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ORIGINAL CONTRIBUTION

Effects of anionic and cationic micelles on the oxidation of D-dextrose by diperiodatoargentate(III)

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Abstract The oxidative behavior of D-dextrose toward diperiodatoargentate(III) (DPA) has been studied in the absence and presence of anionic and cationic micelles of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), respectively. The kinetics is based on the reduction of silver(III) to silver(I) by D-dextrose under pseudo-first-order conditions. The monoperiodatoargentate(III) ions act as active oxidants in comparison to that of DPA. The reactions are first- and fractional-order dependence with respect to [DPA] and [D-dextrose], respectively. The reaction rates decrease with [H^+] and [periodate]. The premicellar environment of SDS and CTAB strongly inhibits the reaction rate. Inhibition is due to favorable thermodynamic/electrostatic binding between the Ag(III) complex and CTAB monomer aggregates. A suitable mechanism involving a one-electron transfer (rate-determining step) from D-dextrose to the silver(III) species has been proposed. Activation parameters have been evaluated and discussed.

Keywords Ionic surfactants · Kinetics · D-Dextrose · Silver(III) · Mechanism

Introduction

The science of surfactant behavior in solution is a rapidly developing field with its wide applications in different industries, medical sciences, and analytical chemistry. Researches on surfactant behavior are completely multidisciplinary in nature. There are no systematic data involving the oxidative behavior of D-glucopyranoside toward silver (III) oxidant although oxidations of aldoses by different oxidants have been studied on several occasions [1–7]. Surfactant micelles in aqueous media resemble enzymes in that they possess distinct regions of hydrophilic and hydrophobic character. The investigations of coupled systems composed of electron transfer reaction and micelle-forming surfactants may contribute in a unique way to our understanding of the redox processes of electron transport enzymes. Literature survey reveals that no attempts have been made for the use of DPA as an oxidant for the oxidation of monosaccharides in presence of cationic and anionic surfactants. To our knowledge, no such investigation has so far been reported. The present paper deals with the oxidative behavior of D-dextrose toward DPA in absence and presence of anionic and cationic micelles of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB), respectively.

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Experimental

Materials

Double distilled (first time from alkaline $KMnO_4$) deionized water was used to prepare the stock solutions of the reactants. D-Dextrose (Merck, India), sodium metabisulfite (BDH), potassium periodate (Qualigens, India), SDS (Fluka, Switzerland), CTAB (Sigma, USA), $HClO_4$ (Fischer, 70% reagent) and sodium hydroxide were of analytical grade. $K_2S_2O_8$ was purified by recrystallization to remove any traces of impurities.

Kinetic procedure

Requisite amounts of DPA and D-dextrose were thermostated in separate two-necked reaction flasks for 10 min at 25.0 °C before mixing. The reaction was initiated by adding DPA as the last component. The progress of the reaction was followed spectrophotometrically by monitoring the decay of absorbance of silver(III) complex at 362 nm at regular time intervals from which the concentration of silver(III) was computed. All kinetic runs were carried out for a period of more than 80% completion with D-dextrose in excess to work under pseudo-first-order conditions. The pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained from the plots of log (absorbance) vs time. Other details of the kinetic procedures are described elsewhere [8, 9]. The same kinetic procedure was also used to evaluate the rate constants in presence of ionic surfactants.

Cmc determination

The critical micelle concentration (cmc) values of the surfactants (CTAB and SDS) in presence and absence of DPA and D-dextrose were determined from plots of the specific conductivity vs surfactant concentration. The break point of nearly two straight-line portions in the plot is taken as an indication of micelle formation and this corresponds to the cmc of surfactant [10]. The cmc values of surfactants in different solvent are given in Table 1.

Results and discussion

Product identification and free radical intervention

The reduction product of silver(III) complex, Ag(I), in solution was detected by adding KCl solution, which produced turbidity of AgCl. Paper chromatographic technique was used to identify the oxidation product of D-dextrose using a mixture of *n*-butanol-acetic acid–water (4:1:5) as the eluent. Paper chromatograms were developed by $AgNO_3$–NaOH–$Na_2S_2O_3$ (specific for the detection of aldonic acids [11, 12]. Seemingly, lactone, which was formed in the rate determining step, was hydrolyzed to form the gluconic acid in neutral medium [13].

The presence of free radical in situ was checked by polymerization of acrylonitrile (white gel formation) in the experimental conditions ([D-dextrose] = 1.0×10^{-2} mol dm^{-3}, [DPA] = 1.0×10^{-4} and temperature = 25.0 °C). Blank experiments in the absence of DPA and D-dextrose did not show gel formation.

Preparation and hydrolysis of diperiodatoargentate(III)

In a typical experiment, 8.5 g $AgNO_3$ was added to a solution containing 28 g NaOH and 23 g KIO_4 in 100 cm^3 of water. The solution was shaken thoroughly and heated to boil, and 20 g $K_2S_2O_8$ was added slowly. A dark red solution mixed with black oxides of silver was obtained. The black precipitate was filtered off on porosity-4 sintered-glass crucible. The NaOH pellets were added to the filtrate till fine crystals of orange color appeared. The electronic spectrum of resulting complex was recorded on a spectronic 21-D spectrophotometer. In aqueous solution, the complex showed three peaks at 214, 255, and 362 nm [14]. It has been reported that aqueous solutions of DPA are unstable [15]. Therefore, a series of kinetic runs were performed for the hydrolysis of DPA in presence of $[H^+]$ and $[OH^-]$ maintained by adding the required amount of $HClO_4$ and NaOH, respectively. The observed results are summarized in Table 2. It was observed that the absorbance of DPA solution decreased gradually with increasing $[H^+]$ from 1.0×10^{-4} to 1.0×10^{-2} mol dm^{-3} in absence of D-dextrose. These results clearly indicate that DPA solution undergoes acid hydrolysis or is unstable in aqueous solutions of $[H^+] > 1.0\times10^{-4}$ mol dm^{-3}. It was also observed that DPA was stable in alkaline medium, whereas reaction rate increased with $[H^+]$. The change in absorbance was also observed in presence of water, which is evidently due to the aquation of DPA complex. Therefore, all the silver(III) complex may exist in the form of $[Ag^{III}(H_2IO_6)$

Table 1 Critical micelle concentration (cmc) values of CTAB and SDS in the absence and presence of 1.0×10^{-4} mol dm^{-3} oxidant and 1.0×10^{-3} mol dm^{-3}D-dextrose at 25.0 °C

Solution	10^4 cmc (mol dm^{-3})	
	CTAB	SDS
Water	10.1 (9.8)[a]	80.1 (80.2)[a]
Water + DPA	9.2	80.1
Water + D-dextrose	10.0	80.2
Water + DPA + D-dextrose	9.2	80.0

[a] The literature values are quoted in the parentheses (25.0 °C) [10].

Table 2 Effect of $[H^+]$ and $[OH^-]$ on the rate constant (k_H) for the hydrolysis of DPA at 25.0 °C

10^4 $[H^+]$ (mol dm^{-3})	$10^4 k_H$ (s^{-1})	10^3 $[OH^-]$ (mol dm^{-3})	$10^4 k_H$ (s^{-1})
1.0	7.6	0.06	No reaction
2.0	9.5	6.0	No reaction
3.0	11.5	12.0	No reaction
4.0	14.3	20.0	No reaction
6.0	19.1	40.0	No reaction
8.0	23.0	50.0	No reaction
9.0	28.7		

$(H_2O)_2$]. The decay in absorbance of DPA clearly suggests that the aquation was very slow after 6 h. Therefore, DPA solution was used after 12 h preparation, which is quite stable, and its absorbance remained unchanged for several days.

Kinetic data analysis

To see whether the bromide ion was capable for reaction with silver(III) complex under our kinetic conditions, some experiments were also performed in absence of D-dextrose (DPA + CTAB). The absorbance of DPA remained constant for the entire range of [CTAB] used in the kinetic experiments. This suggests that the oxidation of bromide ion by DPA was not involved even as a side reaction in the D-dextrose oxidation by DPA in presence of CTAB. Furthermore, a series of kinetic experiments performed with varying [Br^-] at constant [DPA] = 1.0×10^{-4} mol dm^{-3} and temperature = 25.0 °C showed constancy of absorbance up to 30 min (time required for complete reduction of D-dextrose is 15 min under the same kinetic conditions). These results confirm that there was no reduction of DPA by bromide ion.

Tondre et al. [16, 17] have advised to avoid the use of even buffer solutions to maintain pH of micellar solutions. Therefore, no electrolyte was used to maintain ionic strength. The sigmoid nature in the plots of log (absorbance) vs time suggests the existence of an autocatalytic reaction path (Fig. 1). The extent of induction period (noncatalytic reaction path) depends on the experimental conditions, i.e., [DPA], [D-dextrose], [H^+], and [periodate].

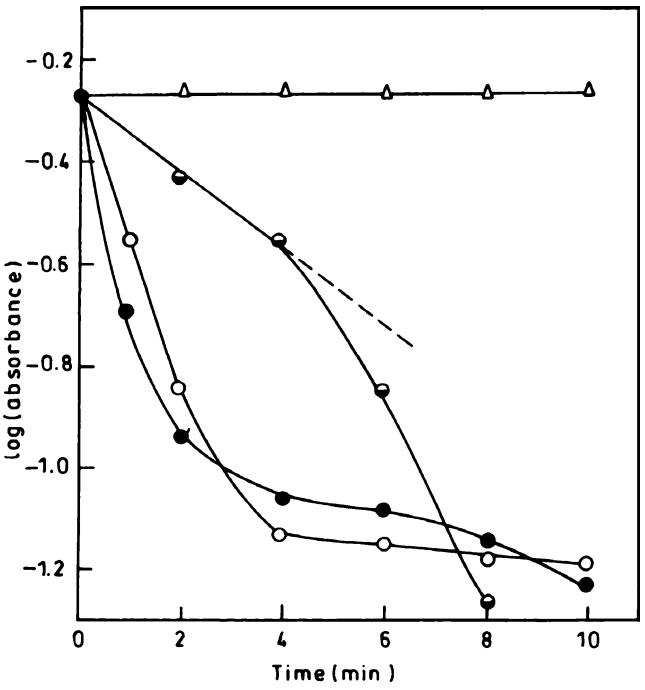
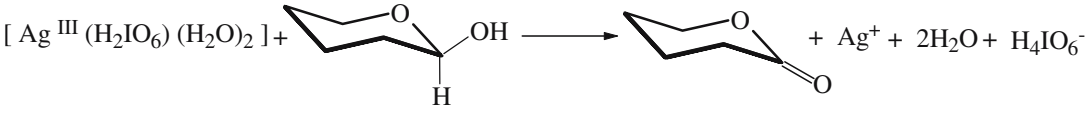


Fig. 1 Plots of log (absorbance) vs time for the oxidation of [D-dextrose] = 1.0×10^{-3} mol dm^{-3} by [DPA] = 1.0×10^{-4} mol dm^{-3} at 25.0 °C. *Reaction conditions* [KIO_4] = 0.6 (*half-filled/half-empty circles*), 3.0 (*empty circles*), and 4.5×10^{-4} mol dm^{-3} (*filled circles*), [D-dextrose] = 0.0 mol dm^{-3} (*triangles*)

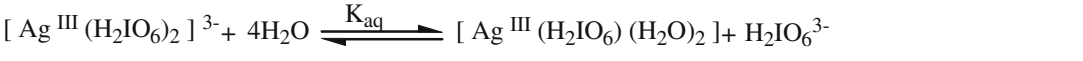
To determine the stoichiometry of the reaction, spectrophotometric titrations were used. The absorbance of residual DPA was monitored at 362 nm. D-Dextrose consumed one equivalent of DPA in 30 min at 25.0 °C. The stoichiometric equation can therefore be expressed as:



(1)

The pseudo-first-order rate constants were calculated for [D-dextrose] at constant [DPA] and temperature. The values of rate constants were summarized in (Table 3). The plot of rate constant vs [D-dextrose] yielded a concave curve, and a plot between k_{obs}^{-1} and [D-dextrose]$^{-1}$ was linear with a positive intercept on the *y*-axis (Fig. 2). Such a plot is indicative of Michaelis–Menten catalysis. Hence, the complex formation between D-dextrose and DPA occurs initially. The values of rate constant were found to be independent on [DPA] indicating first-order dependence on [DPA].

The effects of [H^+] that often accompany silver(III) complex were studied by adding different amounts of [H^+] at constant [D-dextrose] (=1.0×10^{-3} mol dm^{-3}). The results are depicted graphically in Fig. 3. At lower [H^+] $\leq0.3\times10^{-5}$ mol dm^{-3}, no kinetic effects are observed. At higher [H^+] $>0.3\times10^{-5}$ mol dm^{-3}, k_{obs} decreases steeply by increasing [H^+] (Table 4). The decreasing rate constant may be due to the hydrolysis of silver(III) complex or removal of reactive silver(III) species from the reaction site. On the other hand, the addition of periodate also retards the reaction rate (Table 4). The rate constants decreased as the [periodate] was increased (Fig. 3), which indicates that probably, a dissociation equilibrium existed between diperiodatoargentate(III) and monoperiodatoargentate(III) (silver (III) moiety loses a periodate ligand). Periodic acid



(2)

Table 3 Pseudo-first-order rate constants (k_{obs}) for the oxidation of D-dextrose by DPA at 25.0 °C

10^4 [DPA] (mol dm^{-3})	10^3 [D-dextrose] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})
0.2	1.0	26.0
0.4		21.8
0.6		15.3
0.8		14.2
1.0		12.2
	0.8	10.2
	1.0	12.2
	1.2	13.4
	1.4	14.5
	1.6	15.3

themselves are strong and usually oxidants that are often selective. Under our experimental conditions, (pH≈8.0) periodate did not interfere as an oxidant because silver(III) was a stronger oxidant.

An aqueous solution of D-dextrose is in equilibrium with α- and β-anomers. It has been established in the oxidations of aldoses/ketoses by metal ions that the anomer having OH-1 equatorial undergoes faster oxidation than the corresponding anomer having OH-1 axial. On the basis of the above results and discussion, Scheme 1 mechanism has been proposed for the oxidation of D-dextrose by DPA. Equation 7 explains all the experimental observations and is coherent with the fractional-order dependence found for the rate of reaction on the [D-dextrose]. On rearrangement, Eq. 7 can be written as

$$\frac{1}{k_{obs}} == \frac{(1 + K_{aq})}{k K_c K_{aq} [D - dextrose]} + \frac{1}{k} \quad (8)$$

According to Eq. 8, the plot k_{obs}^{-1} vs [D-dextrose]$^{-1}$ should be linear with positive intercept on *y*-axis.

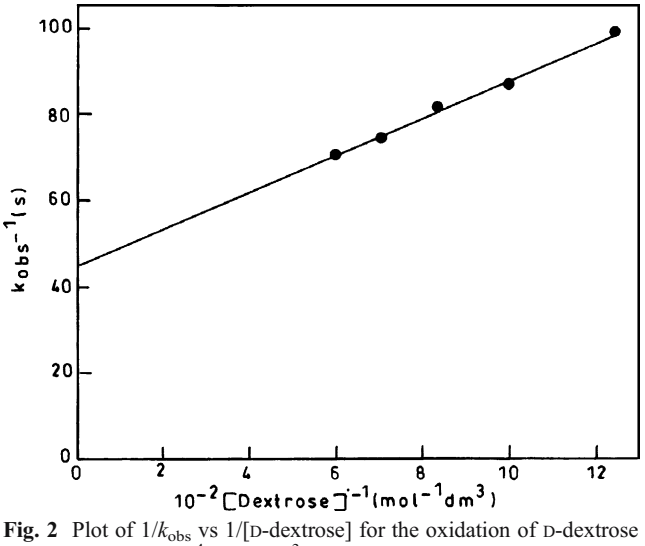


Fig. 2 Plot of $1/k_{obs}$ vs 1/[D-dextrose] for the oxidation of D-dextrose by [DPA] = 1.0×10^{-4} mol dm^{-3} at 25.0 °C

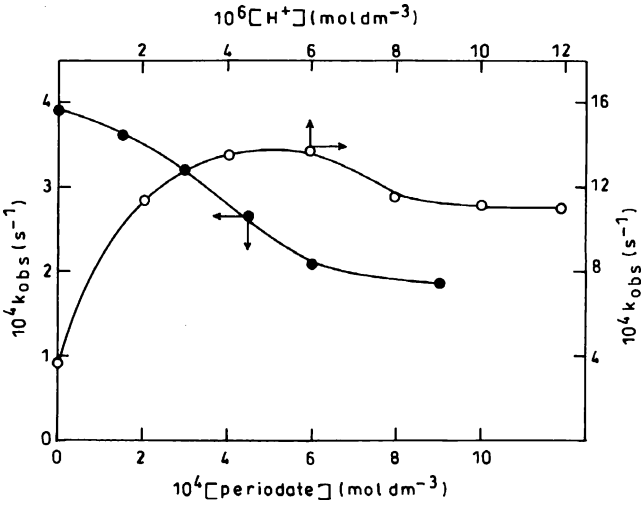


Fig. 3 Effects of [periodate] (**a**) and [H$^+$] (**b**) on the k_{obs}. [DPA], [D-dextrose], and temperature were the same as in Fig. 1

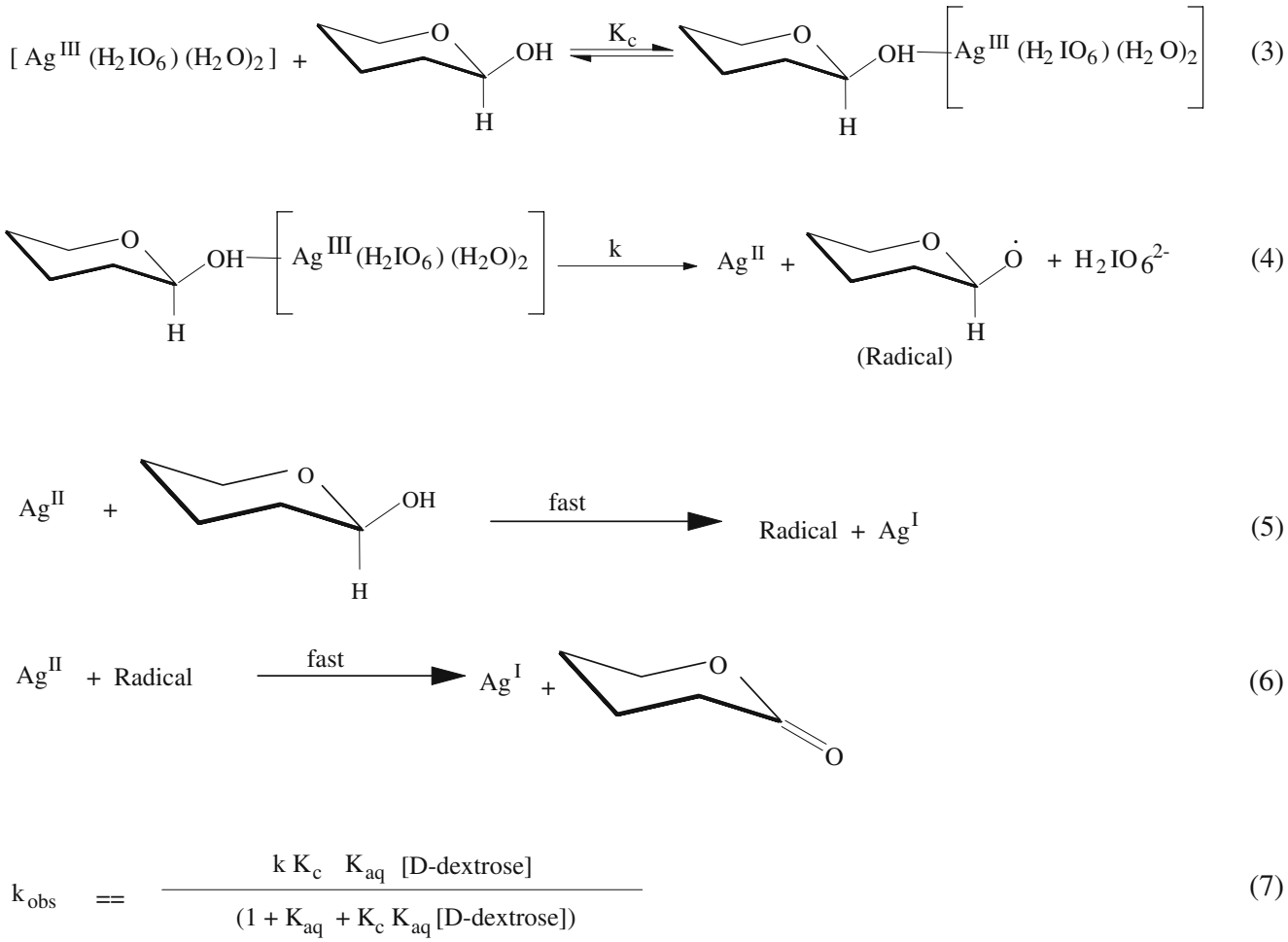
Reaction in presence of anionic and cationic surfactants

To see the effects of surfactants in the oxidation of D-dextrose by DPA, SDS and CTAB were chosen. The effect of varying the surfactant concentrations on the reaction rate (k_{obs}) was studied, keeping other variables constant—[DPA] (=1.0×10^{-4} mol dm^{-3}), [D-dextrose] (=1.0×10^{-3} mol dm^{-3}), and temperature (=25.0 °C). The results are illustrated in Fig. 4 as k_{obs}-[surfactant] profiles, which clearly demonstrate the surfactants' inhibitory effects not only above but even below cmc, i.e., micellar as well as submicellar inhibitions are observed. From Fig. 4, one can see that the rate constant decreases by increasing [CTAB] and [SDS] for surfactant concentrations lower than the cmc. On the other hand, micellized CTAB or SDS has no effect on the rate constant, and its value is less than that obtained in pure water (Fig. 4). The premicellar surfactant kinetic effects as well as the micellar surfactant effects on the oxidation rate can be rationalized by considering the distribution of the diperiodatoargentate(III) molecules among the different pseudo phases present in the reaction

Table 4 Effects of [periodate] and [H$^+$] on the k_{obs} for the oxidation of D-dextrose by DPA at 25.0 °C

10^4 [periodate][a] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	10^6 [H$^+$] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
0.0	3.9	0.0	4.0
1.5	3.6	2.0	11.5
3.0	3.2	4.0	13.5
4.5	2.7	6.0	13.8
6.0	2.1	8.0	11.5
9.0	1.9	10.0	11.0
		12.0	11.0

[a] [DPA] = 1.0×10^{-4} mol dm^{-3}, [D-dextrose] = 1.0×10^{-3} mol dm^{-3}



Scheme 1 Mechanism proposed for the oxidation of D-dextrose by DPA

medium. The first-order rate constant in bulk water (k_w) is higher than first-order rate constant in the micellar aggregates. Hence, there is thermodynamic stabilization of the complex with respect to dissociation via Eq. 2. This is a reasonable explanation for the observed inhibitions in the present work.

The kinetic cmc of CTAB is lower than in water (Table 1), suggesting that the anions $[Ag^{III}(H_2IO_6)_2]^{3-}$ interact with the cationic surfactant, and submicellar aggregates may be formed [18, 19]. The anions $[Ag^{III}(H_2IO_6)_2]^{3-}$ will be preferentially located at the positively charged interphase of the CTAB aggregated molecules and, therefore, the environment will be less polar than in pure water [20]. On the other hand, the cmc of SDS is not affected by the presence of the silver(III) complex at the concentration used throughout the studies.

Micelles are not fixed entities but have a transient character [21]. Surfactant monomers rapidly join and leave micelles, and the aggregation number represents only an average over time. According to the multiple equilibrium model, therefore, the distribution of surfactant (D_1) between various states of aggregation is controlled by a series of dynamic association–dissociation equilibria:

$$D_1 + D_1 \rightleftharpoons D_2$$

$$D_2 + D_1 \rightleftharpoons D_3$$

$$\vdots$$

$$D_{n-1} + D_1 \rightleftharpoons D_n$$

The effect of surfactant below cmc (i.e., submicellar effect) is not new and conforms to various available results [22–24]. The nonfeasibility can be sought in the fact that small aggregates of the surfactant (dimmers, trimers, tetramers, etc.) exist below the cmc; these small submicellar aggregates can interact physically with the reactants forming inactive entities. This effect becomes less important once micellization becomes significant.

On the basis of the above description, the possible causes of the rate retardation may be discussed. The presence of high and negative charge on the silver(III)

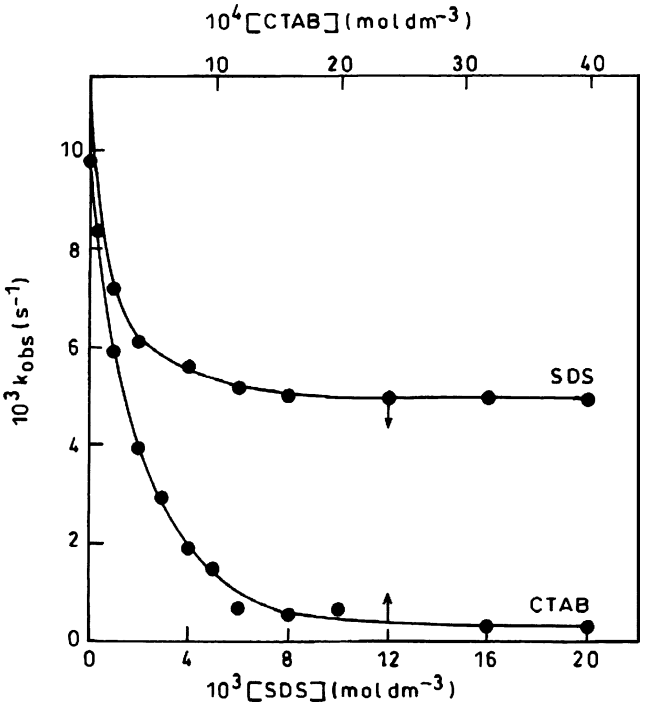


Fig. 4 Effects of [SDS] and [CTAB] on k_{obs}. *Reaction conditions* s[D-dextrose] = 1.0×10^{-3} mol dm^{-3} by [DPA] = 1.0×10^{-4} mol dm^{-3} at 25.0 °C

complex must be considered. It is certainly possible that this negative charge forms an ion pair with the positive head group of CTAB molecules, which brings a large hydrophobic cetyltrimethyl group in the vicinity of the D-dextrose, and orients (freezes) the solvent in the region of the C1-OH of D-dextrose [20].

From the present data, one can obtain the preliminary picture of the reaction sites. The key facts are: (1) the reaction proceeds more slowly in the micellar phase than in the bulk phase (aqueous phase), (2) the cationic and anionic surfactants cause a considerable decrease in the reaction rate constant (ca. eight- and fivefold), and (3) only one reactant [monoperiodatoargentate(III)] proceeds toward the cationic micellar phase. The second reactant (D-dextrose) has no any degree of hydrophobic character; therefore, it exists only in the water phase. The head groups of the ionic micelles are generally about 30% ionized, i.e., 70% neutralized by the counter-ions in the Stern layer. The degree of counter-ion binding depends on several factors [25, 26]. Counter-ions interact with the head groups not only electrostatically but also hydrophobically and coulombically. Added salts inhibit micellar catalysis by excluding ionic reagents from the micellar surfaces. In the present study, sodium salt of silver(III) periodate complex was used to oxidize the D-dextrose in presence of surfactants. The free Na^+ counter-ion concentration can neutralize or screen the SDS aggregates and micelles charge. At the same time, Na^+ can compete with the neutral D-dextrose molecules for surface sites, thereby lowering the amount of D-dextrose molecules present in the Stern layer and, thus, decreasing the effective concentrations of the neutral silver(III) complex, i.e., $[Ag^{III}(H_2IO_6)(H_2O)_2]$ and D-dextrose. Thus, we may safely conclude that SDS micelles have no effect on the oxidation rate.

The negatively charged $[Ag^{III}(H_2IO_6)_2]^{3-}$ complex is expected to be mainly in the bulk aqueous phase. The decrease in the oxidation rate in premicellar region of SDS can be explained in terms of ionic strength of the reaction mixture [27]. As the [SDS] increases, the ionic strength of the medium increases and, therefore, the release of the periodate molecule (Eq. 2) from the inner coordination shell of Ag^{3+} to the bulk is more difficult, which, in turn, decreases the oxidation rate. These results and explanations are in good agreement with the observations of Ige and Soriyan [28].

Comparison with other oxidants

Table 5 summarizes the values of second-order rate constant (k^{II}, mol^{-1} dm^3 s^{-1}) for the reactivity of D-dextrose toward different oxidants. It is interesting to note that the reactivity of silver(III) toward D-dextrose is much higher than the corresponding reduction of many other oxidants. The comparison of the second-order rate constant shows that the reactivity decreases in the order silver(III) > Cr(VI)> Ce(IV) > Pt(IV) > Tl (III) > V(V) (caution: one should keep in mind the reaction conditions; different [H^+], temperature, etc.).

Table 5 Kinetic data (second-order rate constant) for the oxidation of D-dextrose by different metal ion oxidants

Oxidant	Medium (mol dm^{-3})	Temp. (°C)	k^{II} (mol^{-1} dm^3 s^{-1})	Reference
Ag(III)[a]	Aqueous (pH=8.0)	25	16.5	Present work
Cr(VI)[b]	$HClO_4$ (2.4)	35	34.0×10^{-2}	[11]
Ce(IV)[c]	H_2SO_4 (0.5)	25	6.0×10^{-3}	[5]
Pt(IV)[d]	NaOH (1.0×10^{-2})	30	3.4×10^{-2}	[6]
Tl(III)[e]	$HClO_4$ (1.0)	65	1.45×10^{-3}	[7]
V(V)[f]	$HClO_4$ (2.0)	50	0.65×10^{-3}	[4]

[a–f][Oxidant] = 1.0×10^{-4} (*a*), 1.6×10^{-4} (*b*), 2.5×10^{-3} (*c*), 1.0×10^{-3} (*d*), 1.0×10^{-2} (*e*), 2.0×10^{-2} (*f*) mol dm^{-3}

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