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Kinetics of the MnO_4^- Oxidation of Anionic Surfactant (Sodiumdodecyl Sulphate): Evidence for the Formation of Soluble Colloidal MnO_2

Raju and Zaheer Khan*

Department of Chemistry, Jamia Millia Islamia, (Central University), Jamia Nagar, New Delhi 110025, India

Received July 20, 2004; E-mail: drkhanchem@yahoo.co.in

A conventional spectrophotometric technique was used to study the oxidation of SDS by permanganate in a perchloric acid medium. It was observed that the reaction proceeded in two stages (fast first stage followed by a relatively slow second stage). Plots of log(absorbance) versus time deviate from linearity. The kinetic and spectroscopic data are consistent with the formation of soluble colloidal MnO_2. The first-order kinetics with respect to [SDS] at low concentrations shifted to second-order at higher concentrations. The kinetics of oxidation is first-order with respect to both [MnO_4^-] and [$HClO_4$]. The oxidation rate was decreased by the addition of $P_2O_7^{4-}$ and Mn(II) ions. Second-step oxidation is not a true path for the oxidation of the Mn(IV)–SDS reaction. In the presence of Mn(II) (a reaction product), the MnO_4^- oxidation of SDS becomes more complicated, and an exact dependence on [Mn(II)] can not be estimated. Different activation parameters have been evaluated. Mechanisms consistent with the kinetic data have been proposed and discussed. The $–O–SO_3^-$ group is responsible for the oxidative degradation of SDS by MnO_4^-.

In a previous publication we showed that a non-ionic, TX-100, surfactant is unstable in aqueous solution, and acts as a reductant for cerium(IV).[1] At that time we pointed out that a primary –OH group of a polyoxyethylene chain of TX-100 was responsible for the oxidative degradation of TX-100. In the present study, we explored a related family of reactions involving the anionic surfactant (sodiumdodecyl sulphate) and potassium permanganate. In this paper, we wish to report on the results of our work on the oxidation of SDS by MnO_4^-.

A large number of books and review articles are available concerning the role of surfactants in a variety of organic and inorganic reactions.[2–15] The common behavior of micelle-catalyzed reactions is the solubilization of the substrate(s). However, despite extensive research on the effect of the surfactant, the kinetics and mechanistic aspects of the reaction involving micelle as a reductant have not been studied so far, except for a recent report by a few researchers.[1,16]

Experimental

Sodiumdodecyl sulphate (Merck, India, 99%), potassium permanganate (Merck, India, 99%), mercuric chloride (Merck, India, 99%), hydrochloric acid (Merck, India, 36%), 2,4-dinitrophenylhydrazine (Qualigens, India, 98%), dimethylsulphoxide-d_6 (Merck, Germany, 99.8%), manganese(II) chloride ($MnCl_2 \cdot 4H_2O$, Qualigens, India, 98%), and sodium pyrophosphate (Merck, India, 99%) were used as such without further purification. In order to check the purity of SDS, the critical micelle concentration (cmc) was determined conductometrically, and the obtained value was found to be in good agreement with the reported cmc. The [H^+] of the medium was adjusted with the required [$HClO_4$] (Merck, India, 60% reagent). Solutions of the entire reagent were prepared in double-distilled, deionized and boiled water. MnO_4^- solutions were prepared and tested by the vogel method.

A permanganate solution ($=6.0$ cm^3, 1.0×10^{-3} mol dm^{-3}) was added to a mixture of SDS ($=5.0$ cm^3, 0.1 mol dm^{-3}), $HClO_4$ ($=6.0$ cm^3, 11.63 mol dm^{-3}), and $HgCl_2$ ($=1.2$ g) in a volume of 50 cm^3. The reaction mixture was heated to 40 °C for 30 min. A white precipitate of mercurous chloride appeared slowly, showing free-radical intervention. No precipitate formation could be observed under the experimental conditions with either MnO_4^- or SDS alone.

The kinetics measurement was carried out by mixing the solutions in a three-necked reaction flask fitted with a condenser (to arrest evaporation). The reaction flask was kept in a thermostate controlled at the desired temperature within ±0.1 °C. The progress of the reaction was followed spectrophotometrically by pipetting aliquots of the reaction mixture at definite time intervals, and the absorbance was measured at 525 nm (λ_{max} for MnO_4^-). The concentrations of SDS were always much in excess over that of permanganate. The pseudo-first-order rate constants were calculated from the slope of the conventional log(absorbance) versus t (time) plots. The reactions were usually followed by the complete disappearance of MnO_4^- color. However, a few runs were also performed at 425 nm to confirm the autocatalytic nature of the oxidation. Other details of the kinetic procedure are described elsewhere.[17–20]

Results and Discussion

The rate of disappearance of permanganate ion is shown in Fig. 1 as a log(absorbance)–time profile. The sigmoid nature of these plots suggests the existence of an autocatalytic reaction path. The extent of the induction period (non autocatalytic reaction path) depends on the experimental conditions, i.e., [SDS], [$HClO_4$], and temperature. Therefore, choice of the best experimental conditions for the kinetic experiments is a crucial problem that we address first. In order to examine the effects of the variables, experiments were tried at 1.2×10^{-4} to 2.4×10^{-4} mol dm^{-3}, 4.0×10^{-3} to 30.6×10^{-3} mol dm^{-3}, and 0.73 to 3.28 mol dm^{-3} of permanganate, SDS, and $HClO_4$, respectively. $HClO_4$ was used as an acidifying agent due to the

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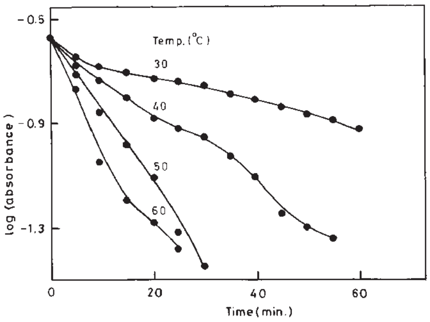


Fig. 1. Plots of log(absorbance) versus time at 525 nm for the MnO_4^- oxidation of SDS at different temperatures. *Reaction conditions*: $[SDS] = 10.0 \times 10^{-3}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] = 1.46$ mol dm^{-3}.

Table 1. Pseudo-First-Order Rate Constants for the Oxidation of SDS by MnO_4^- at 313 K

$[MnO_4] \times 10^4$ /mol dm^{-3}	$[SDS] \times 10^3$ /mol dm^{-3}	$[HClO_4]$ /mol dm^{-3}	$k_{obs1} \times 10^4$ /s^{-1}	$k_{obs2} \times 10^4$ /s^{-1}
1.2	10.0	1.46	3.4	1.9
1.4			3.0	1.5
1.6			2.3	1.5
1.8			1.5	1.5
2.0			1.5	0.7
2.4			1.5	0.7
1.2	4.0	1.46	1.5	not observed
	8.0		2.3	not observed
	10.0		3.4	1.9
	14.0		5.3	4.2
	18.0		6.1	5.3
	22.0		8.4	7.6
	26.0		10.7	7.6
	30.0		13.8	9.2
1.2	10.0	0.73	1.5	not observed
		1.46	3.4	1.9
		1.82	5.3	3.8
		2.55	6.6	5.3
		2.92	7.6	6.1
		3.28	9.2	6.9

non-complexing nature of ClO_4^-. The rate constants of the non-autocatalytic route were determined by measuring the slopes of the lines extended over the induction period. The oxidation of SDS proceeded in two stages, i.e., initial fast stage followed by a relatively slower step.

At constant $[H^+]$, the pseudo-first-order rate constants increased with increases in [SDS] from 4.0 to 30.0×10^{-3} mol dm^{-3} (Table 1). The plot of k_{obs1} versus [SDS] was a curve passing through the origin; Figure 2 shows the relevant curve. The reaction order in SDS changes from first towards second as the [SDS] is increased. Generally, H_2SO_4 and $HClO_4$ are used as sources of hydrogen ion in the redox reaction of permanganate. H_2SO_4 contains at least two catalyzing species, namely, H^+ ion and HSO_4^-, which complicate the mechanism. The investigations were made in the presence of $HClO_4$, because the perchlorate ion is a weak ligand (unlike HSO_4^- and SO_4^{2-}). To maintain the concentration of the H^+ ion constant, HCl cannot be used as a source of H^+ ion. The effect of the H^+ ion concentration was investigated by keeping the $[MnO_4^-]$ and [SDS] constants and varying $[H^+]$ of the solution. There was an increase in the rate of the reaction with an increase in $[HClO_4]$ (Table 1). The values of k_{obs} were plotted against $[HClO_4]$, which gave a straight line passing through the origin with a slope of 1.0 (Fig. 3A). The reaction was, therefore, first-order with respect to $[HClO_4]$. The reactions were also studied in the temperature range 30–60 °C (Table 2). The plot of $\log k_{obs1}$ versus $1/T$ was linear (Fig. 3B). The value of E_a (activation energy) was calculated from the slope of Fig. 3B, plot, and is recorded in Table 2 along with other parameters. A useful explanation of the activation of enthalpy and the activation of entropy is not possible, because the k_{obs1} does not represent a single elementary step; it is a complex function of ionization, the true rate, and binding constants. However, the large negative values of the entropy of the activation show that the transition state is well-structured and highly solvated. Thus, the oxidation of SDS is an entropy-controlled rather than an enthalpy-controlled one. The order with respect to $[MnO_4^-]$ was determined by studying the reaction at different initial $[MnO_4^-]$ values. The plots of log(absorbance) versus time were linear, indicating a first-order dependence on $[MnO_4^-]$ in the initial stages of the reactions.

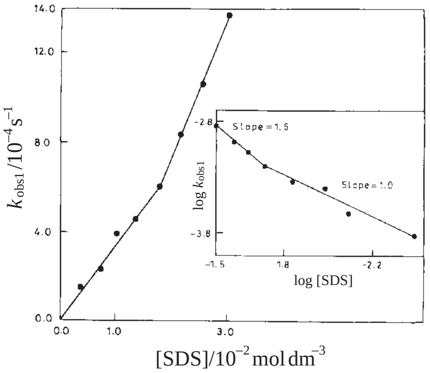


Fig. 2. Plot of k_{obs1} versus [SDS]. Inset: log–log plot between k_{obs1} and [SDS]. *Reaction conditions*: $[SDS] = 0.0$ to 30.0×10^{-3} mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] = 1.46$ mol dm^{-3}, temperature = 40 °C.

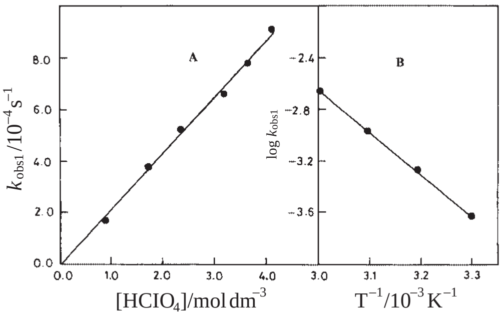


Fig. 3. A-Plot of k_{obs1} versus $[HClO_4]$. *Reaction conditions*: $[SDS] = 10.0 \times 10^{-3}$ mol dm^{-3}, $[MnO_4^-] = 1.2 \times 10^{-4}$ mol dm^{-3}, temperature at 40 °C. B-Arrhenius plot for the MnO_4^- oxidation of SDS. Reaction conditions were the same as in Fig. 1.

Table 2. Pseudo-First-Order Rate Constants and Activation Parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$) For the Oxidation of SDS ($=14.0 \times 10^{-3}$ mol dm^{-3}) by MnO_4^- ($=1.2 \times 10^{-4}$ mol dm^{-3}), [$HClO_4$] ($=1.46$ mol dm^{-3})

Temperature /K	$k_{obs1} \times 10^4$ /s^{-1}	$k_{obs2} \times 10^4$ /s^{-1}
303	2.3	1.5
313	5.3	4.2
323	10.7	7.3
333	20.7	9.2
Activation Parameters:		
E_a (kJ mol^{-1})	57	80
$\Delta H^{\#}$ (kJ mol^{-1})	54	77
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−122	−88

On the other hand, the pseudo-first-order rate constants decreased with an increase in [MnO_4^-], which may be due to the possible flocculation of the colloidal MnO_2 particles (intermediate). This type of behavior (dependent of pseudo-first-order rate constant on the initial concentration of the reactant in defect) has been observed in many permanganate reactions, and especially for those reactions, which has an autocatalytic reaction path.[21–23]

It has been established that the oxidation of organic substrates by permanganate is characterized by two principal processes:[24]

$$\text{Mn(VII)} + \text{organic reductant(s)} \longrightarrow \text{Intermediate}, \tag{1}$$

$$\text{Intermediate} \longrightarrow \text{Mn(II)}, \tag{2}$$

where Int. = one (or several) reaction intermediate(s).

Therefore, in order to obtain insight into the autocatalytic reaction path and to confirm the formation of an intermediate (Fig. 4), the oxidation of SDS was also studied by monitoring the absorbance of the reaction mixture at 420 nm, where the contribution from MnO_4^- is negligible. A plot of the absorbance at 525 nm versus absorbance at 420 nm was linear (Fig. 4, inset), indicating that product formation occurred at the same rates as the reaction of permanganate ion.[25] The species, which absorbs light at 420 and 525 nm, is a soluble species of Mn(IV). In addition, some experiments were also carried out at 420 and 525 nm. These results are shown graphically in Fig. 5 as an absorbance time profile at different [$HClO_4$] values. At 420 nm, the absorbance increases until it reaches a maximum, and then decreases with time. This behavior indicates the formation and disappearance of intermediate (water soluble colloidal MnO_2) during the course of the reaction. The formation of an intermediate was very sensitive to [$HClO_4$]. Surprisingly, as the $HClO_4$ increased from 0.73 to 3.28 mol dm^{-3}, the formation of intermediate was not observed. In the case of MnO_4^- as an oxidizing agent, the possible intermediates are Mn(VI), Mn(V), Mn(IV), and Mn(III). The presence of Mn(VI) and Mn(V) is ruled out by the fact that they are highly unstable in an acidic medium.[25] As far as the formation of Mn(III) is concerned, some experiments were also performed where the 470 nm (characteristic of Mn(III))[26] was used to monitor the formation of Mn(III) during the course of the reaction, but failed to detect any build up of Mn(III). Thus, we may safely conclude that the intermediate was a Mn(IV) species (Mn(IV) is commonly involved in the permanganate oxidation of organic reductants). The spectra of Mn(IV) depend on the experimental conditions as well as the nature of the reducing agent. The spectra of this intermediate showed a maximum absorption at 390 nm, and the absorbance uniformly decreased with the wavelength over the whole visible region.[27,28] In addition, some experiments were also carried out at 420 nm. On the other hand, the plot of log absorbance versus log wavelength is also linear,[29] suggesting that the formation of water-soluble colloidal species of Mn(IV) as an intermediate product during the SDS oxidation of MnO_4^- in the presence of $HClO_4$.

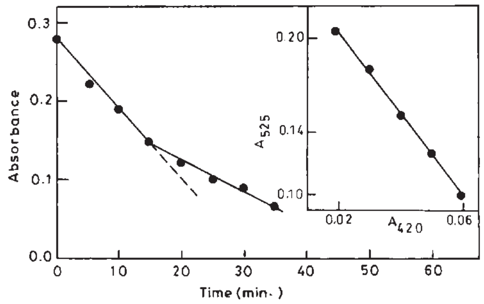


Fig. 4. Plot of absorbance versus time at 525 nm. Inset: plot of absorbance at 525 nm versus absorbance at 420 nm for the MnO_4^- oxidation of SDS. *Reaction conditions*: [SDS] = 10.0×10^{-3} mol dm^{-3}, [MnO_4^-] = 1.2×10^{-4} mol dm^{-3}, [$HClO_4$] = 1.46 mol dm^{-3}, temperature = 40 °C.

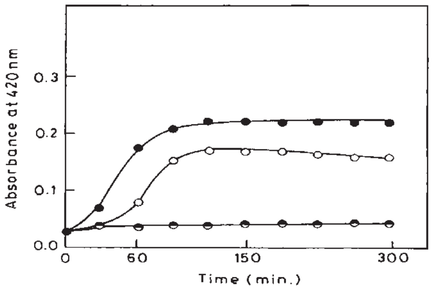
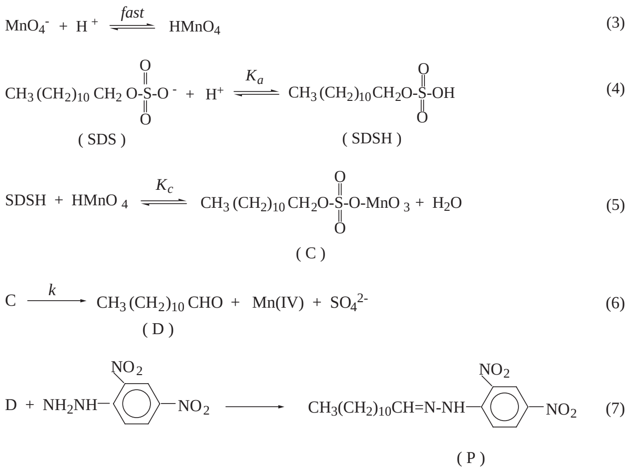


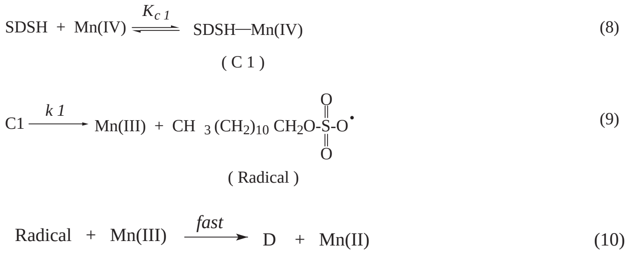
Fig. 5. Plots of absorbance versus time for the formation of intermediate (colloidal MnO_2) during the oxidation of [SDS] (= 10.0×10^{-3} mol dm^{-3}) by [MnO_4^-] (=1.2×10^{-4} mol dm^{-3}) at 40 °C and [$HClO_4$] = 0.73 (●), 1.46 (○), and 2.92 (◒) mol dm^{-3}.

The kinetic parameters experimentally found in this work are consistent with the following tentative mechanism for the formation of Mn(IV) as an intermediate.

In Scheme 1, reaction (5) represents the formation of a complex (C) with permanganate and protonated SDS. By analogy with previous results,[24,25] we assume that C decomposes by a one-stop, three-electron oxidation–reduction mechanism directly to manganese(IV) and dodecanal (D). The oxidation product of SDS, dodecanal, was characterized as follows. In a typical experiment SDS (=10.0×10^{-2} mol dm^{-3}), $HClO_4$ (=2.14 mol dm^{-3}), and potassium permanganate (=5.8×10^{-4} mol dm^{-3}) were allowed to react at 30 °C. After completion of the reaction (complete disappearance of purple color), a saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl was added to the reaction mixtures and the dinitrophenylhydra-



Scheme 1.



Scheme 2.

zone was filtered, washed, and dried. The product was identified as dodecanal 2,4-dinitrophenylhydrazone (P) by comparing the ^{1}H NMR spectrum in (DMSO-d_6) with that of an authentic sample of SDS. The ^{1}H NMR spectra were run at room temperature (27 °C) in a solution of DMSO on a Bruker DPX-300 spectrospin instrument operating at 300.13 MHz.

In order to establish the reduction of Mn(IV) (intermediate product) and to confirm the formation of Mn(III) as an intermediate, a series of kinetic experiments were carried out in the presence of $P_2O_7^{4-}$ (a complexing agent). It was found that the oxidation rate of SDS decreased upon adding $P_2O_7^{4-}$ ions. For example, under the conditions [SDS] ($=10.0 \times 10^{-3}$ mol dm^{-3}), [MnO_4^-] ($=1.2 \times 10^{-4}$ mol dm^{-3}), [$HClO_4$] ($=1.46$ mol dm^{-3}), temperature ($=40$ °C), 10^4 k_{obs} values were found to be 3.4, 2.3, 1.5, 1.5, 1.5, and 1.5 s^{-1} at 10^4 [$P_2O_7^{4-}$] of 0.0, 2.0, 4.0, 8.0, 12.0, and 14.0 mol dm^{-3}, respectively. This indicates that Mn(III) is the principal species responsible for the oxidation of SDS in an autocatalytic reaction path (although our attempts failed to observe the appearance of this ion, vide supra). The decrease in the reaction rate with an increase in [$P_2O_7^{4-}$] may be due to the one-step one-electron oxidation–reduction while passing through Mn(III) as an intermediate. The proposed mechanism is shown in Scheme 2 for the reduction of Mn(IV).

The rate law, which can be deduced from the proposed mechanism (Scheme 1), is

$$\frac{-\mathrm{d}[\mathrm{MnO_4}^-]}{\mathrm{d}t} = \frac{kK_\mathrm{c}K_\mathrm{a}[\mathrm{SDS}]_\mathrm{T}[\mathrm{H}^+][\mathrm{MnO_4}^-]}{(1+K_\mathrm{a}[\mathrm{H}^+])}, \tag{11}$$

and

$$k_\mathrm{obs1} = \frac{kK_\mathrm{c}K_\mathrm{a}[\mathrm{SDS}]_\mathrm{T}[\mathrm{H}^+]}{(1+K_\mathrm{a}[\mathrm{H}^+])}. \tag{12}$$

The inequality $1 \gg K_\mathrm{a}[\mathrm{H}^+]$ is evident, and the rate equation 12 reduces to

$$k_\mathrm{obs1} = kK_\mathrm{c}K_\mathrm{a}[\mathrm{SDS}]_\mathrm{T}[\mathrm{H}^+], \tag{13}$$

which is in complete according to the observations, and thus supports the mechanism. The derived rate-law is only known to apply at lower [SDS], and could be different for the higher [SDS] values.

The following rate equation has been derived based on the proposed mechanism (Scheme 2):

$$\frac{-\mathrm{d}[\mathrm{Mn(IV)}]}{\mathrm{d}t} = \frac{k_1K_\mathrm{c1}K_\mathrm{a}[\mathrm{SDS}]_\mathrm{T}[\mathrm{H}^+][\mathrm{Mn(IV)}]}{(1+K_\mathrm{a}[\mathrm{H}^+])}, \tag{14}$$

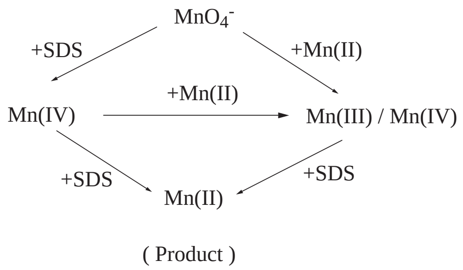
$$k_\mathrm{obs2} = \frac{k_1K_\mathrm{c1}K_\mathrm{a}[\mathrm{SDS}]_\mathrm{T}[\mathrm{H}^+]}{(1+K_\mathrm{a}[\mathrm{H}^+])}. \tag{15}$$

Interestingly, the autocatalytic reaction path (k_obs2) is not a true value of the oxidation of SDS. It may be a mixture of the rates of SDS and manganese(II); the exact dependence of the k_obs2 on [SDS] and [H$^+$] can not be estimated.

In order to further explain the autocatalytic path, the oxidation kinetics of SDS was carried out in presence of Mn(II) (a reaction product). The kinetic curve between log(absorbance) and time is linear. It was observed that the extent of the noncatalytic reaction pathway disappeared completely. These results are summarized in Table 3. The decrease in the oxidation rate with increasing [Mn(II)] indicates that Mn(IV) is involved in

Table 3. Pseudo-First-Order Rate Constants for the Oxidation of SDS by MnO_4^- in Presence of Mn(II) at 313 K, [$HClO_4$] ($=1.46$ mol dm^{-3})

[SDS] $\times 10^3$ /mol dm^{-3}	[MnO_4^-] $\times 10^4$ /mol dm^{-3}	[Mn(II)] $\times 10^4$ /mol dm^{-3}	$k_\mathrm{obs1} \times 10^4$ /s^{-1}	$k_\mathrm{obs2} \times 10^4$ /s^{-1}
10.0	1.2	1.0	1.9	2.0
		2.0	not observed	1.9
		4.0	not observed	1.5
		8.0	not observed	1.5
		12.0	not observed	1.5
10.0	1.2	0.0	3.4	1.9
14.0			5.3	4.2
0.0	1.2	1.0	0.28	not observed
		2.0	0.28	not observed
		4.0	0.28	not observed



Scheme 3.

the autocatalytic reaction path. In order to confirm the observations of previous investigators,[30–32] the kinetics of Mn(II) oxidation to Mn(III) by MnO_4^- as studied spectrophotometrically at 525 nm (Table 3). Based on their results, we conclude that in presence of externally added Mn(II), the path of oxidation of SDS by MnO_4^- may become more complicated (Scheme 3).

Table 1 clearly demonstrates that the MnO_4^- oxidizes both the monomeric molecules of SDS as well as the aggregated units (micelles). Surfactant monomers rapidly join and leave micelles, and the aggregation number represents only an average over time. Micelles are not fixed entities, but have a transient character.[33] Therefore, according to the multiple equilibrium models, the distribution of the surfactant (D_1) between various states of aggregation is controlled by a series of dynamic association–dissociation equilibria:

$$D_1 + D_1 \rightleftharpoons D_2, \quad (16)$$

$$D_2 + D_1 \rightleftharpoons D_3, \quad (17)$$

$$D_{n-1} + D_1 \rightleftharpoons D_n. \quad (18)$$

The small aggregates of the surfactant (dimers, trimers, tetramers, etc.) exist below the cmc.[33] These small submicellar aggregates are responsible for the oxidation of SDS by MnO_4^-. The equilibrium between the micelles and sub-micellar aggregates is fast. In the presence MnO_4^-, the equilibrium shifts towards the right-hand side because monomeric SDS is consumed, and is oxidized to the product. On the other hand, in the micellar pseudo phase, the aggregated SDS molecules (D_n) are oxidized by the MnO_4^-. It has been proved that the exact reaction site cannot be proposed because the micellar pseudo phase is regarded as a microenvironment having varying degrees of water activity.[34] The oxidation of SDS was found to increase with increases in the [H^+] value (Table 1). $HClO_4$ is a strong acid, which dissociates completely. Therefore, due to the electrostatic interactions between the anionic head group of SDS micelle ($–OSO_3^-$) and H^+, the local concentration of H^+ increases in the Stern layer (water-rich region as activity of water at the surface of ions micelles is not different from water activities in the aqueous pseudo phase). As a result, $–OSO_3^-$ converted to $–OSO_3H$. On the other hand, MnO_4^- acts as $HMnO_4$ at the interfacial junction at the region of the Stern and Gouy-Chapman layers; as the reaction proceeds the $–OSO_3H$ form an intermediate with the $HMnO_4$ (Scheme 1). The probable reaction site may be the Stern and Gouy-Chapman layers' junctural region.

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