

Contents lists available at ScienceDirect

# Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Role of cationic gemini surfactants (m-s-m type) on the oxidation of D-glucose by permanganate



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#### ARTICLE INFO

Article history: Received 25 September 2015 Received in revised form 31 December 2015 Accepted 16 January 2016 Available online xxxx

Keywords: Cationic gemini surfactant Micellar catalysis D-Glucose Permanganate

#### ABSTRACT

Cationic gemini (m-s-m type; m = 16, s = 4,5,6) surfactants were used to determine the micelles assisted kinetics parameters, mechanism of permanganate-D-glucose redox system in an aqueous solution by means of UVvisible spectroscopy at 40 °C. Effects of different [gemini surfactant], [permanganate], [D-glucose] and temperature on the reaction rate were investigated. Various activation parameters such as activation energy (Ea), enthalpy of activation ( $\Delta H^{\pm}$ ), free energy of activation ( $\Delta G^{\pm}$ ), and entropy of activation ( $\Delta S^{\pm}$ ) have been evaluated. Menger-Portony pseudo-phase model modified by Bunton was used to analyze the role of gemini surfactant on the rate constant. Spacer chain length of surfactants has significant impact on the oxidation -reduction kinetics. A suitable mechanism reliable with the experimental results has been proposed and discussed. The cationic gemini surfactant micellar media are relatively more efficient than conventional monomeric surfactant i.e. cetyltrimethylammonium bromide (CTAB).

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# 1. Introduction

Surfactant oriented research has become the topic of interest because of their physicochemical properties and potential application in chemical and technological areas like mineral processing, petroleum, pharmaceutical, food science and cosmetics [1-7]. They play a significant role in resolving many hazardous environmental problems caused by toxic polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons are formed by the pyrolysis of organic compounds during fossil fuel utilization, forest fires, etc. Surfactant-enhanced remediation (SER) process has been developed for the remediation of polycyclic aromatic hydrocarbons from contaminated soil and water system [8]. The structure of the surfactant molecule under consideration determines the physicochemical properties of surfactant molecules. For instance, when two long alkyl chains with polar head groups are bonded covalently by spacer of methylene units. Gemini surfactants are considered a unique class of surfactant. The unique physicochemical properties and enhanced performance in micellar catalysis have provided gemini surfactants a wide range attention from different scientific fields. Owing to these excellent properties, gemini surfactants have been used in industrial detergency, gene transfection, and also as corrosion inhibitors [9,10]. The dimeric or gemini surfactants are different from conventional surfactants because they have two hydrophobic chains

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and two hydrophilic groups covalently bonded through a spacer, which provides them special attention in both academic and industrial research fields [11–14]. The chemical structure of the two-headed, two-tailed surfactant connected at the level of the head groups by a spacer (s) is shown in Fig. 1. The various surface active properties of gemini surfactant molecules are superior to those of corresponding conventional surfactants having one hydrophilic and hydrophobic group. They are the new generation surfactants with very low critical micelle concentration, low Krafft points, unusual aggregation morphologies, better wetting properties and have capability in lowering the surface tension of water [15–21].

One of the widely used reaction media for various important organic reactions is the micelle forming surfactant media and their catalytic behavior toward organic reactions is an interesting topic of discussion. The esterolytic cleavage of phosphate and carboxylate esters in the presence of cationic gemini surfactants is well documented in the literature [22]. The micellization kinetic effects and micellar growth of cationic dimeric surfactant 12-s-12,  $2Br^{-}$  (spacer = 2–6) have been investigated in aqueous and organic solvents [23,24]. The effect of gemini surfactants on the chemical reaction rate has been the topic of interest for many research groups from the last many years [25–27]. For understanding several complex aspects about gemini micelles, kinetic investigations are one of the best tools that can help for better observations [28-30]. Different kinetic and thermodynamic investigations have been made on the micellization and micellar growth of different cationic dimeric surfactants both in aqueous and organic media [31–34]. The permanganate ion is an important oxidizing agent in neutral, alkaline and acidic media.

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Fig. 1. Chemical structure of gemini surfactant (16-s-16).

It is an eco-friendly and versatile oxidizing agent used for studying the kinetics of oxidation of various organic and inorganic reactions. It has achieved lot of importance in green chemistry as one of the most used oxidants for water treatment [35]. Permanganate is stable in neutral or slightly alkaline media but disproportionates in strongly alkaline media to form manganese(V) (hypomanganate) or manganese(VI) (manganate) [36]. The role of gemini surfactants in the oxidation of D-glucose by permanganate has not yet been reported. Therefore in the present study we are reporting the oxidation of D-glucose by permanganate in the presence of three gemini surfactants.

# 2. Experimental

## 2.1. Materials

The water (doubly distilled deionized with a conductivity of  $(1-2) \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ ) was used as solvent to the preparation of all regents solutions. D-Glucose, potassium permanganate (KMnO<sub>4</sub>), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, N,N-dimethylhexadecylamine, ethyl acetate and ethanol absolute were purchased from Aldrich and used as received. All the solvents and reagents used were of AR grade.

#### 2.2. Synthesis of dimeric gemini surfactant

Alkanediyl- $\alpha$ , $\Omega$ -bis(dimethylhexadecylammonium bromide) type of gemini surfactant, containing  $-N(CH_3)_2$  head groups has been prepared by the reported method [37,38] as shown in Scheme 1. In a three necked round bottom flask a mixture of N,Ndimethylhexadecylamine and  $\alpha$ , $\Omega$ -dibromoalkane (molar ratio 2.1:1) was stirred in dry ethanol at 80 °C for about 48 h to ensure the highest bisquaternization possible. The progress of the reaction was scrutinized by thin layer chromatography. Hexane/ethyl acetate mixture was used for washing the synthesized crude white solid. The product was recrystallized from methanol/acetone



**Scheme 1.** Synthetic route for synthesis of the gemini surfactant (16-s-16) (spacer (s) = 4,5,6).

mixture for two to three times till the purity of the compound was established through TLC. The percentage yield of the synthesized product was observed to be about 70–75%. The IR spectrum of the gemini surfactants was recorded on a Bruker Tensor II FT-IR Spectrometer. Perkin-Elmer series II analyzer was used for the elemental analysis of the surfactants. <sup>1</sup>H NMR spectra of the synthesized cationic gemini surfactants were recorded on a 600-MHz Bruker NMR spectrometer in CDCl<sub>3</sub>.

#### 2.3. Determination of critical micellar concentration (cmc)

Conventional conductivity technique was used to determine the cmc (the concentration over which monomeric surfactant molecules rapidly aggregate to form micelles) of the gemini (16-s-16, s = 4, 5, 6) surfactants. Aqueous KCl solutions in the proper concentration range were used for the calibration of the conductivity cell (cell constant = 1.02). All conductivity measurements of the desired solution were carried out at 40 °C. The cmc was achieved from the break points of nearly two straight lines of the specific conductivity versus [surfactant] [39] and their values under different experimental conditions, i.e., gemini + water, gemini +  $MnO_4^-$ , gemini + glucose, and gemini +  $H_2SO_4$  are summarized in Table 1.

#### 2.4. Reaction product analysis

In order to identify the oxidation product of D-glucose, a series of experiments were performed under different experimental conditions. After the completion of the kinetic experiment, alkaline hydroxylamine solution was added to the oxidized reaction mixture and the lactone presence was examined by FeCl<sub>3</sub>–HCl blue test [40]. In order to neutralize the reaction mixture barium carbonate was added to the reaction mixture. On adding FeCl<sub>3</sub> solution that had been colored violet with phenol, turned bright-yellow, indicating that aldonic acid is formed as the oxidation product. Apparently, the lactone, which formed in the rate determining step, hydrolyzed to the aldonic acid in neutral medium in a fast step [41]. In addition, lactone was identified against an authentic sample (1,4-d-glucolactone) using 4:1:5 n-butanol-acetic acid-water eluent. A three-stage dip of AgNO<sub>3</sub>, NaOH, and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used to visualize the paper chromatograms [42].

Table 1

The cmc values of gemini surfactants under different experimental conditions at 40 °C.

Reaction solution <sup>a</sup>	16-4-16 16-5-16		16-6-16		
	$10^4 \mathrm{cmc} (\mathrm{mol} \mathrm{dm}^{-3})$				
Water + 16-s-16 16 c 16 + $MpO^{-}$	0.41 (.30)	0.35 (0.34)	0.31 (0.39)		
$16-s-16 + H_2SO_4$	0.28	0.23	0.23		
16-s-16 + glucose	0.38	0.30	0.28		

The literature values of cmc are given in the parenthesis.

 $^a$  [Glucose] = 4.0  $\times$  10  $^{-3}$  mol dm  $^{-3}$ ; [MnO  $_4$ ] = 4.0  $\times$  10  $^{-4}$  mol dm  $^{-3}$ ; [H<sub>2</sub>SO<sub>4</sub>] = 1.0  $\times$  10  $^{-4}$  mol dm  $^{-3}$ .

# 2.5. Kinetic measurements

The required volumes of MnO<sub>4</sub><sup>-</sup>, 16-s-16 gemini surfactant and  $H_2SO_4$  (for maintaining the desired [H<sup>+</sup>]) were introduced into a three necked reaction vessel fitted with a double-walled condenser to arrest evaporation. The reaction vessel was kept in a thermostat maintained at a desired temperature (40 °C). The reaction was started by adding the required and thermally equilibrated solution of D-glucose. The zero time was taken when half of the D-glucose solution has been added. The reaction progress was followed at 525 nm ( $\lambda_{max}$  of MnO<sub>4</sub><sup>-</sup>) using a sampling technique and UV/vis spectrophotometer (UV-260 Shimadzu, with 1 cm quartz cuvettes) was used for absorbance measurements at specific time intervals. A control dynamic pH-meter fitted with a combination electrode was used to measure the pH of the working solutions. Pseudo-first-order conditions were used to determine the rate constants  $(k_{obs}, s^{-1})$  by using a large excess of D-glucose over MnO<sub>4</sub><sup>-</sup> in all kinetic runs. Duplicate runs gave results that were reproducible to within  $\pm 4\%$ . Other details of the kinetic measurements were the same as described earlier [43].

# 3. Results and discussion

#### 3.1. Effect of [16-s-16] on reaction rate

The effect of [16-s-16] (s = 4,5,6) on the reaction rate was observed by varying different concentrations of gemini surfactants (from  $1.0 \times 10^{-4}$  to  $22.0 \times 10^{-4}$  mol dm<sup>-3</sup>) and keeping all other reaction conditions constant, i.e.  $[MnO_4^- = 4.0 \times 10^{-4} \text{ mol } dm^{-3}, [D-glucose] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}, [H_2SO_4] = 1.00 \times 10^{-4} \text{ mol } dm^{-3}$  and temperature = 40  $^{\circ}$ C. It was observed that reaction rate first increases with [surfactant], remains constant up to certain concentration and increases sharply at higher concentrations (Fig. 2). Inspection of data clearly indicates that used surfactant has pre- and post-micellar catalytic effects on the redox reaction, which might be due to the preponement of micellization by reactants and/or the presence of premicelles [44]. Generally, micellar catalysis has been interpreted in terms of the pseudophase ion exchange model and pseudophase model [45]. The catalytic effect of gemini surfactants on the reaction rate is explained in terms of the Menger and Portnoy [46] pseudo-phase model (Scheme 2), later developed by Bunton [47]. Micelles are dynamic structures which are influenced by counterions, ionic strength, polarity of the medium and temperature, etc. [48]. The effects of structural variation of the surfactants have been analyzed by various models and theories [49-51]. The



**Fig. 2.** Plot showing the effects [16-s-16] on  $k_{obs}$  of the oxidation of D-glucose by permanganate. *Reaction conditions*:  $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[D\text{-glucose}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$ , temperature = 40 °C.

interfacial ion exchange and the binding constant of the substrate are the key factors for the efficiency of micellar catalysis. It seems reasonable to expect that a factor of importance for the relative rates in the aqueous and micellar pseudophase would be the orientation of the substrate molecule within the surfactant aggregate. The overall kinetic behavior of the surfactants is described in the framework of the pseudo-phase model. It has been established that the rate enhancement is mainly due to the reagent concentration in the micellar pseudophase. In this system, substrate is distributed between the bulk and micellar phases (Scheme 2).

In Scheme 2, subscripts w and m represent aqueous and micellar pseudo-phases.  $k_w$  and  $k_m$  are the second order rate constants in aqueous phase and micellar pseudophase, respectively.  $K_n$  and  $K_s$  are the binding constants of D-glucose and  $MnO_4^-$  to the micelles, respectively and [Dn] = the concentration of the micellized surfactant =  $([16-s-16]_T-cmc)$ .

Corresponding to the Scheme 2, the following rate equation can be obtained as Eq. (1) and modified as Eq. (2):

$$k_{obs} = \frac{k_w + k_m K_s [D_n]}{(1 + K_s [D_n])} \tag{1} \label{eq:kobs}$$

$$\begin{split} k_{obs} &= \frac{k'_w [D\text{-}glucose]_T + (K_s k'_m - k'_w) MG^s [D_n]}{(1 + K_s [D_n])} \\ k'_w &= \frac{k_w}{[D\text{-}glucose]} \quad k'_m = \frac{k_m}{MG^s} \quad MG^s = \frac{[D\text{-}glucose]}{[D_n]} \end{split}$$

The following equilibrium was used to obtain the value  $MG^S$ . Using Eq. (4) and the mass balance of glucose,  $[D-glucose]_T = [(D-glucose)_w] + [(D-glucose)_m]$ , a quadratic Eq. (5) can be obtained which is solved for  $[(D-glucose)_m]$  with the help of a computer program with  $K_n$  as an adjustable parameter [52]. The cmc values were determined under experimental conditions and a non-linear least-square technique was used for the calculation of  $k'_m$  and  $K_n$ . These values are summarized in Table 2.

$$(D-glucose)_{w} + D_{n} \stackrel{\kappa_{n}}{\rightleftharpoons} (D-glucose)_{m}$$
 (3)

$$K_{n} = \frac{\left[ (D-glucose)_{m} \right]}{\left[ (D-glucose)_{w} \right] + \left( [D_{n}] - \left[ (D-glucose)_{m} \right] \right)}$$
(4)

$$\begin{array}{l} K_n \big[ (D\mbox{-}glucose)_m \big]^2 - (1 + K_n [D_n] + K_n [D\mbox{-}glucose]_T) \\ \times \big[ (D\mbox{-}glucose)_m \big] + K_n \big( [D_n] \big[ (D\mbox{-}glucose)_T \big] \big) = 0 \end{array}$$

$$\tag{5} \label{eq:starses}$$

Under the present experimental condition it was observed that the rate constant values are more at 16-4-16 as compared to 16-5-16 and 16-6-16 and follow the order 16-4-16 > 16-5-16 > 16-6-16 among the gemini molecules. It is well documented in the literature that the length of the spacer and the type of the moiety dictate the conformation of the gemini surfactant molecule [53]. Because of shorter spacer length the micelle formation is more in 16-4-16 as compared to 16-5-16 and 16-6-16 gemini molecules. The shorter spacer is the reason for the increasing geometrical constraints in the formation of aggregates with decreasing the spacer unit length [54]. The cmc values decrease with increased in hydrophobic chain length of the surfactant molecule. The micellar morphology tends to be less ellipsoidal with increasing spacer in gemini surfactants is well supported by microviscosity and SANS data [55]. As a result the spacer greatly controls the surfactant morphology and the rate constant values obtained in the present study are consistent with the expectation being maximum at spacer = 4, beyond which looping of the spacer (to minimize its contact with water [56]) will progressively make the Stern layer more wet with the resultant rate constant decrease. Thus, increasing the hydrophobicity of spacer from 4 to 6 entirely changes the whole scenario of the reaction kinetics.



Scheme 2. Schematic representation for the distribution of D-glucose and  $MnO_4^-$  in micelles according to pseudophase model.

Inspection of Table 1 clearly suggests that the corresponding cmc values of 16-s-16 surfactants in aqueous solution are in close agreement with the values reported in the literature [57]. The small change in the cmc with  $MnO_4^-$  could be associated to the formation of ion-pair between permanganate ion and surfactant molecules through electrostatic interactions. This behavior indicates the electrostatic interaction between the positive head group of 16-s-16 surfactants and permanganate ion or the association of the  $MnO_4^-$  into the stern layer of the 16-s-16 micelles, which results in the formation of ion-pair complex between  $MnO_4^-$  and cationic gemini surfactant. In the present study,  $H_2SO_4$  was used to maintain  $[H^+]$  constant. Therefore, cmc values were also determined in the presence of  $H_2SO_4$ , which might be attributed due to the electrostatic interactions and/or association of  $HSO_4^-$  ions with the positive head group of 16-s-16 cationic micelles.

# 3.2. Probable reaction site

It has been established that electrostatic, hydrophobic, and hydrogen bonding were the main driving force for the solubilization and/or incorporation of reactants ( $MnO_4^-$  and glucose) into the micellar pseudo-phases. Due to the electrostatic interactions,  $MnO_4^-$  formed ion-pair with the positive head group ( $-N^+(CH_3)_2$ ) of surfactant. As the spacer chain length increases between the two cationic head groups of used gemini surfactants, surface area of the solubilized reactants decreases, which in turn, decreases the reaction rates (Table 2). In the present case, the maximum rate enhancement is found with the

#### Table 2

Activation parameters, rate and binding constant values for the D-glucose oxidation by permanganate. *Reaction conditions*:  $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[p-glucose] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}$ ,  $[16\text{-s}\text{-}16] = 3.0 \times 10^{-4} \text{ mol } dm^{-3}$  and  $[H_2SO_4] = 1.00 \times 10^{-4} \text{ mol } dm^{-3}$ .

Temperature (°C)	$10^4 k_{obs} (s^{-1})$				
	16-6-16	16-5-16	16-4-16		
40	1.02	1.25	1.50		
45	1.40	1.70	2.0		
50	1.95	2.25	2.55		
55	2.65	3.0	3.55		
60	3.40	3.90	4.35		
Parameters					
Ea (kJ mol <sup>-1</sup> )	52	48	44		
$\Delta H^{\#}$ (kJ mol <sup>-1</sup> )	49	45	41		
$\Delta S^{\#}$ (JK <sup>-1</sup> mol <sup>-1</sup> )	-213	-205	-199		
$\Delta G^{\#}$ (kJ mol <sup>-1</sup> )	115	109	103		
$10^3 \mathrm{k_m}(\mathrm{s}^{-1})$	9.2	7.3	8.1		
$K_{s} (mol^{-1} dm^{3})$	110	105	92		
$K_n (mol^{-1} dm^3)$	88.2	76.7	85.2		

shortest spacer (s = 4). It is due to the fact that a decrease in spacer chain length increases the surface charge density of the micelles. Thus, 16-4-16 interacts more strongly with the MnO<sub>4</sub><sup>--</sup> as compared to the other largest spacer geminis (16-5-16 and 16-6-16). Reactions take place between the micellar solubilized MnO<sub>4</sub><sup>--</sup> and D-glucose and the bound counter ions in the Stern and Gouy-Chapman layers' junctural region. Micellization increases the reaction rate because on micellization counterions can be attracted or repelled more effectively. Micellar surfaces are water-rich and do not provide a uniform reaction medium because a micelle is a porous cluster with a rough surface and deep-waterfilled cavities. Therefore, it is not possible to precisely locate the exact site to the micelle-assisted reactions. However, localization of the reactants can be considered. A highly schematic (possible solubilization and/or incorporation) could be that as shown in Scheme 3.

# 3.3. Effect of [reactants] on reaction rate

To find the effect of  $[MnO_4^-]$  on the reaction rate,  $[MnO_4^-]$  was varied from 2.0 to  $8.0 \times 10^{-4}$  mol dm<sup>-3</sup> at fixed [D-glucose] =  $4.0 \times 10^{-3}$ mol dm<sup>-3</sup>,  $[H_2SO_4] = 1.00 \times 10^{-4}$  mol dm<sup>-3</sup> and temperature = 40 °C in the presence of constant gemini surfactants [16-s-16] = $3.0 \times 10^{-4}$  mol dm<sup>-3</sup>. The reaction rate remains constant and did not show any significant effect, indicating pseudo-first kinetics with respect to [MnO<sub>4</sub><sup>-</sup>]. To investigate the effect of [D-glucose] on the reaction rate, [D-glucose] was varied from  $1.0 \times 10^{-3}$  to  $10.0 \times 10^{-3}$  mol dm<sup>-3</sup> at constant [MnO<sub>4</sub>] = 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [16-s-16] =  $3.0 \times 10^{-4}$  mol dm<sup>-3</sup> and temperature =  $40 \degree$ C. The reaction rate increases with [D-glucose] (Fig. 3). The plot of log k<sub>obs</sub> versus log [D-glucose] gave a straight line with a slope of 0.93, 0.86, 0.72, in the presence of gemini surfactants 16-6-16, 16-5-16 and 16-4-16 respectively, shows that the oxidation reaction was fractional order with respect to [D-glucose]. The double reciprocal plot of 1/k<sub>obs</sub> versus 1/[D-glucose] gave a straight line with a definite intercept, indicating the reaction follow Michaelis-Menten type of kinetic. Initially the kinetic runs were carried out in absence of H<sub>2</sub>SO<sub>4</sub> and it was observed that the reaction does not take place. This suggests that the reaction is highly dependent on [H<sup>+</sup>]. The rate constant, obtained as a function of  $[H_2SO_4]$  at constant  $[MnO_4^-] = 4.0 \times 10^{-4}$  mol dm<sup>-3</sup>,  $[D-glucose] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}, [16-s-16] =$  $3.0 \times 10^{-4} \text{ mol } \text{dm}^{-3}$  and temperature = 40 °C, was found to reach a maximum at  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, and then fall drastically. The plot between log[H<sub>2</sub>SO<sub>4</sub>] and logk<sub>obs</sub> was found to be linear with positive slopes = 0.87, 0.82, 0.79 for 16-6-16, 16-5-16 and 16-4-16, respectively. Thus the reaction follows fractional-order kinetics with respect to [H<sub>2</sub>SO<sub>4</sub>]. Interestingly, the kinetics and mechanism of D-glucose-MnO<sub>4</sub><sup>-</sup> redox system is the same in the absence and presence of gemini surfactants. It is also concluded from the observed results that the order of reaction in the presence of cationic surfactants do not differ in any way as that of aqueous medium.

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Scheme 3. Schematic model showing probable location of reactants for the micellar-catalyzed reaction between D-glucose and MnO<sub>4</sub><sup>-</sup>.

#### 3.4. Effect of temperature and activation parameters

Activation parameters are believed to provide useful information regarding the environment in which chemical reactions take place. In order to determine the activation parameters, a series of kinetic experiments for oxidation of D-glucose by MnO<sub>4</sub><sup>-</sup> were carried out at four different temperatures (40–60 °C) and other reactant concentration constant (i.e. [MnO<sub>4</sub><sup>-</sup>] = 4.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> and [D-glucose] =  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>) in presence of m-s-m type gemini surfactant micelles =  $(3.0 \times 10^{-4} \text{ mol dm}^{-4})$ . Arrhenius plots (lnk<sub>obs</sub> and 1/T) are shown in Fig. 4. The values of activation energy (Ea) were calculated from the slopes of Fig. 4. Activation enthalpy ( $\Delta$ H<sup>#</sup>), activation entropy ( $\Delta$ S<sup>#</sup>) and the free energy ( $\Delta$ G<sup>#</sup>) are determined by using Eyring equations (Table 2). It is observed from the derived results that gemini surfactants lower the values of activation enthalpy ( $\Delta$ H<sup>#</sup>) and activation entropy ( $\Delta$ S<sup>#</sup>) than aqueous. This lowering may occur not only through the



**Fig. 3.** Plot showing the effect of [D-glucose] on  $k_{obs}$ . Reaction conditions:  $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[16\text{-s}-16] = 3.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4] = 1.00 \times 10^{-4} \text{ mol } dm^{-3}$ , temperature = 40 °C.

adsorption of  $MnO_4^-$  and D-glucose on micellar surface but also through stabilization of transition state. The decline in the  $\Delta S^{\#}$  proposes that the transition state is well structured in case of gemini surfactant micelles (spacer = 4) in comparison to gemini surfactants (spacer = 05 and spacer = 6). However, a more meaningful mechanistic explanation of the apparent values of  $\Delta H^{\#}$  and  $\Delta S^{\#}$  is not possible because the rate constant does not represent a single elementary kinetic step as it is a complex function of true rate, binding and ionization constants.

### 3.5. Mechanism and rate law

Kinetic method is the most important one, which establishes the most refined mechanism at the molecular level for any reaction. The most predominant form of D-glucose is  $\alpha$ -D-glucopyranose followed by  $\beta$ -D-glucopyranose. Among these  $\beta$ -D-glucopyranose is considered as the reaction species of D-glucose. Glucopyranose possess three different alcohol functionalities including a primary alcohol, three secondary



**Fig. 4.** Arrhenius plots for D-glucose oxidation by permanganate. *Reaction conditions*:  $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[16\text{-s}\text{-}16] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H_2SO_4] = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[p\text{-glucose}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ .



Scheme 4. Oxidation of D-glucose by permanganate.

alcohol groups and one hemiacetal hydroxyl group. Each of these OH groups can be oxidized to corresponding sugar derivatives as shown below.



In the light of above observations and observed results, the following mechanism given in Scheme 4 has been proposed for the oxidation of D-glucose by permanganate.

In Scheme 4, Eq. (6) represents the protonation of  $MnO_4^-$  to  $HMnO_4$ . The next reaction shows formation of complex between p-glucose and  $HMnO_4$  (Eq. (7)). It has been established that different species of manganese (Mn(VI), Mn(V), Mn(IV) and Mn(III)) are formed as an intermediate(s) during the reduction of permanganate. The stability of these species strongly depended on the experimental conditions and pH of the working media, i.e., acidic, alkaline and neutral. Out of these, Mn(IV) species is commonly involved in the permanganate oxidation of various reductants [58]. In analogy with previous studies [59], we assume that it decomposes in a one-step, two electron oxidation-reduction mechanism to  $MnO_4^{3-}$  (Mn(V)) and radical (Eq. (8)). Mn(V) is highly unstable in an acidic medium [60] with respect to disproportionation and immediately gets converted into  $MnO_2$  (Mn(IV)). Other oxidation states of Mn are obviously involved in the reaction; they are extremely unstable under the experimental conditions used in this study.

After the slow steps, the following fast reactions may also take place.

$$HO \xrightarrow{H}_{HO} \xrightarrow{H}_{H} \xrightarrow{OH}_{OH} + Mn(IV) \xrightarrow{Fast} redical + Mn(III)$$
(10)

$$Radical + Mn(III) \xrightarrow{Fast} Lactone + Mn(II)$$
(11)

The reduction of colloidal  $MnO_2$  to Mn(III) by Mn(II) has also been reported on several occasions [60].

A rate law consistent with Scheme 4 may be expressed as Eq. (12).

$$\frac{d[MnO_{4}^{\text{-}}]}{dt} = \frac{k \ K \ K_{a}[H^{+}][MnO_{4}^{\text{-}}]_{T}[D\text{-}glucose]}{(1 + K_{a}[H^{+}] + K \ K_{a}[H^{+}][D\text{-}glucose])}$$
(12)

and

$$k_{obs} = \frac{k \ K \ K_a[H^+][D-glucose]}{1 + K_a[H^+] + K \ K_a[H^+][D-glucose]}$$
(13)



**Fig. 5.** Plot of log 1/k<sub>obs</sub> vs. 1/[D-glucose] for the oxidation of D-glucose by permanganate. *Reaction conditions*:  $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[16\text{-s-16}] = 3.0 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[H_2SO_4] = 1.00 \times 10^{-4} \text{ mol } dm^{-3}$ ,  $[D\text{-glucose}] = 4.0 \times 10^{-3} \text{ mol } dm^{-3}$ , temperature = 40 °C.

# Table 3

Effect of [D-glucose] on the oxidation of D-glucose by permanganate and comparison of the kobs and kcal for the oxidation of D-glucose by permanganate. Reaction conditions:  $[MnO_{4}^{-}] = 4.0 \times 10^{-4} \text{ mol } dm^{-3}, [16-s-16] = 3.0 \times 10^{-4} \text{ mol } dm^{-3}, [H_2SO_{4}] = 1.00 \times 10^{-4} \text{ mol } dm^{-3}, \text{temperature} = 40 ^{\circ}C.$ 

$10^3$ [D-glucose] (mol dm <sup>-3</sup> )	$10^4 k_{obs} (s^{-1})$			$10^4 k_{cal} (s^{-1})$		$(k_{obs} - k_{cal}  /  k_{obs})$			
	16-6-16	16-5-16	16-4-16	16-6-16	16-5-16	16-4-16	16-6-16	16-5-16	16-4-16
1	0.24	0.32	0.47	0.22	0.30	0.47	0.08	0.06	0.00
2	0.49	0.64	0.82	0.48	0.60	0.79	0.02	0.06	0.03
3	0.77	0.92	1.15	0.75	0.94	1.12	0.02	-0.02	0.00
4	1.02	1.25	1.50	1.02	1.27	1.53	0.00	-0.01	0.02
5	1.21	1.47	1.70	1.18	1.50	1.74	0.02	-0.02	-0.02
6	1.40	1.67	1.86	1.37	1.67	1.81	0.02	0.00	0.02
7	1.61	1.86	2.05	1.60	1.88	2.07	0.00	-0.01	-0.01
8	1.79	2.04	2.20	1.81	2.02	2.15	-0.01	0.01	0.02
9	1.97	2.20	2.36	2.00	2.24	2.30	-0.01	-0.01	0.02
10	2.08	2.34	2.48	2.04	2.28	2.54	0.01	0.02	-0.02

On the other hand, the rate law, Eq. (13), which is consistent between the extreme conditions, has been verified by rewriting it as Eq. (14).

$$\frac{1}{k_{obs}} = \frac{1 + K_a [H^+]}{k \ K \ K_a [H^+] [D-glucose]} + \frac{1}{k}$$
(14)

According to Eq. (14), the plot of 1/k<sub>obs</sub> versus 1/[D-glucose] should be linear (Fig. 5) with a positive intercept on the y-axis. The values of k and K were calculated from the intercept and slope of figure and were found to be slopes = 4.09, 2.99, 1.92 and intercepts = 0.02, 0.10, 0.21 for 16-6-16, 16-5-16 and 16-4-16, respectively. In order to conform the validity of rate law (Eq. (13)), the values of k, K, K<sub>a</sub>, [H<sup>+</sup>] and [D-glucose] are substituted and k<sub>cal</sub> has been calculated in various kinetic runs (Table 3). These values are found in good agreement with the experimental kobs, which provides supporting evidence for the proposed mechanism (Scheme 4) and to Eq. (13) and confirming the Michaelis-Menten reciprocal relationship, which is a kinetic proof for complex formation between the reactants.

#### 4. Conclusions

The micellar catalyzed oxidation of D-glucose by  $MnO_4^-$  was studied in the presence of different gemini surfactant (16-s-16) concentrations at 40 °C. The observed results clearly demonstrate that the reaction rate is enhanced in the presence of gemini surfactants as compared to cationic surfactant cetyltrimethylammonium bromide. A plausible mechanism and related rate law have been derived on the basis of observed kinetic results. The effect of different reactant concentrations was also carried out to provide the complete information regarding the order of the reaction. It seems that the increased hydrophobicity was responsible for higher concentration of D-glucose in the Stern layer of the micelles. Activation parameters were also evaluated at different temperatures. The activation energy (Ea), activation enthalpy ( $\Delta H^{\#}$ ), activation entropy ( $\Delta S^{\#}$ ) and free energy ( $\Delta G^{\#}$ ) values have been calculated and interpreted accordingly.

#### References

- [1] M.S. Bakshi, K. Singh, J. Singh, J. Colloid Interface Sci. 297 (2006) 284-291.
- [2] D. Tikariha, B. Kumar, S. Ghosh, A.K. Tiwari, N. Barbero, P. Quagliotto, K.K. Ghosh, J. Nanofluids. 2 (2013) 316-324. [3] A. Rodriguez, M.M. Graciani, M. Vargas, M.L. Moya, J. Phys. Chem. B 112 (2008)
- 11942-11949
- [4] T. Chakraborty, I. Chakraborty, S. Ghosh, Arab. J. Chem. 4 (2011) 265-270.
- S. Ghosh, J. Colloid Interface Sci. 244 (2001) 128-138.
- [6] G. Basu Ray, I. Chakraborty, S. Ghosh, S.P. Moulik, C. Holgate, K. Glenn, R.M. Palepu, J. Phys. Chem. B 111 (2007) 9828-9837.
- T. Chakraborty, S. Ghosh, J. Surfactant Deterg. 11 (2008) 323-334.
- A.A. Dar, G.M. Rather, A.R. Das, J. Phys. Chem. 111 (2007) 3122-3132. [8]
- C. Keyes-Baig, J. Duhamel, S. Wetting, Langmuir 27 (2011) 3361-3371. [10] K. Sakai, K. Matsuhashi, A. Honya, T. Oguchi, H. Sakai, M. Abe, Langmuir 26 (2010) 17119-17125.
- [11] S. Ghosh, T. Chakraborty, J. Phys. Chem. B 111 (2007) 8080-8088.

- [12] M.S. Sheikh, Kabir-ud-din, A.A. Dar, Colloids Surf, A Physicochem, Eng. Asp. 378 (2011) 60-66
- [13] T. Chakraborty, S. Ghosh, Colloid Polym. Sci. 285 (2007) 1665-1673.
- [14] P. Sharma, S. Sachar, G. Kaur, P. Thakur, M.S. Bakshi, T.S. Banipal, J. Surf. Sci. Technol. 23 (2007) 131-147.
- T. Lu, Z. Li, J. Huang, H. Fu, Langmuir 24 (2008) 10723–10728. [15]
- S. De, V.K. Aswal, P.S. Goyal, S. Bhattacharya, J. Phys. Chem. B 101 (1997) 5639–5645. [16]
- [17] K. Tsubone, S. Ghosh, J. Surfactant Deterg. 6 (2003) 225-229.
- K. Tsubone, S. Ghosh, J. Surfactant Deterg. 7 (2004) 47-52.
- A.O. Mingqi, H. Peipei, X. Guiying, Y. Xiaodeng, W. Yajing, Colloid Polym. Sci. 287 [19] (2009) 395-402
- [20] T Yoshimura K Esumi Colloid Interface Sci 276 (2004) 231–238
- 21 S. Das, B. Naskar, S. Ghosh, Soft Matter 10 (2014) 2863-2875.
- S. Bhattacharya, V.P. Kumar, J. Org. Chem. 69 (2004) 559-562.
- [23] A. Rodriguez, M.D.M. Graciani, M. Angulo, M.L. Moya, Langmuir 23 (2007) 11496-11505
- [24] A. Rodriguez, M.M. Graciani, F. Cordobes, M.L. Moya, J. Phys. Chem. B 113 (2009) 7767-7779
- [25] L. Qiu, G. Jiang, X. Gu, L.N.G. Hu, J. Mol. Catal. A Chem. 277 (2007) 15-20.
- [26] L.G. Qiu, A.J. Xie, Y.H. Shen, Colloid Polym. Sci. 283 (2005) 1343-1348.
- M.N. Khan, C.T. Fui, J. Mol. Liq. 147 (2009) 170–177. 127
- C. Oelschlaeger, G. Waton, S.J. Candau, M.E. Cates, Langmuir 18 (2002) 7265-7271. Ì28Ì [29] S. Bal, M.L. Satnami, S. Kolay, R.M. Palepu, P.R. Dafonte, K.K. Ghosh, J. Surf. Sci. Technol. 23 (2007) 33-48.
- [30] W. Jiang, B. Xuc, Q. Lina, J. Li, H. Fu, X.Z.H. Chen, Colloid Interface Sci. 311 (2007) 530-536
- [31] M.M. Graciani, A. Rodriguez, M.L. Moya, J. Colloid Interface Sci. 328 (2008) 324–330. [32] M.M. Graciani, A. Rodriguez, M.L. Moya, V.I. Martín, J. Colloid Interface Sci. 342 (2010) 382-391.
- [33] K.K. Ghosh, S. Kolay, S. Bal, M.L. Satnami, P. Quagliotto, P.R. Dafonte, Colloid Polym. Sci. 286 (2008) 293-303.
- [34] S. Kolay, K.K. Ghosh, A.M. Donald, J. Moulins, R.M. Palepu, J. Solut. Chem. 37 (2008) 59 - 72
- [35] R.H. Waldemer, P.G. Tratnyek, Environ. Sci. Technol. 40 (2006) 1055–1061.
- F. Freeman, Rev. React. Species Chem. React. 1 (1976) 179–184. [36]
- F.M. Menger, J.S. Keiper, Angew. Chem. 39 (2000) 1906–1920. Ì37İ
- V. Sharma, M. Borse, V.K. Aswal, N.K. Pokhriyal, J.V. Joshi, P.S. Goyal, S. Devi, J. Colloid [38] Interface Sci. 277 (2004) 450-455
- [39] P. Mukerjee, K.J. Mysels, Critical Micelle Concentrations of Aqueous Surfactant Systems, Superintendent of Documents, Washington, DC, 1971.
- [40] Z. Khan, P. Kumar, Kabir-ud-Din, Colloids Surf. A Physicochem. Eng. Asp. 248 (2004) 25-31.
- K.K.S. Gupta, B.A. Begum, Carbohydr. Res. 315 (1999) 70-75.
- ĺ42ĺ L.F. Sala, S.R. Signorella, M. Rizotto, M.I. Frascaroli, F. Gandolfo, Can. J. Chem. 70 (1992) 2046-2052.
- [43] S.A. Al-Thabaiti, Z. Khan, S. Hussain, O. Bashir, J. Mol. Liq. 207 (2015) 200-205. [44] Y.L. Sim, N.S.M. Yusof, A. Ariffin, M.N. Khan, J. Colloid Interface Sci. 360 (2011) 182-188.
- [45] F.M. Menger, C.E. Portnoy, J. Am. Chem. Soc. 89 (1967) 4698-4703.
- C.A. Bunton, Catal. Rev. Sci. Eng. 20 (1979) 1–56. i46i
- J.M. Rathman, Curr. Opin. Colloid Interface Sci. 1 (1996) 514-518. [47]
- ĺ48ĺ K.K. Ghosh, D. Sinha, M.L. Satnami, D.K. Dubey, P.R. Dafonte, G.L. Mundhara, Langmuir 21 (2005) 8664-8669.
- [49] K.K. Ghosh, S. Bal, M.L. Satnami, P.R. Dafonte, R.M. Palepu, J. Disperson, Sci. Technol. 27 (2006) 349-355.
- [50] Kabir-ud-Din, K. Hartani, Z. Khan, Colloids Surf. A Physicochem. Eng. Asp. 193 (2001) 1-13.
- [51] S. Das, S. Maiti, S. Ghosh, RSC Adv. 4 (2014) 12275-12286.
- [52] R. Zana, Y. Talmon, Nature 362 (1993) 228-230.
- [53] R. Zana, J. Colloid Interface Sci. 248 (2002) 203-220.
- [54] Kabir-ud-Din, U.S. Siddiqui, Colloid J. 72 (2010) 14-22
- Ì55Ì R. Zana, M. Benrraou, R. Rueff, Langmuir 7 (1991) 1072-1075.
- [56]
- L. Simándi, M. Jáky, J. Am. Chem. Soc. 98 (1976) 1995–1997. D. Tikariha, N. Singh, M.L. Satnami, K.K. Ghosh, N. Barberob, P. Quagliotto, Colloids 57 Surf. A Physicochem. Eng. Asp. 411 (2012) 1-11.
- Raju, Z. Khan, Kabir-Ud-Din, Colloid Polym. Sci. 284 (2005) 26-35.
- P. Kumar, Z. Khan, Colloid Polym. Sci. 284 (2006) 1155-1162. 59
- [60] J.F. Perez-Benito, J. Colloid Interface Sci. 248 (2002) 130–135.