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## Micelle Catalyzed Oxidation of D-Mannose by Cerium (IV) in Sulfuric Acid

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**Abstract:** Kinetics of D-mannose oxidation by cerium (IV) was studied in a sulfuric acid medium at 40 °C both in absence and presence of ionic micelles. In both cases, the rate of the reaction was first-order in D-mannose and in cerium (IV), which decreased with increasing [H<sub>2</sub>SO<sub>4</sub>]. This suggested that the redox reaction followed the same mechanism. The reaction proceeded through formation of an intermediate complex, which was proved by kinetic method. The complex underwent slow unimolecular decomposition to a free radical that reacted with cerium (IV) to afford the product. The catalytic role of cationic cetyltrimethylammonium bromide (CTAB) micelles was best explained by the Menger-Portnoy model. The study of the effect of CTAB also indicated that a negatively charged species was reactive form of cerium (IV). From the kinetic data, micelle-cerium (IV) binding and rate constants in micellar medium were evaluated. The anionic micelle of sodium dodecyl sulfate plays no catalytic role. The oxidation has the rate expression:

$$-d[\text{Ce(IV)}]=k_1K_{cl}[\text{D-mannose}][\text{Ce(IV)}]dt$$

Different activation parameters for micelle catalyzed and uncatalyzed paths were also calculated and discussed.

**Key Words:** Kinetics; D-Mannose; Cerium (IV); Cationic micelles; Anionic micelles

In the carbohydrate field, many researchers have investigated the oxidative degradation of monosaccharides (aldoses and ketoses) and their derivatives. This was done by different oxidants such as chromium (VI), vanadium (V), cerium (IV), cobalt (III), and iron (III) in aqueous sulfuric, perchloric acids and alkaline medium<sup>[1–13]</sup>. However, despite the extensive study made on the kinetics of the oxidation of monosaccharides by these oxidants, the use of surfactants in similar studies is not so common<sup>[14–18]</sup>.

In a homogenous surfactant solution (above the critical micelle concentration), the reactive site might exist in one or more of the following environments: the micelle interior (hydrophobic region), the hydrophilic region (Stern layer), the micelle water-interface, and the bulk solvent<sup>[19–23]</sup>. Preliminary observations indicated that the addition of cationic surfactant, CTAB, enhanced the reaction rate. It was thought important to investigate the kinetics and mechanism of D-mannose oxidation by cerium (IV) in the presence of surfactants. For comparison, the reaction was also studied in the absence of surfactants.

## 1 Experimental

### 1.1 Materials and reagents

D-mannose (≥99%, s.d. fine, India), ceric ammonium nitrate (99%, Qualigens, India), sulfuric acid (98%, Merck, India), CTAB (99%, BDH, England), sodium dodecyl sulfate (SDS)

(99%, Sigma, USA), sodium sulfate (98%, Merck, India), sodium nitrate (99%, Merck, India), sodium chloride (99.9%, BDH, India), and acrylonitrile (99%, s.d. fine, India) were used as received. All the solutions were prepared in doubly distilled water (specific conductivity:  $1.5 \times 10^{-5} \Omega^{-1} \cdot \text{cm}^{-1}$ ).

### 1.2 Kinetic measurements

Known amounts of cerium (IV) (oxidant) in H<sub>2</sub>SO<sub>4</sub> and D-mannose (reductant) solutions were heated separately to desired temperature (±0.1 °C) before mixing. The course of the reaction was followed (under excess D-mannose) using the disappearance of cerium (IV) at 385 nm with a Bausch & Lomb Spectronic-20 spectrophotometer. The pseudo first-order rate constants were estimated from the linear parts of the plots of  $\lg A$  versus time ( $A$ : absorbance) by carrying out reactions upto ca 80% completion. Other details of the kinetic procedure were similar to that described previously<sup>[14–18, 24]</sup>.

### 1.3 Free radical test

The generation of free radicals during the course of the oxidation was confirmed by using acrylonitrile monomer<sup>[25]</sup>. To a reaction mixture (containing [Ce (IV)]= $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , [D-mannose]= $4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ , and [H<sub>2</sub>SO<sub>4</sub>]= $1.83 \text{ mol} \cdot \text{dm}^{-3}$ ), a known amount of acrylonitrile (20 cm<sup>3</sup>) was added. Formation of a polymer (white precipitate) appeared slowly. The positive response indicated *in situ* generation of free radicals<sup>[25]</sup>.

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### 1.4 Product identification

Qualitative analysis of the oxidized reaction mixture with the excess [D-mannose] over [Ce(IV)] (the kinetic condition) in presence of H<sub>2</sub>SO<sub>4</sub> was performed. After the kinetic experiment was completed, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution, and the presence of lactone in the reaction mixture was tested by FeCl<sub>3</sub>-HCl blue test<sup>[26]</sup>.

To the other part of the reaction mixture, barium carbonate was added to make the solution neutral<sup>[4]</sup>. FeCl<sub>3</sub> solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration<sup>[27]</sup>, indicating the presence of aldonic acid. It is concluded that lactone, formed in the rate determining step, is hydrolyzed to aldonic acid in neutral medium in a fast step. At higher pH, the [lactone] is reduced because of the formation of aldonic acid anion that shifts the equilibrium away from lactone<sup>[28]</sup>.

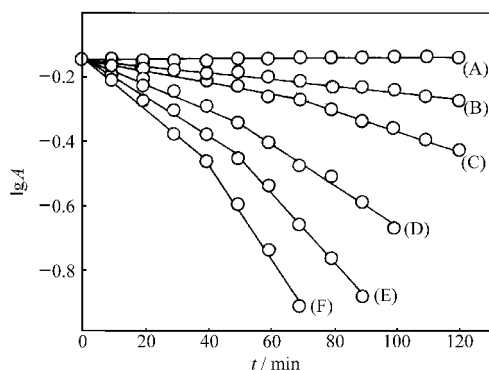
### 1.5 Critical micelle concentration measurement

The critical micelle concentration (cmc) values of the CTAB in the presence and absence of reactants were obtained from surface tensiometry by the ring detachment method using a S.D. Hardson tensiometer. Experiments were made under different conditions, i.e., solvent being water, water + cerium (IV) (1.0 × 10<sup>-3</sup> mol · dm<sup>-3</sup>), and water + D-mannose (4.0 × 10<sup>-2</sup> mol · dm<sup>-3</sup>); and the respective cmc values were 9.9 × 10<sup>-4</sup>, 2.0 × 10<sup>-4</sup>, and 8.3 × 10<sup>-4</sup> mol · dm<sup>-3</sup> at 40 °C. However, under the experimental conditions ([Ce(IV)] = 1.0 × 10<sup>-3</sup> mol · dm<sup>-3</sup>, [D-mannose] = 4.0 × 10<sup>-2</sup> mol · dm<sup>-3</sup>, and [H<sub>2</sub>SO<sub>4</sub>] = 1.83 mol · dm<sup>-3</sup>), the obtained value was 1.26 × 10<sup>-5</sup> mol · dm<sup>-3</sup>.

## 2 Results and discussion

### 2.1 Reaction-time curve and stoichiometry

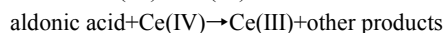
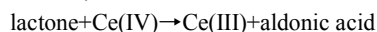
Fig.1 shows the plots of lgA versus time for the oxidation of D-mannose by cerium (IV) at different reductant concentrations. As the plots deviate from linearity, it is clear that the oxidation kinetics proceed in two stages, i.e., initial slow stage and a relatively faster step. However, the faster step oxidation (auto-catalytic reaction path) is not a true reaction path for the oxida-



**Fig.1 Plots of lgA versus time for the oxidation of D-mannose by cerium (IV)**

reaction conditions: [Ce(IV)] = 1.0 × 10<sup>-3</sup> mol · dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 1.83 mol · dm<sup>-3</sup>; [D-mannose]/(mol · dm<sup>-3</sup>): 0.00 (A), 0.01 (B), 0.02 (C), 0.04 (D), 0.06 (E), 0.08 (F); T = 40 °C

tion of D-mannose by cerium (IV). It might be the mixture of rates of oxidation of D-mannose and its products (lactone and aldonic acid).



The time, at which the deviation commenced, was found to decrease with an increase in [D-mannose] (Fig.1) and temperature. This might be because the oxidation rate of one of the oxidation products (lactone, whose concentration is small at lower [D-mannose]) becomes reasonable and shows up at higher [reductant]. Sala and coworkers<sup>[29,30]</sup> studied the oxidation of lactones and found that the rates of their oxidation are at least 10-fold higher in comparison to the corresponding monosaccharides. Therefore, the pseudo first-order rate constants in absence ( $k_{\text{obs}}$ , s<sup>-1</sup>) and presence of surfactant ( $k_{\text{p1}}$ , s<sup>-1</sup>) were calculated from the slopes of the initial parts of the linear plots.

Several reaction mixtures with [Ce(IV)] > [D-mannose], ([Ce(IV)] = 5.0 × 10<sup>-4</sup> mol · dm<sup>-3</sup>, [D-mannose] = (0.5–4.5) × 10<sup>-4</sup> mol · dm<sup>-3</sup> at constant [H<sup>+</sup>] = 1.83 mol · dm<sup>-3</sup>) were prepared. After completion of the reaction, unreacted cerium (IV) was estimated spectrophotometrically. The observed results suggest that two cerium (IV) ions are required for the oxidation of one molecule of D-mannose. However, due to the autoaccelerative nature of the reaction, the exact stoichiometry equation is difficult to predict.

### 2.2 Dependence on [Ce(IV)]

To evaluate the order of the reaction with respect to [Ce(IV)], a series of kinetic runs were carried out at different [Ce(IV)] (0.6 × 10<sup>-3</sup> to 1.8 × 10<sup>-3</sup> mol · dm<sup>-3</sup>) at fixed [D-mannose] and [H<sub>2</sub>SO<sub>4</sub>]. The rate constants were independent of initial [Ce(IV)] both in the absence and presence of surfactant (Table 1), indicating an approximate first-order dependence on [Ce(IV)]. The dependence can be given by

$$-d[\text{Ce(IV)}]/dt = k_{\text{obs}}[\text{Ce(IV)}] \quad (1)$$

Hardwick and Robertson<sup>[31]</sup> have reported the hydrolysis of cerium (IV) ion by water. Therefore, the rate of hydrolysis was also determined under the same kinetic conditions. The value of rate constant was found to be 6.3 × 10<sup>-6</sup> s<sup>-1</sup> at [Ce(IV)] = 1.0 × 10<sup>-3</sup> mol · dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 1.83 mol · dm<sup>-3</sup>, and T = 40 °C. The decay in absorbance of cerium (IV) is also shown in Fig.1 (A). It was observed that the change in absorbance of cerium (IV) aqueous solution was negligible after 12 h. Therefore, the stock solution of cerium (IV) was stored in a dark glass bottle and always used after 12 h.

### 2.3 Dependence on [D-mannose]

At [Ce(IV)] = 1.0 × 10<sup>-3</sup> mol · dm<sup>-3</sup> and [H<sub>2</sub>SO<sub>4</sub>] = 1.83 mol · dm<sup>-3</sup>, the effect of [D-mannose] (range: 1.0 × 10<sup>-2</sup>–9.0 × 10<sup>-2</sup> mol · dm<sup>-3</sup>) on the observed rate constant was followed both in aqueous and micellar media (Table 1). The linear plots of rate constants versus [D-mannose] pass through the origin (Fig.2), indicating first-order dependence on [D-mannose].

### 2.4 Dependence on temperature

From the rate constants obtained at 30, 35, 40, 45, and 50 °C,

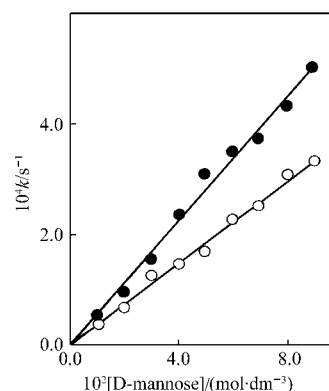
**Table 1** Effect of [Ce(IV)], [D-mannose], [H<sub>2</sub>SO<sub>4</sub>], and [HSO<sub>4</sub><sup>-</sup>] on the oxidation rate of D-mannose by cerium (IV) in absence ( $k_{\text{obs}}$ ) and presence ( $k_{\text{vt}}$ ) of surfactant ( $50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ) at 40 °C

$10^3[\text{Ce(IV)}]$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$[\text{H}_2\text{SO}_4]$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$10^2[\text{D-mannose}]$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$10^2[\text{HSO}_4^-]$ ( $\text{mol} \cdot \text{dm}^{-3}$ )	$10^4 k_{\text{obs}}$ $\text{s}^{-1}$	$10^4 k_{\text{vt}}$ $\text{s}^{-1}$
0.6	1.83	4.0		1.6	2.7
0.8				1.6	2.6
0.9				1.5	2.4
1.0				1.5	2.4
1.1				1.5	2.3
1.2				1.6	2.4
1.3				1.5	2.4
1.4				1.2	2.2
1.6				1.3	1.5
1.8				1.3	1.5
1.0	0.73	4.0		1.5	turbidity
	1.10			1.5	turbidity
	1.47			1.5	turbidity
	1.83			1.5	2.4
	2.20			1.2	2.1
	2.57			1.0	1.8
	2.94			0.8	1.7
	3.30			0.7	1.2
	3.67			0.5	1.2
1.0	1.83	1.0		0.4	0.6
		2.0		0.7	1.0
		3.0		1.4	1.6
		4.0		1.5	2.4
		5.0		1.7	3.1
		6.0		2.3	3.5
		7.0		2.5	3.7
		8.0		3.1	4.3
		9.0		3.3	5.0
1.0	1.83	4.0	5.0	1.5	
			10.0	1.4	
			15.0	1.3	
			20.0	1.3	
			25.0	1.2	
			30.0	1.0	
			35.0	0.9	
			40.0	0.8	

activation parameters were computed using Arrhenius (Fig.3) and Eyring plots. The values are given in Table 2. A lower value of activation energy in presence of CTAB confirms the catalytic role of cationic micelles in the redox reaction of D-mannose and cerium (IV).

### 2.5 Dependence on [H<sub>2</sub>SO<sub>4</sub>]

To observe the behavior of H<sub>2</sub>SO<sub>4</sub> (assuming [H<sub>2</sub>SO<sub>4</sub>]=[H<sup>+</sup>]) on rate constant, the acid concentration was varied in the range of 0.73–3.67 mol·dm<sup>-3</sup>. The rate was inhibited with increasing [H<sub>2</sub>SO<sub>4</sub>] (Table 1). Because of the involvement of large number of proton dependent equilibria in the cerium (IV), the exact computation on [H<sup>+</sup>] was not possible. The inhibition of reaction



**Fig.2** Effect of [D-mannose] on the rate constant  
reaction conditions: [Ce(IV)]= $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , [H<sub>2</sub>SO<sub>4</sub>]= $1.83 \text{ mol} \cdot \text{dm}^{-3}$ , [CTAB]= $0.0$  (○),  $50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  (●),  $T=40 \text{ }^\circ\text{C}$

rate by the addition of H<sub>2</sub>SO<sub>4</sub> may be due to the removal of reactive species of cerium (IV). A rate increase was found with the increase in [SO<sub>4</sub><sup>2-</sup>] (Na<sub>2</sub>SO<sub>4</sub> was added). Under the conditions of [D-mannose]= $4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ , [Ce(IV)]= $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , and [H<sub>2</sub>SO<sub>4</sub>]= $1.83 \text{ mol} \cdot \text{dm}^{-3}$  at 40 °C, the values of rate constants were  $1.5 \times 10^{-4}$ ,  $1.5 \times 10^{-4}$ ,  $1.6 \times 10^{-4}$ ,  $1.7 \times 10^{-4}$ ,  $1.7 \times 10^{-4}$ , and  $1.8 \times 10^{-4} \text{ s}^{-1}$  at [Na<sub>2</sub>SO<sub>4</sub>] values of 0.0,  $1.0 \times 10^{-4}$ ,  $2.0 \times 10^{-4}$ ,  $4.0 \times 10^{-4}$ ,  $5.0 \times 10^{-4}$ , and  $10.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ , respectively. The results indicate the involvement of cerium (IV)-sulfato species as the reactive species.

### 2.6 Dependence on [HSO<sub>4</sub><sup>-</sup>] at constant [H<sup>+</sup>]

To confirm the reactive species of cerium (IV), a series of kinetic runs were also performed at different [HSO<sub>4</sub><sup>-</sup>] (range: 0.0– $40.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ) at constant [H<sub>2</sub>SO<sub>4</sub>] ( $1.83 \text{ mol} \cdot \text{dm}^{-3}$ , ignoring the dissociation of HSO<sub>4</sub><sup>-</sup>)<sup>[32]</sup>. The reaction rate is retarded by an increase in [HSO<sub>4</sub><sup>-</sup>] (Table 1). The retardation in the rate with increasing [HSO<sub>4</sub><sup>-</sup>] suggests the removal of reactive species of cerium (IV).

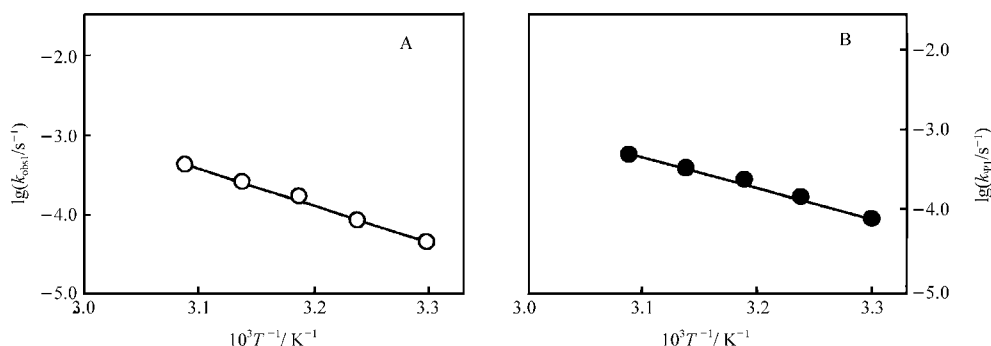
### 2.7 Effect of surfactants

To observe whether the bromide ion is capable for reaction with cerium (IV) under our kinetic conditions, some experiments were also performed in the absence of D-mannose (Ce(IV)+CTAB+H<sub>2</sub>SO<sub>4</sub>). The absorbance of cerium (IV) remained con-

**Table 2** Values of rate constants and activation parameters for the oxidation of D-mannose by cerium (IV) in absence and presence of surfactant

$T/^\circ\text{C}$	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^4 k_{\text{vt}}/\text{s}^{-1}$	$E_a$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J} \cdot \text{mol}^{-1} \text{K}^{-1}$ )
30	0.4	0.7			
35	0.8	1.4			
40	1.5	2.4			
45	2.4	3.3			
50	3.8	4.8			
			94 <sup>a</sup>	91 <sup>a</sup>	-28 <sup>a</sup>
			79 <sup>b</sup>	76 <sup>b</sup>	-73 <sup>b</sup>

reaction conditions: [Ce(IV)]= $1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , [H<sub>2</sub>SO<sub>4</sub>]= $1.83 \text{ mol} \cdot \text{dm}^{-3}$ , [D-mannose]= $4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ , [CTAB]= $0.0$  ( $k_{\text{obs}}$ ),  $50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  ( $k_{\text{vt}}$ );  
a: obtained from  $k_{\text{obs}}$ , b: obtained from  $k_{\text{vt}}$



**Fig.3 Arrhenius plots for the oxidation of D-mannose by cerium (IV)**

reaction conditions:  $[Ce(IV)]=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[H_2SO_4]=1.83 \text{ mol} \cdot \text{dm}^{-3}$ ,  $[D\text{-mannose}]=4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[CTAB]=0.0$  ( $\circ$ ),  $50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$  ( $\bullet$ )

stant for the entire range of  $[CTAB]$  used in the kinetic experiments. This suggests that the oxidation of bromide ion by cerium (IV) is not involved (Fig. 1(A)) even as a side reaction in the D-mannose oxidation by cerium (IV) in presence of CTAB. Furthermore, a series of kinetic experiments performed with varying  $[Br^-]$  ( $10.0 \times 10^{-4}$  to  $50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ) at constant  $[H_2SO_4]=1.83 \text{ mol} \cdot \text{dm}^{-3}$ ,  $[Ce(IV)]=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , and  $T=40^\circ \text{C}$  showed constancy of absorbance upto 90 min. The time required for complete oxidation of D-mannose is also 90 min under the same kinetic conditions. These results confirm that there is no reduction of cerium (IV) by bromide ion.

Several redox reactions in micellar media are influenced by the hydrophobic and electrostatic forces and for a given set of reactions, the observed rate depends on the extent of association between the reactants and micellar aggregates. Therefore, in order to observe the role of surfactants and to confirm the active species of cerium (IV), a series of kinetic runs were performed in presence of varying amounts of SDS and CTAB at constant  $[Ce(IV)]$  ( $=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ),  $[D\text{-mannose}]$  ( $=4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ),  $[H_2SO_4]$  ( $=1.83 \text{ mol} \cdot \text{dm}^{-3}$ ), and  $T=40^\circ \text{C}$ . The observed pseudo first-order rate constants are summarized in Table 3. It is observed that the rate constant increases with the increase in  $[CTAB]$  but SDS has no effect (Fig.4). The positive catalytic effect of CTAB indicates the incorporation/association of the reactants into or at

the surface of the cationic CTAB micelles. In case of SDS, there is a repulsion between the anionic head group ( $-\text{OSO}_3^-$ ) and the reactive cerium (IV) species (negatively charged), whereas the latter may form an ion-pair with the positive head group of CTAB micelles. Thus, an increase in the effective concentration of cerium (IV) within a small volume takes place. In addition, the partitioning of D-mannose in the micellar pseudophase cannot be ruled out because the Stern layer is water rich (the water activity in the aqueous phase and in the micellar pseudophase is similar<sup>[33]</sup>).

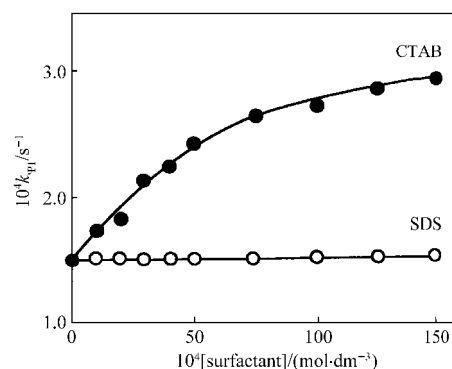
## 2.8 Mechanism and rate law

Aldoses exist predominantly as cyclic hemiacetals that are in equilibrium with the cyclic form and an open chain. The monosaccharides are considered as a polyol and the reactivities of  $-\text{OH}$  groups can be influenced by the presence of the carbonyl group. It has been established that the reactivity of D-glucose and D-mannose is higher in comparison to glycol<sup>[34]</sup>. Aldohexoses exist mainly as pyranoid and furanoid forms, the former being more stable. The pyranoid form mainly exists in a chair conformation. The presence of  $\alpha$ - and  $\beta$ -pyranose forms of D-mannose has been calculated from NMR studies<sup>[35]</sup> at  $30^\circ \text{C}$  and found to be 64:36. Out of these two forms,  $\beta$ -anomer is more reactive<sup>[36]</sup>. On the contrary, various species of cerium (IV) ( $Ce(OH)^{3+}$ ,  $CeSO_4^{2+}$ ,  $Ce(SO_4)_2$ ,  $H_2Ce(SO_4)_3^-$ ,  $H_3Ce(SO_4)_4^{2-}$ , and  $Ce(SO_4)_3^{3-}$ ) are known to be present in  $H_2SO_4$  media and various equilibria between ceri-

**Table 3 Effect of [CTAB] on the pseudo first-order rate constant for the oxidation of D-mannose by cerium (IV)**

$10^4[CTAB]/(\text{mol} \cdot \text{dm}^{-3})$	$10^4k_{\text{pfi}}/\text{s}^{-1}$	$10^4k_{\text{pfi}}/\text{s}^{-1}$	$(k_{\text{pfi}}-k_{\text{pfi}}^0)/k_{\text{pfi}}^0$
0.0	1.5		
10.0	1.7	1.7	0.00
20.0	1.8	1.8	0.00
30.0	2.1	2.0	0.05
40.0	2.2	2.1	0.05
50.0	2.4	2.3	0.04
75.0	2.6	2.5	0.04
100.0	2.7	2.7	0.00
125.0	2.8	2.9	-0.04
150.0	2.9	3.0	-0.03

$[Ce(IV)]=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[D\text{-mannose}]=4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ,  
 $[H_2SO_4]=1.83 \text{ mol} \cdot \text{dm}^{-3}$ ;  $T=40^\circ \text{C}$



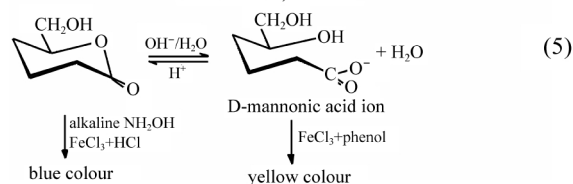
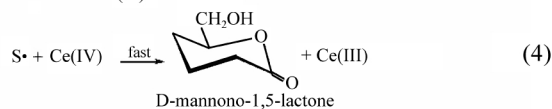
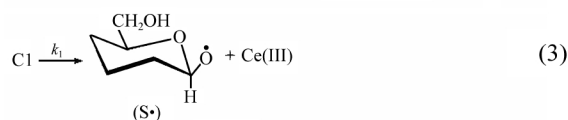
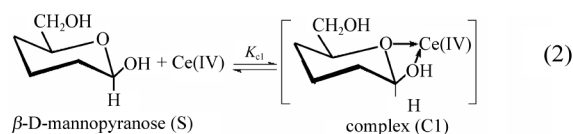
**Fig.4 Effect of surfactants on  $k_{\text{pfi}}$**

reaction conditions:  $[Ce(IV)]=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[H_2SO_4]=1.83 \text{ mol} \cdot \text{dm}^{-3}$ ,  
 $[D\text{-mannose}]=4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ ;  $T=40^\circ \text{C}$

um (IV) and  $\text{HSO}_4^-$  are reported in literature on several occasions<sup>[31,37-40]</sup>. On the basis of rate retarding effects of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$ ,  $\text{Ce}(\text{SO}_4)_2$  has been considered to be the reactive form in most of the reactions of cerium (IV)<sup>[39,41,42]</sup>. Alternatively,  $\text{HSO}_4^-$  and  $\text{H}_2\text{SO}_4$  dependencies also suggest the participation of  $\text{HCe}(\text{SO}_4)_3^-$  and  $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$ , respectively, as the reactive species<sup>[42,43]</sup>. In the present case, the catalytic role of CTAB micelles clearly suggests the involvement of a negatively charged species of cerium (IV). It completely excludes the possibility of  $\text{Ce}(\text{SO}_4)_2$  being the reactive species. Thus, we may safely conclude that  $\text{Ce}(\text{SO}_4)_2^{2-}$ ,  $\text{HCe}(\text{SO}_4)_3^-$ , and  $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$  might be considered to be the most active species in the present system. Further, reaction rate is inversely proportional to  $[\text{H}_2\text{SO}_4]$  which shows that  $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$  can not be kinetically active. Hardwick and Robertson<sup>[31]</sup> have proposed the equilibrium  $\text{Ce}(\text{SO}_4)_2 + \text{HSO}_4^- \rightleftharpoons \text{Ce}(\text{SO}_4)_3^{2-} + \text{H}^+$  and the formation of  $\text{Ce}(\text{SO}_4)_3^{2-}$  has been questioned<sup>[37,38]</sup>. If we consider  $\text{Ce}(\text{SO}_4)_3^{2-}$  as the reactive species, simultaneous formation of  $\text{HCe}(\text{SO}_4)_3^-$  is equivalent to the formation of  $\text{Ce}(\text{SO}_4)_3^{2-} + \text{H}^+$  in solution. Presently, it is difficult to answer which of the two negatively charged species ( $\text{Ce}(\text{SO}_4)_3^{2-}$  or  $\text{HCe}(\text{SO}_4)_3^-$ ) is the active form of Ce(IV).

Evidence for the formation of stable coordination complexes has been obtained by kinetic and spectrophotometric methods for cerium (IV) oxidations of many compounds in perchloric and nitric acids<sup>[1,44-46]</sup>. Complex formation in cerium (IV) oxidations in sulfuric acid solution, has been indicated only in a few literatures<sup>[47,48]</sup>. However, in none of these was spectrophotometric evidence provided for the complex. Thus, in aqueous  $\text{H}_2\text{SO}_4$  media, complexation of organic substrate with Ce (IV)-sulfato species is a rare possibility<sup>[49]</sup>. However, there might be a weak association and the following steps given in Scheme 1 are quite reasonable.

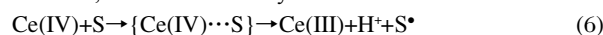
Scheme 1 is similar to that proposed by Mehrotra *et al.*<sup>[5]</sup>. Here, the complex C1 unimolecularly disproportionates in the



**Scheme 1** Probable mechanism for Ce(IV) and D-mannose reaction

rate determining step to give Ce(III) and  $\text{S}\cdot$ .

An alternate mechanism (Eq.(6)) might be given assuming the substrate to be directly oxidized by Ce(IV) in a bimolecular step. In this case, the interaction may occur at transition state



However, when the  $K_{cl}$  value is very small then it is not possible to discriminate between Scheme 1 and Eq.(6). Scheme 1 and Eq.(6), cerium (IV) actually denotes the kinetically active cerium (IV) species.

The derived rate law for Scheme 1 is

$$-d[\text{Ce(IV)}]/dt = k_1 K_{cl} [\text{D-mannose}] [\text{Ce(IV)}] \quad (7)$$

which is in accordance with the observations, i.e., first-order dependence both in [D-mannose] and cerium (IV). As explained above, exact equation for observing the inverse-order kinetics each in  $[\text{H}_2\text{SO}_4]$  and  $[\text{HSO}_4^-]$  can not be derived due to uncertainty of the involved protonic equilibria producing the active cerium (IV) species.

## 2.9 Analysis of $k_{\psi}$ -[surfactant] profile

In the present study, as the rate dependence on all the variables ( $[\text{Ce(IV)}]$ ,  $[\text{H}_2\text{SO}_4]$ , [D-mannose], and temperature) is the same for aqueous medium and in presence of CTAB, there is no change in the mechanism in presence of the surfactant. Thus the reaction proceeds through the same mechanism in both media.

Several models have been advanced to explain the catalysis of rate in presence of micelles<sup>[19-23]</sup>. The variation of rate constant with surfactant is treated on the assumption that the substrate (Ce(IV)) is distributed between the aqueous and micellar pseudophases as given in Scheme 2 (where  $(\text{Ce(IV)})_m$  is the micelle incorporated cerium (IV),  $[\text{D}_n] = [\text{surfactant}]_T - \text{cmc}$ ,  $K_s$  is the micelle-Ce (IV) binding constant, and  $k_w$  and  $k_m$  are first-order rate constants in aqueous and micellar pseudophases, respectively).

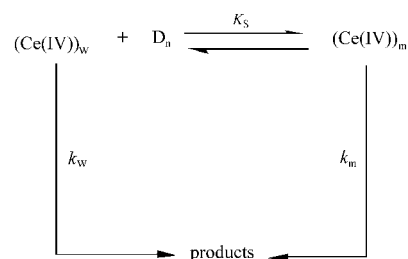
According to Scheme 2, the observed rate constant is expressed as a function of  $[\text{D}_n]$ , Eq.(8),

$$k_{\psi} = \frac{k_w + k_m K_s [\text{D}_n]}{1 + K_s [\text{D}_n]} \quad (8)$$

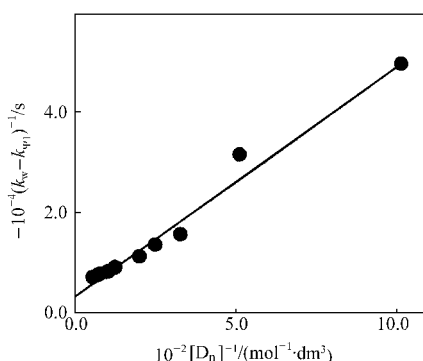
which may be rearranged in the form

$$\frac{1}{(k_w - k_{\psi})} = \frac{1}{(k_w - k_m)} + \frac{1}{(k_w - k_m) K_s [\text{D}_n]} \quad (9)$$

Thus, a linear plot of  $1/(k_w - k_{\psi})$  versus  $1/[\text{D}_n]$  should suggest the applicability of the Scheme 2 model. In the present investigation the plot is indeed linear (Fig.5), implying that this model is adequate for the present reaction. The intercept and slope give values of  $k_m$  and  $K_s$ , respectively. Under the experimental condi-

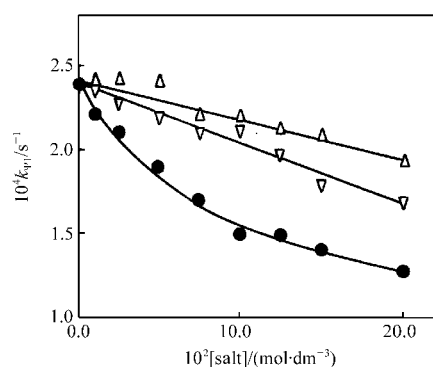


**Scheme 2** Distribution of Ce (IV) in aqueous and micellar pseudophases



**Fig.5** Plot of  $1/(k_w - k_{v1})$  versus  $1/[Dn]$  for the reaction in CTAB

Reaction conditions are the same as that in Fig.4.



**Fig.6** Effect of  $[Na_2SO_4]$  (●),  $[NaNO_3]$  (▽), and  $[NaCl]$  (△) on  $k_{v1}$

Reaction conditions are the same as that in Fig.4.  $[CTAB]=50.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$

tions,  $[Ce(IV)]=1.0 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $[D\text{-mannose}]=4.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ , and  $[H_2SO_4]=1.83 \text{ mol} \cdot \text{dm}^{-3}$  at  $40^\circ \text{C}$ , the values of  $k_m$  and  $K_s$  were found to be  $4.8 \times 10^{-4} \text{ s}^{-1}$  and  $58.2 \text{ mol}^{-1} \cdot \text{dm}^3$ , respectively. To obtain the  $k_{v\text{calc}}$ , the values of  $k_m$ ,  $K_s$ , and  $[D_n]$  were substituted in Eq.(8); the  $k_{v\text{calc}}$  is in excellent agreement with the observed  $k_{v1}$  (Table 3).

### 2.10 Salt effect

Added salts inhibit the micellar catalysis (Fig.6), which is a general phenomenon. The inhibition has been explained by assuming that the counterions compete with an ionic reactant for a site on the ionic micelle. Electrolytes have also been found to increase the aggregation number, decrease the  $\text{cmc}^{[50,51]}$ , and cause shape change from spherical to rod-like micelles. The redox reaction between cerium (IV) and D-mannose is catalyzed by CTAB. The added salts ( $Na_2SO_4$ ,  $NaNO_3$ ,  $NaCl$ ) inhibit the rate of reaction. As the concentration of these electrolytes increases, the concentration of cerium (IV) at the reaction site decreases due to salting-out effect of the salts. Thus, exclusion effect seems to be responsible for rate decrease in presence of inorganic electrolytes.

## 3 Conclusions

The oxidation of D-mannose by cerium (IV) in sulfuric acid medium (studying the kinetics in the absence and presence of cationic and anionic surfactants) is proposed to take place between the negatively charged species of cerium (IV) and pyra-

noid form of the monosaccharide. The reaction starts through the formation of an intermediate complex, which undergoes slowly unimolecular decomposition to a free radical. The free radical then reacts with cerium (IV) species to form the product.

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