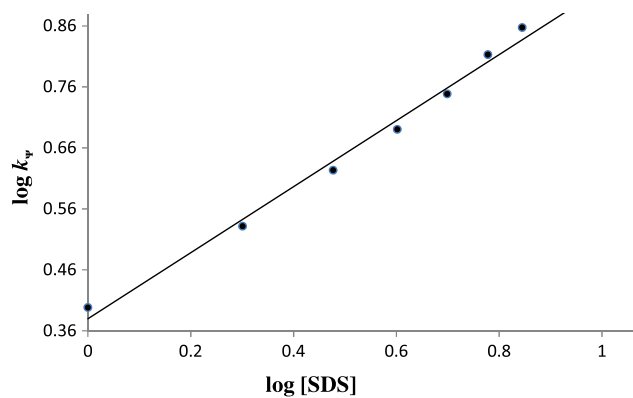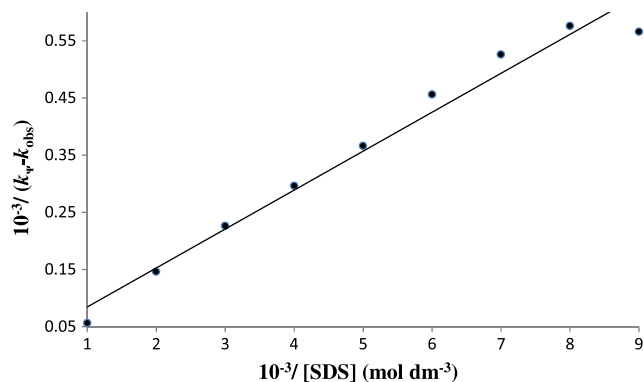
conditions were kept constant (Table S3). This may be due to the enhancement of the reaction between Mn(II) and MnO_2 [69–71] when PCM is present to suggest that in the process of consumption of colloidal MnO_2, some intermediate complex has probably been formed between Mn(II) and PCM both in SDS solution and aqueous medium to significantly increase the rate of the reaction (Fig. S2).

Elucidation of the mechanism of oxidation of PCM by colloidal MnO_2 in aqueous solution

Kinetic results in the "Oxidation of PCM by colloidal MnO_2" section have been used for elucidation of the mechanism of the oxidation of PCM by colloidal MnO_2 in aqueous solution and in the presence of SDS.

Effect of [salt]

At constant [PCM], [MnO$_2$] and [H$_2$SO$_4$], the effect of added salts like KCl, KBr and Na$_2$SO$_4$ on the reaction rate at 298 K was investigated in aqueous medium and in the presence of SDS. No significant change on the reaction rate could be observed with change in concentration of the salt (Table S3).

Mechanism of the reaction in aqueous solution in the absence of SDS

Scheme 1 (Eqs. 5, 6, and 7) shows the illustration of the reaction in acidic medium in the absence of the surfactant. Considering that 1 mol of PCM is oxidized by 1 mol of MnO_2, the rate of reaction can be expressed as

Effect of temperature

The kinetics of the reaction exhibited expected change with temperature in the reaction rate both in the absence and presence of the surfactant in aqueous media. The rate constant

$$\text{Rate} = k \, [C_2] \tag{8}$$

Scheme 4 Schematic representation of the probable reaction site for the oxidation of paracetamol by colloidal MnO_2 in the presence of SDS micelles

Fig. 9 $1/(k_\Psi - k_{obs})$ versus $1/$[SDS] for the oxidation of paracetamol by colloidal MnO_2 at 298 K. (Conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, [MnO$_2$] = 1.2×10^{-4} mol dm^{-3} and [H$_2$SO$_4$] = 1.0×10^{-4} mol dm^{-3})
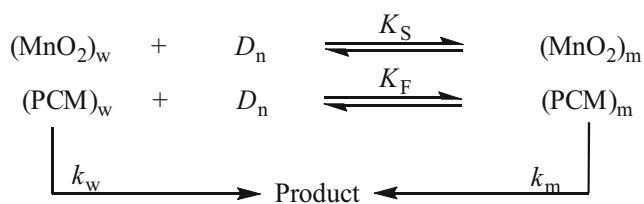
Scheme 5 The variation of the rate constant with concentration of the detergent [D] is usually treated on the consideration that the substrate (S) is distributed between aqueous and micellar media

$$[C_1] = K_1 [MnO_2] [PCM] \tag{9}$$

$$[C_2] = K_2 [C_1] [H^+] \tag{10}$$

The rate law in an aqueous media on the basis of the observed kinetic orders with respect to each reactant involved in the reaction is

$$Rate = kK_1K_2 [MnO_2] [PCM] [H^+] \tag{11}$$

Equation (11) can be rewritten as

$$\frac{[MnO_2]}{rate} = \frac{1}{k_{obs}} = \frac{1}{K_1K_2[PCM][H^+]} \tag{12}$$

Plots of $1/k_{obs}$ versus $1/[PCM]$ and $1/k_{obs}$ versus $1/[H^+]$ show the expected linearity with zero intercept (Figs. 6 and 7) to support the proposition.

Scheme 2 (Eqs. 13, 14, 15,16, 17, and 18) illustrates the detailed reaction mechanism in the absence of SDS. According to Scheme 2, PCM reacts with MnO_2 to form a C_1 complex in the first equilibrium step; the C_1 complex combines with H^+ to give a cationic C_2 complex in the following step. In Eqs. 13 and 14, K_1 and K_2 are the equilibrium constants. The cationic complex, C_2, in the rate determining step decomposes to form a free radical complex, C_3, and $HMnO_2$. This free radical again reacts with $HMnO_2$ to give a C_4 complex and H_2MnO_2. Further, H_2MnO_2 reacts with H^+ to form Mn^{2+} and C_4 complex,
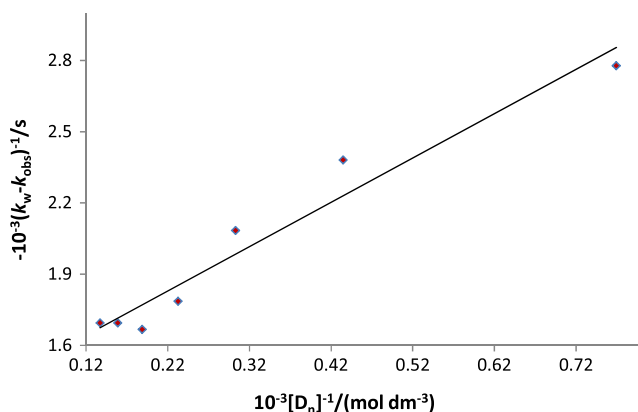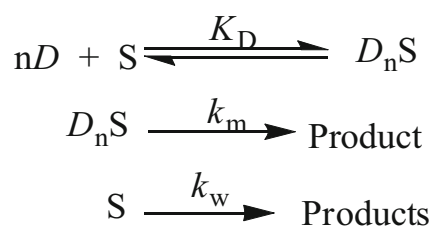
Scheme 6 Substrate (S) and an n number of detergent molecules (D) aggregate/associate to form the active micelle (D_nS) that can react to produce a product

which is hydrolyzed to produce benzoquinone as the oxidative product of PCM. In this reaction mechanism, the cationic complex is treated as a reactive species for the oxidation of PCM in the acidic medium.

Mechanism of the reaction in aqueous solution the presence of SDS

Scheme 3 (Eqs. 19, 20, 21, and 22) shows a probable mechanism of the reaction in the presence of SDS. According to Scheme 3, the final rate law on the basis of the observed kinetic orders with respect to each reactant can be expressed as

$$Rate = kK_1K_2K_3[D_n][PCM][MnO_2][H^+] \tag{23}$$

where $[D_n]$ represents concentration of the micellized surfactant (i.e. $[D_n]$ = [SDS] − CMC). Equation (23) may be converted to Eq. (24) as

$$\frac{rate}{[MnO_2]} = \frac{1}{k_{obs}} = \frac{1}{k\ K_1K_2K_3[D_n][PCM][MnO_2][H^+]} \tag{24}$$

Other conditions being constant, plots of $1/k_{obs}$ versus $1/[PCM]$ and $1/k_{obs}$ versus $1/[H^+]$ exhibit the expected linearity with zero intercept in the presence of micellar system (Figs. 6 and 7).

Fig. 10 $1/(k_w − k_{obs})$ versus $1/[D_n]$ for the oxidation of paracetamol by colloidal MnO_2 in the presence of SDS at 298 K
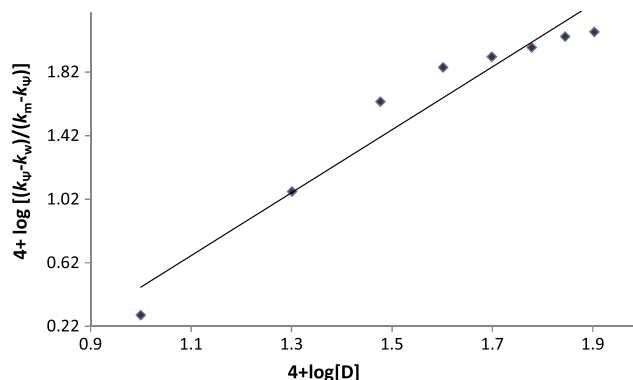

Fig. 11 Fitting of kinetic results to Piszkiewicz model for SDS-mediated reaction. (Conditions: [PCM] = 1.2×10^{-3} mol dm^{-3}, [MnO$_2$] = 1.2×10^{-4} mol dm^{-3} and [H$_2$SO$_4$] = 1.0×10^{-4} mol dm^{-3} at 298 K)

Table 3 Optimized parameters from theoretical treatments of kinetic results for the oxidation of paracetamol by colloidal MnO₂ in the presence of SDS

Parameters	In the presence of SDS
k_m (s⁻¹)	5.15×10^4
K_S mol⁻¹ dm³	7.59×10^{-2}
N	1.98
$-\log K_D$	1.511

Catalysis of oxidation of PCM by colloidal MnO₂ in aqueous solution of SDS

The catalytic effect of SDS in aqueous solution on the oxidation of PCM by colloidal MnO₂ in aqueous solution was studied at various [SDS]. Table 2 lists the observed rate constants (k_{obs}) at different concentrations both below and above the critical micelle concentration (CMC) of SDS at 298 K (7.9×10^{-3} mol dm⁻³). It may be worth mentioning that the CMC value decreased further in the presence of additives such as MnO₂, PCM and H₂SO₄. In a typical kinetic run, the CMC value of the mixture was determined from specific conductance measurements (data not shown) as 2.7×10^{-3} mol dm⁻³ at 25 °C. The k_{obs} increases with increase in SDS concentration in aqueous solution and increases significantly in micellar solutions to ultimately reach a limiting value at high SDS concentrations above the CMC of SDS (Fig.S4, Table 2). The rate is enhanced up to more than fourfold in micellar solutions of SDS. For example, the k_{obs} for the oxidation of 1.2×10^{-3} mol dm⁻³ PCM by 1.2×10^{-4} mol dm⁻³ MnO₂ in the presence of 1.0×10^{-4} mol dm⁻³ of [H₂SO₄] is 0.19×10^{-4} s⁻¹ at 298 K; under identical experimental conditions, the rate constant becomes 0.77×10^{-4} s⁻¹ in 8.0×10^{-3} mol dm⁻³ in micellar solution of SDS. The k_ψ–[SDS] profile thereby represents positive catalysis. This is ascribable to increasing solubilization and association or adsorption of the reactive species of PCM and MnO₂ with increasing [SDS] which ultimately reaches a limiting value. It is the micelle that is responsible for enhancing the rate of the oxidation of PCM. PCM is easily solubilized into the hydrophobic core of micelle in aqueous solution, and the concentration of PCM is much higher in the core of micelles compared with that in the bulk. The observed rate is the average rate of the oxidation in two different environments: outside the micelle core and inside the micelle core. But enhancement of the concentration in the micellar pseudophase can bring about significant increase in the reaction rate. The probable reaction site is the junction of the regions of the Stern and Gouy-Chapman layers; the PCM, MnO₂ and H⁺ form a cationic complex which easily reacts with anionic species of SDS to enhance the rate of reaction with increase in the concentration of SDS (Scheme 4). The kinetic results are consistent with the observations of catalysis of reactions by other surfactants for instance, SDS, cetyltrimethylammonium bromide and Triton X-100, towards various types of organic substrates such as D-glucose, tricyclazole, glycyl-leucin, L-tyrosine, DL-malic acid, oxalic acid, glycolic acid, glycyl-glycine and aspartic acid oxidized by colloidal MnO₂ [30, 32, 66, 67, 71–75].

Theoretical treatment of catalysis of oxidation of PCM by colloidal MnO₂ in aqueous solution of SDS

The kinetic results of the oxidation of PCM by colloidal MnO₂ in aqueous solution were treated with several theoretical models available in the literature.

Mathematical model

The micellar catalytic effect of SDS may be interpreted following a mathematical model by Tuncay et al. [76].

$$\log k_\Psi = a\log[\text{SDS}] + b \tag{25}$$

where k_Ψ is the pseudo first-order rate constant of the oxidation of PCM in the presence of SDS and a and b are constants. The plot of log k_Ψ versus log [SDS] gives a straight line with $a = 0.541$ and $b = 0.379$ ($R^2 = 0.990$) (Fig. 8), and the model is followed. In order to further explain the catalytic role of [SDS], Eq. (26) is also suggested by Tuncay et al. [76].

$$\frac{1}{k_\psi - k_{obs}} = \frac{c + d}{[\text{SDS}]} \tag{26}$$

The plot of $1/(k_\Psi - k_{obs})$ versus $1/[\text{SDS}]$ (Fig. 9) was linear, and the values of c and d were evaluated as 0.068 and 0.016, respectively ($R^2 = 0.974$). The validity of Eqs. (25) and (26) confirms that the oxidative degradation of PCM by MnO₂ in the presence of SDS follows the Tuncay model [76].

Menger and Portnoy model

The catalysis of the reaction in the presence of aqueous micellar solution of SDS may also be explained by the micellar kinetic pseudo phase model proposed by Menger and Portnoy [77] and modified by Bunton et al. [78–80]. The variation of the rate constant with concentration of the detergent [D] is usually treated on the consideration that the substrate (S) is distributed between aqueous and micellar media (Scheme 5).

The rate law is expressed from Scheme 5 as

$$k_{obs} = \frac{k_w + k_m K_s[D_n]}{1 + K_s[D_n]} \tag{27}$$

The following relationship is established.

$$\frac{1}{(k_w - k_{obs})} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m)(K_s)[D_n]} \tag{28}$$

Here, $[D_n]$ is concentration of micellized surfactant and k_w represents the rate constant in the absence of surfactant. The plot of $1/k_w - k_{obs}$ versus $1/[D_n]$ was linear following Eq. (28) (Fig. 10). The binding constant (K_s) and the rate constant in the micellar phase (k_m) evaluated from the slope and intercept were found to be 5.15×10^4 s^{-1} and 7.59×10^{-2} mol dm^{-3}, respectively. The substrate binding to micelle is thereby apparent.

Piszkiewicz model

At lower concentrations of a surfactant, the micellar catalysis has been explained by the kinetic model developed by Piszkiewicz [81] which is analogous to Hill model [82]. This model assumes that the substrate (S) and an *n* number of detergent molecules (*D*) aggregate/associate to form the active micelle (D_nS) that can react to produce a product as given in Scheme 6, where K_D represents the dissociation constant of micelle back to its free components; *n* and *D* express the index of cooperativity and total surfactant, respectively,

Positive cooperativity shows the catalysis of the reaction by micelles. The observed rate constant may be expressed as a function of the detergent concentration by

$$k_{obs} = \frac{k_m[D]^n + k_w K_D}{K_D - [D]^n} \tag{29}$$

After rearrangement of Eq. (29) and taking the logarithm, the rate constant is obtained as

$$\log \frac{k_{obs} - k_w}{k_m - k_{obs}} = n \ \log[D] - K_D \tag{30}$$

The value of k_m was determined by using the Menger-Portnoy model. The plot $\log \{(k_{obs} - k_w) / (k_m - k_{obs})\}$ and $\log [D]$ showed linearity, and the values of *n* and K_D could be determined (Fig. 11) as 1.98 and 32.43, respectively (Table 3). These are in good agreement with early observations of Piszkiewicz [81]. The index of positive cooperativity refers to interaction of the additional substrate molecule because of the interaction of micelle with the first substrate molecule.

Conclusion

The kinetics of the oxidation of PCM by colloidal MnO_2 in the absence and presence of anionic (SDS) surfactant has been investigated for the first time in aqueous acidic medium. In both uncatalyzed and micellar catalyzed reactions, the reactions follow the first-order kinetics with respect to PCM, MnO_2 and H_2SO_4 under pseudo first-order reaction conditions. The micellar (SDS)-catalyzed reaction behaviour could be explained by theoretical models: Tuncay, Menger and Portnoy, and Piszkiewicz models. The catalysis of the reaction

by micelles of SDS correlates well with the enhancement of concentration of the substrate in the hydrophobic core of micelles, the substrate to micelle binding, the high degree of dissociation of the micellar head group and positive cooperativity due to interaction of micelles with the substrate.

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