Research Article

The Catalytic Influence of Polymers and Surfactants on the Rate Constants of Reaction of Maltose with Cerium (IV) in Acidic Aqueous Medium

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Kinetics of the reaction of maltose with cerium ammonium sulfate were analyzed spectrophotometrically by observing the decrease of the absorbance of cerium (IV) at 385 nm in the presence and absence of polyethylene glycols (600, 1500, and 4000) and polyvinylpyrrolidone (PVP), in addition to anionic micelles of sodium dodecyl sulfate (SDS), cationic micelles of cetyltrimethylammonium bromide (CTAB) and non-ionic micelles of Tween 20 surfactants. Generally, there is little literature about using the polymers (PEGs and PVP) as catalysts in the oxidation-reduction reactions. Therefore, the major target of this work was to investigate the influence of the nature of polymers and surfactants on the oxidation rates of maltose by cerium (IV) in acidic aqueous media, as well as employing the Piszkiewicz model to explain the catalytic effect. The kinetic runs were derived by adaptation of the pseudo first-order reaction conditions with respect to the cerium (IV). The reaction was found to be first-order with respect to the oxidant and fractional-order to maltose and H_2SO_4. The reaction rates were enhanced in the presence of polymer and micellar catalysis. Indeed, the surfactants were found to work perfectly close to their critical micelle concentrations (CMC). Electrostatic interaction and H-bonding appear to play an influential role in binding maltose molecules to polymer/surfactant micelles, while oxidant ions remain at the periphery of the Stern layer within the micelle.

1. Introduction

Carbohydrates including sugars are the major source of energy for human cells, tissues, and organs. Hence, the oxidation products of sugars play a significant role as active intermediates for the synthesis of more complex molecules, which have various biological activities [1]. On the other hand, the cerium (IV) metal ion is an efficient oxidant in acid media with a reduction potential of 1.70 V for the couple Ce (IV)/Ce (III). It is widely employed in the oxidation of organic and inorganic compounds and has only been reduced to a single substance (cerium (III)) without any intermediates compared to other oxidants. As it is in H_2SO_4 and SO_4^{-2} media, several sulfate complexes of cerium (IV) are usually generated as active oxidant species, like $Ce(OH)^{+3}$, $Ce(SO_4)^{+2}$, $Ce(SO_4)_2$, and $Ce(SO_4)_2HSO_4^-$, $H_3Ce(SO_4)_4^-$ [2, 3].

Herein, we give a brief overview of some literature that discusses the kinetics of the redox reactions of sugars with

Ce (IV). For example, Pentii Virtanen and his colleagues studied the kinetics of the oxidation of some sugars such as *D*-mannose, *D*-galactose, *D*-glucose, and *D*-xylose with Ce (IV) in perchloric acid to produce two complexes in the oxidation of each monosaccharide [4]. Agarwal et al. with his group carried out a reaction of mannitol with Ce (IV) in an acidic medium to produce mannose as the final product. They found that the most dominant active Ce (IV) species in the H_2SO_4 medium was $HCe(SO_4)_3{}^-$. Under pseudo first-order reaction conditions, the reaction obeyed first-order kinetics with respect to Ce (IV) and mannitol [5]. Kabir-Ud-Din et al. investigated the effect of surfactants (Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB)) on the kinetics of the reaction of D-fructose with Ce (IV) in an acidic medium, and they reported that the oxidation reaction was first-order with respect to each [Ce (IV)] and [D-fructose]. In addition, SDS did not influence the reaction rate, while CTAB had increased the rate of reaction and this effect was explained by pseudo phase model proposed by Menger and Portnoy [6]. Kabir-Ud-Din et al. have continued their efforts to study the effect of the anionic and cationic surfactants on the reaction of D-glucose, L-(+)-arabinose, and D-Mannose with Ce (IV) spectrophotometrically at 385 nm in H_2SO_4 environment, in all cases, SDS has not increased the reaction rate due to the repulsion of negative heads of SDS with reactive $Ce(SO_4)_3{}^{-2}$, in turn, CTAB has an influential role in the improvement of the rates of reaction [7–9]. Recently, Ghosh et al. investigated the oxidation kinetics of D-mannitol into D-mannose by Ce (IV) in an aqueous medium in the presence of sodium dodecyl sulfate (SDS) in combination with five various metal ions cupper (II), manganese (II), chromium (III), iron (II), and silver (I) as catalysts, the reaction has considerably been enhanced, especially when using Mn (II) with SDS [10].

Recently, polyethylene glycols and polyvinylpyrrolidone have become increasingly important as promising catalysts in the oxidation reactions in the presence of Ce (IV) owing to the ease of their preparation, the commercial availability of many representatives, and low toxicity. Shylaja et al. used PEGs to catalyze the reactions of some xanthine alkaloids with ceric ammonium nitrate to give uric acid derivatives. They found that the rate of reaction increased linearly in the presence of a set of PEGs, and their catalytic activities depended on the nature as well as the molecular weight of the PEGs [11]. Likewise, PEGs catalyzed the reaction of borneol, isoborneol, and camphor with ceric ammonium nitrate acid-free conditions. The reaction followed first-order in both [Ce (IV)] and [alkaloids]. Besides, the rates of reactions were enhanced linearly with an increase in [PEG] [12]. Whilst, Dahadha et al. have employed PEG 4000, PVP, and mixed PEG4000-SDS systems as powerful catalysts in the redox reaction of aspirin under acidic reaction conditions. PEG 4000 and PVD, were found to increase the rate of the reaction and their kinetic catalytic data were successfully analyzed by the Benesi–Hildebrand model [13]. Also, our group studied and explained the catalytic influence of the mixed systems of polyethylene glycol 600, 1500, and 4000 with SDS on the reduction of Ce (IV) via o-Cresol, especially at the critical micelle concentration point of SDS [14].

In the current work, we have performed the reaction of maltose with Ce (IV) under an acidic medium to investigate and explain the catalytic behaviour of each PEG (600, 1500, and 4000) and PVP, in addition to three types of surfactants (SDS, CTAB, and Tween 20).

2. Experimental

2.1. Materials. The homogeneous mixtures of $0.030\,mol\,dm^{-3}$ maltose (≥99%, Merck, India) and $2.0\,mol\,dm^{-3}$ sulfuric acid (95–97%, Sigma-Aldrich, USA) have been prepared using a specific quantity of each component and doubly distilled water. Likewise, homogeneous mixtures of $0.010\,mol\,dm^{-3}$ of CTAB (98%, S. d. fine. Chem. India), $0.050\,mol\,dm^{-3}$ of SDS (99%, AZ Chem), $0.010\,mol\,dm^{-3}$ of TW-20 (molecular biology grade, Sigma-Aldrich), PVD (PVD-K15 with a molar mass of $10,000\,g\,mol^{-1}$; AppliChem, Germany), $1.0 \times 10^{-3}\,mol\,dm^{-3}$ of each PEG 600 (Xilong Chemical Industry Co. Ltd. China), PEG 1500 (AR, Fluka, Germany), and PEG 4000 (Schariau, Spain) and were synthesized at the time of their use. $3.0 \times 10^{-3}\,mol\,dm^{-3}$ ammonium cerium (IV) sulfate solution (AR grade, Caro Erba, Italy) was formed by dissolving the appropriate quantity in $2.0\,mol\,dm^{-3}$ H_2SO_4 solution.

2.2. Kinetic Measurements. All kinetic experiments were done under the pseudo first-order redox reaction conditions with maltose was always made in large excess over that of Ce (IV). The progress of the redox reactions has been tracked by following the decreasing absorbance of Ce (IV) as a function of time at $\lambda = 385\,nm$, which is the absorption maximum wavelength of Ce (IV) as shown in Figure 1 and 1S. The main experimental procedure has been done by mixing 4.0 ml of the maltose solution, 4.0 ml of H_2SO_4 and 8.0 ml of distilled water in the beaker that has been put beside another beaker consisting of 4.0 ml of the oxidant solution in an electronic thermostatic water bath (PRECISION GP20 manufactured by Thermo Scientific, USA) maintained at 293 K for sufficient time to attain the thermal equilibrium. Then, the maltose and Ce (IV) solution have been blended, and the decay of the absorbance of the reaction solution has been instantly estimated by an ultraviolet-visible spectrophotometer (AE-S90-2D, A and E Lab, UK) at specific time intervals. The k_{obs} values were calculated from the slopes of the plots of absorbance versus time interval by utilizing of the nonlinear regression method. The rate constants were considered to be the mean of three independent kinetic runs. The influence of the [Ce (IV)], [maltose], [H_2SO_4], [PEG 600], [PEG 1500], [PEG 4000], [PVP], [SDS], [CTAB], and [Tween 20] on the observed rate constant (k_{obs}) of the reactions have been analyzed in sequential experimental runs through mixing of the particular changeable quantities of each component with the fixed volume of water to assure the total volume of the reaction medium always is 20.0 ml. [surfactants] has been altered to be near to their CMCs, to test the catalytic influence in the presence of pre- and postmicellar quantities.

Samples of raw absorbance versus time data at various concentrations of reactants and additives are given in Tables 1–14S. Unexpectedly, the plots of absorbance versus
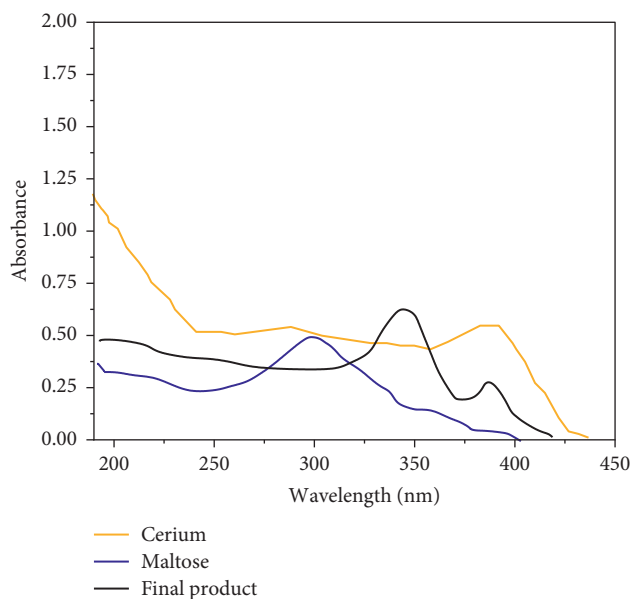
FIGURE 1: Ultra violet-visible spectra of the acidic solution of [maltose] $= 6.0 \times 10^{-3}$ mol dm^{-3} [Ce (IV)] $= 6.0 \times 10^{-4}$ mol dm^{-3} dissolved in 0.40 mol dm^{-3} [H$_2$SO$_4$]. The expected product in reaction medium in the presence of excess [Ce (IV)].

SCHEME 1: The suggested reaction of maltose with cerium (IV) in an acidic medium to produce maltobionic acid as an expected final product.
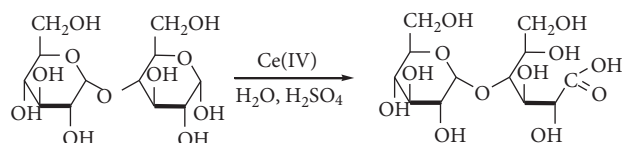
time appeared to diverge from linearity and, instead, adopted a curvature trend. It was reported by Perrin [15] that the employing of the normal first-order integrated equation is expected to deviate from linearity way at the final stages of the chemical reaction owing to the increase of error in evaluating the values of the absorbance with time. Our group has previously investigated some redox reactions by employing the suitable nonlinear obeying to estimate the k_{obs} values and other kinetic parameters [16, 17]. Fortunately, the curvature of the plot of the absorbance and time was found to fit to the following nonlinear equation with regression coefficients $r^2 \geq 0.9995$.

$$A = a + be^{-k_{obs}t}. \tag{1}$$

However, A value indicates to the absorbance of the reaction medium at specific time t, k_{obs} is reaction rate constant in aqueous and micellar pseudophases, and a and b are also constants. Consequently, this procedure was employed to estimate the k_{obs} values from the kinetic data under various conditions.

2.3. Product Identification

2.3.1. Employing of UV-Vis Spectra and Using of 2, 4-Dinitrophenylhydrazine Solution to Identify the Product. Several reaction mixtures with various gros of the concentration of components have been prepared, in which [Ce (IV)] was always in excess over [maltose]. The mixtures were kept for 72 h at 293 K in an inert atmosphere. The remaining unreacted Ce (IV) in each mixture has been evaluated spectrophotometrically. The results indicated that 2 mol of Ce (IV) reacted stoichiometrically with 1 mol of maltose, based on the following Scheme :

The ultraviolet–visible (UV– Vis) spectra for maltose in the acidic medium showed a growing broad peak centered at 310 nm, while the expected product showed two peaks. One of them occurred at 345 nm and the second emerged at 380 nm as shown in Figure 1. Moreover, the occurrence of the carboxylic acid as the probable final product has been proved by reacting the mixture with a saturated solution of 2, 4– dinitrophenylhydrazine, which has been left 24 hrs in a freezer. The mixture remained clear and no precipitate was formed, which is evidence of the absence of aldehydic or ketonic carbonyl groups.

2.3.2. Free Radical Detection. The generation of free radicals during the redox reaction has been tested via employing of acrylonitrile solution. The reaction medium including of [Ce (IV)] $= 6.0 \times 10^{-4}$ mol dm^{-3}, [maltose] $= 6.0 \times 10^{-3}$ mol dm^{-3} and [H$_2$SO$_4$] $= 0.40$ mol dm^{-3} was added to the acrylonitrile solution (30%) at 293 K, resulting in the occurrence of a precipitate, which indicated the presence of free radical intermediates during the reaction.
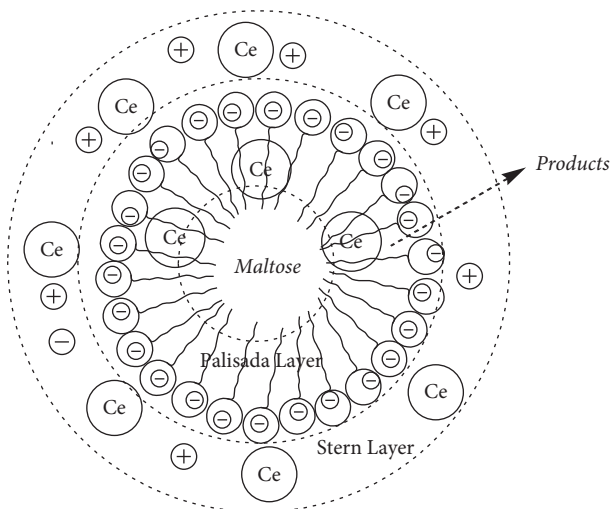
3. Results and Discussion

3.1. Effect of [Ce (IV)]. The [Ce (IV)] has been varied in the range 1.0–4.5×10^{-4} mol dm^{-3}, while [Maltose] has been remained at 6.0×10^{-3} mol dm^{-3}and [H$_2$SO$_4$] at 0.40 mol dm^{-3}, under pseudo first-order conditions at 293 K. The values of reaction rate constants were calculated to be independent of initial [Ce (IV)] in the absence and presence of the polymers and surfactants, indicating an approximate first-order dependence on [Ce (IV)] as shown in Table 1.

3.2. Effect of [Maltose]. The k_{obs} values have been obtained at different initial [Maltose] ranging from 1.5×10^{-3} to 6.0×10^{-3} mol dm^{-3} while the other reaction variables have been kept constant. The rates of reaction have been found to increase linearly with increasing [Maltose], (regression coefficients $r^2 \geq 0.998$, average standard deviation and error are 7.09×10^{-5} and 4.09×10^{-5}, respectively) as illustrated in Figure 2, with a nonzero intercept. The reaction, therefore, followed the fractional-order that ranges from 0 to 1 with respect to maltose. At sufficiently low [Maltose], the reaction approaches unity, while at higher [Maltose], the reaction rate becomes of zeroth order. However, the reaction adopts fractional-order within most of the reaction time. This type of dependence can be represented mathematically by the following equation:

TABLE 1: k_{obs} values at various concentrations of Ce (IV), maltose, and H_2SO_4 at 298 K.

[Ce (IV)] × 10^{-4} mol dm^{-3}	[Maltose] × 10^{-3} mol dm^{-3}	[H$_2$SO$_4$] mol dm^{-3}	k_{obs} (s^{-1})
1.0	6.0	0.40	0.00580
2.5	6.0	0.40	0.00560
3.5	6.0	0.40	0.00580
4.0	6.0	0.40	0.00570
4.5	6.0	0.40	0.00580
6.0	1.5	0.40	0.00198
6.0	2.2	0.40	0.00289
6.0	3.0	0.40	0.00365
6.0	3.7	0.40	0.00441
6.0	4.5	0.40	0.00508
6.0	6.0	0.40	0.00632
6.0	6.0	0.12	0.00414
6.0	6.0	0.14	0.00428
6.0	6.0	0.16	0.00441
6.0	6.0	0.18	0.00452
6.0	6.0	0.20	0.00460

FIGURE 2: k_{obs} versus [Maltose] at the following conditions: [Ce (IV)] = 6.0×10^{-4} mol dm^{-3} and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 298 K.

SCHEME 2: The oxidation of maltose by cerium (IV) within the anionic surfactant micelle.

$$\text{Rate} \, \alpha \, \frac{[\text{Maltyose}]}{1 + [\text{Maltose}]}. \tag{2}$$

3.3. Effect of [H$^+$].
[H$^+$] has been changed (0.12–0.2 mol dm^{-3}) at the fixed concentrations of all other reactants to investigate its influence on k_{obs} as presented in Figure 3. It was noticed that the reaction rates increased with increasing of [H$^+$], whilst the plots of k_{obs} versus [H$^+$] were linear (regression coefficient $r^2 \geq 0.99$, average standard deviation and error were 2.08×10^{-5} and 1.20×10^{-5}, respectively), with a positive intercept on the y-axis, this conformed to a fractional-order dependence with respect to [H$^+$] and followed a trend similar to that given in equation (2).

3.4. Effect of Salts.
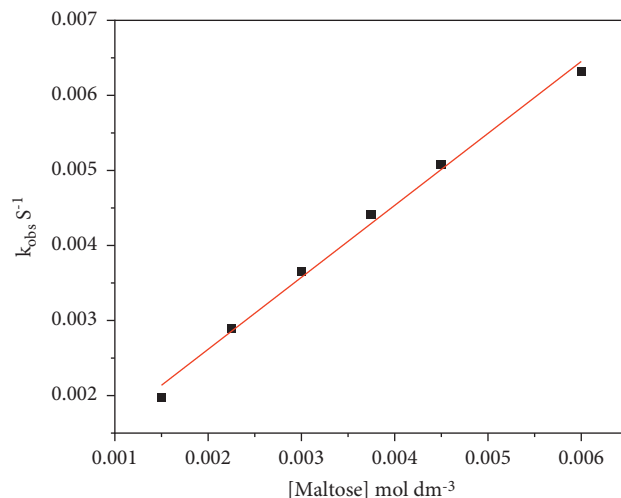Several experiments were run with varying the ionic strength of the reaction mixture by the addition of Na_2SO_4, KCl, NaI, and $NaIO_4$ into the redox reaction, while other variables have been kept constant at 293 K. However, the observed reaction rates were not influenced by any variation of [salts]. Consequently, this means the ionic strength had no impact on the kinetics of the reaction. Hence, the chemical reacting species that are included in the step of determining the rate of the reaction are expected to be both or at least one of them uncharged [18].

3.5. Effect of Temperature.
Some experimental runs have been achieved at various temperatures in the range 290–310 K to examine the effect of temperature on the reaction rate and obtain the kinetic parameter: activation energy E_a, activation enthalpy $H^{\neq}$, activation entropy $S^{\neq}$, and activation free energy $G^{\neq}$. The activation energy was obtained by linear fitting the following form of the Arrhenius equation:

$$\ln k_{obs} = \ln A - \frac{E_a}{RT}. \tag{3}$$

The natural logarithm of k_{obs} at different temperatures is plotted against the temperature inverse in Figure 4. It appears that the equation is obeyed with a regression coefficient >0.99. From the slope of the plot, the activation energy was calculated and found to be 27.570 kJ mol^{-1}. The activation enthalpy was obtained from the following form of the Eyring equation:

$$\ln \frac{k_{obs}}{T} = -\frac{H^{\neq}}{RT} + \ln \frac{kT}{h} + \frac{S^{\neq}}{R}, \tag{4}$$

where k and h are Boltzmann and planks' constantans, respectively. The plot of $\ln k_{obs}/T$ vs $1/T$ as in the inset of Figure 4, shows the successful fitting of the equation to a straight line. The values of $H^{\neq}$ and $S^{\neq}$ were calculated from the slope and intercept, respectively, and found to be 25.075 kJ mol^{-1} and −256.354 J K^{-1} mol^{-1}, respectively. The positive value of activation enthalpy indicates the endothermic nature of the formation of the activated complex,
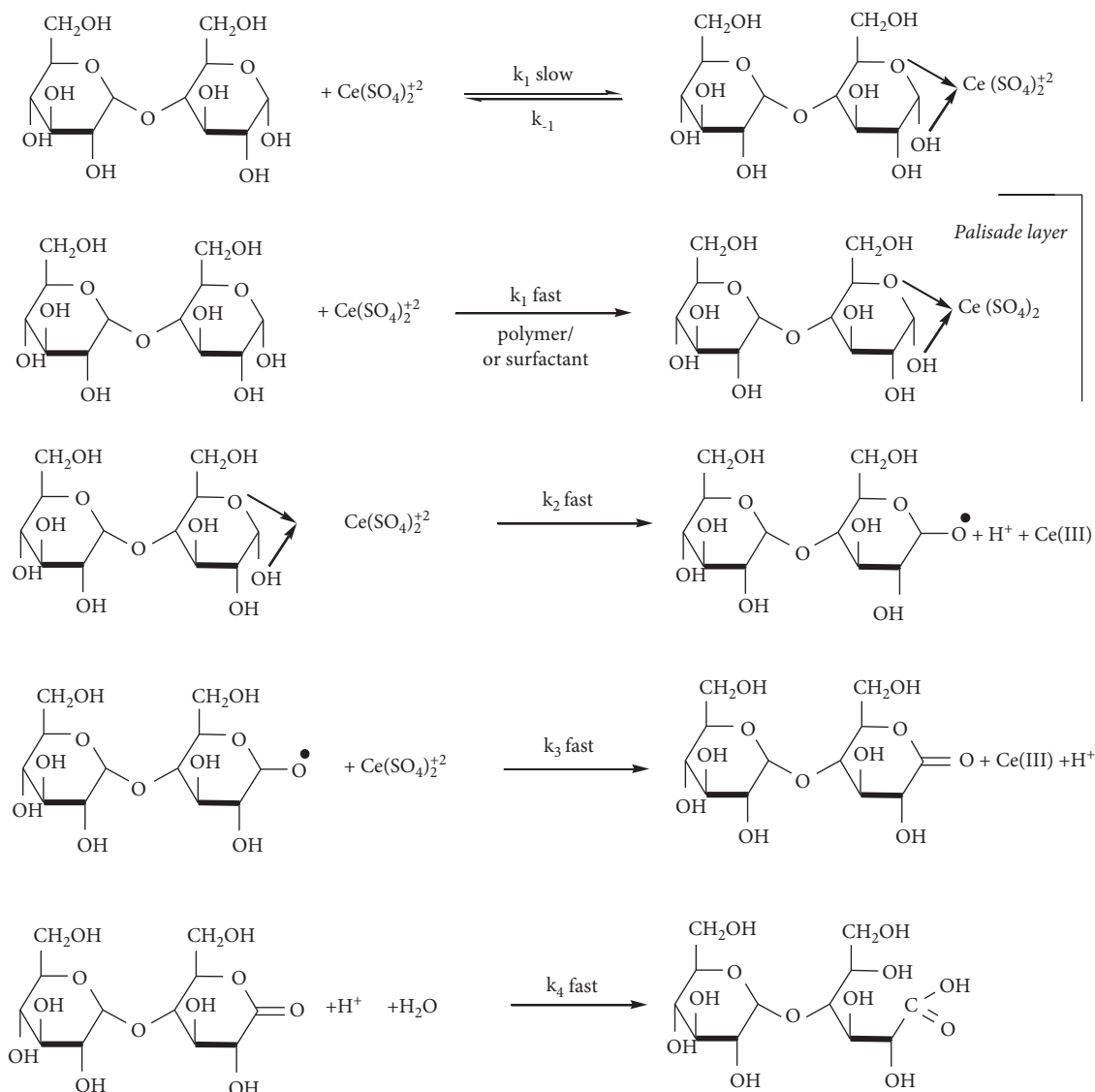
Scheme 3: A suggested mechanism for the redox reaction of maltose by Ce (IV) in the acidic medium solution.

and the negative value of entropy reflects the ordered structure of the complex compared to the reactants. The activation free energy was calculated using the following formula:

$$G^{\neq} = H^{\neq} - TS^{\neq}. \tag{5}$$

The value of $G^{\neq}$ at 298 is 101.468 kJ mol^{-1}. The positive sign of $G^{\neq}$ indicates that the formation of the activated complex is a nonspontaneous process, which explains the relative sluggishness of the reaction.

3.6. Effect of PEG 600, 1500, and 4000. In recent years, several kinds of polyethylene glycol (PEG) have been used as efficient catalysts and catalyst supports in various chemical reactions owing to their low cost, low toxicity, and commercial availability [19, 20]. To assure the inertness of the polymers against the redox reactions, some experimental runs have been derived in the presence of 1.25×10^{-4} mol dm^{-3} of PEGs (600, 1500 and 4000) and PVP in the absence of maltose. The absorbance of the reaction mixture slightly decreased at the primary reaction time stages, then the absorbance of the mixture at 385 nm kept almost steady with time (Tables 4S–7S). The initial slight decline in the absorbance might be due to the adsorption of some Ce (IV) ions on PEGs and PVP chain surfaces and not to the participation of the polymers in redox reaction with Ce (IV). Anywise, the influence of PEG 600, 1500, and 4000 as an efficient catalyst on the reaction rates of maltose with Ce (IV) was investigated under the similar concentrations of the reaction component and conditions as shown graphically in Figure 5, to disclose that the reaction rates have increased linearly with the increasing of [PEG 600, 1500 and 4000], (Regression coefficients $r^2 \geq 0.99$, average standard deviation and error are 2.22×10^{-5} and 1.98×10^{-5}, respectively). In the same connection, compared to the uncatalyzed
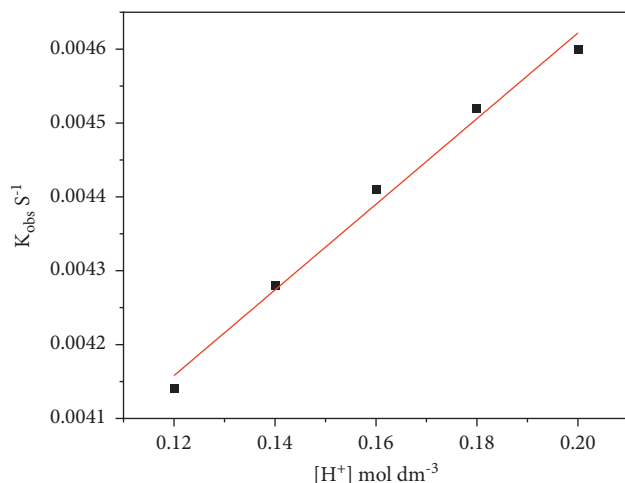
FIGURE 3: k_{obs} versus [H$^+$] at the following conditions: [Ce (IV)] = 6.0×10^{-4} mol dm^{-3} and [Maltose] = 6.0×10^{-3} mol dm^{-3} at 298 K.
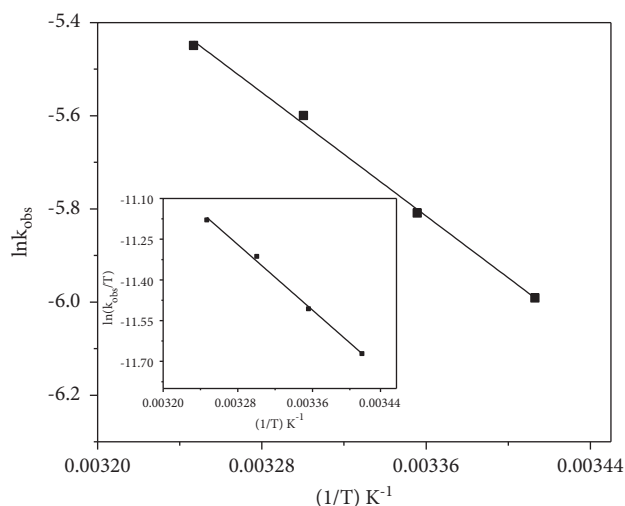

FIGURE 4: Plot of Arrhenius relation at the following conditions: [Ce (IV)] = 6.0×10^{-4} mol dm^{-3} and [Maltose] = 6.0×10^{-3} mol dm^{-3} and [H$^+$] = 0.4 mol dm^{-3}. The inset shows plot of Eyring equation.

FIGURE 5: k_{obs} versus [PEG 600, 1500 and 4000] at the following reaction conditions: [Ce (IV)] = 0.003 mol dm^{-3}, [Maltose] = 0.03 mol dm^{-3}, and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 298 K.

the model has been employed to investigate the effect of the presence of the very low concentrations of the polymers and surfactants in the reaction media through the interactions of the maltose molecules with the polymer or surfactant micelles to increase the concentration of maltose molecules inside the micelles, which behave as nanoreactors in the aqueous medium. In turn, the palisade layer of the micelles can be broken through by the active Ce (IV) ions to be close to the substrate molecules, and then the reaction might be efficiently commenced as illustrated in the following scheme .

$$\log\left[\frac{k_{obs} - k_w}{k_m - k_{obs}}\right] = \log(P) = n\log[D]_T - \log K_D. \qquad (6)$$

K_D constant indicates to the degradation of the micellized polymer/surfactant reactants aggregate to its original ingredients, while n value is the index of cooperativity of surfactant, and $[D]_T$ provides the entire [surfactant/or polymer]. k_w is the observed reaction rate in aqueous medium, and k_m is the k_{obs} value with the higher quantity of polymer or surfactant. However, the cooperativity of interaction between micelles and substrate molecules will be positive if the n value is grater the 1. On the other hand, if n value is less than 1, the cooperativity of interaction will be inhibited, but if its value is equal to 1, the interaction is noncooperative [20–22]. Based on this model, the plotting of log ($k_{obs} - k_{kw}/k_{km} - k_{obs}$) against log [PEG 600, 1500, and 4000] was found to generate a straight line with slope values (n) for PEG 600 1500, and 4000 were 2.07, 1.98, and 1.98, respectively (Figure 2S). This indicates affirmative cooperativity, and this influence may be imputed to strong interactions among the maltose and polyethylene glycol molecules via hydrogen bonding over the adsorption of oxidant particles.

maltose oxidation by Ce (IV) ($k_{obs} = 2.5 \times 10^{-3}$ s^{-1}), the reaction rates were obviously enhanced up to more than fourfold in the presence of PEG 600, 1500, and 4000. Overall, the catalytic activity was found to be in the order of PEG 600 < PEG 1500 < PEG 4000.

The noncovalent bonds between both the maltose and Ce (IV) with the hydroxyl groups of hydrophilic PEGs may play a remarkable role in the enhancement of the reaction rates via the production of active aggregates during the course of the reaction. In the same context, the Piszkiewicz cooperativity model has been also utilized to explain the catalytic behaviors of the polymers in these reactions, as shown in equation (5) [20]. However, the PEG chains in aqueous media are analogous to the structure of nonionic micelles of Triton-X and Tween 20. Consequently, the catalytic impact of PEGs on the kinetics of reactions could be explicated via the cooperative Piszkiewicz model [11, 19–21]. In this work,
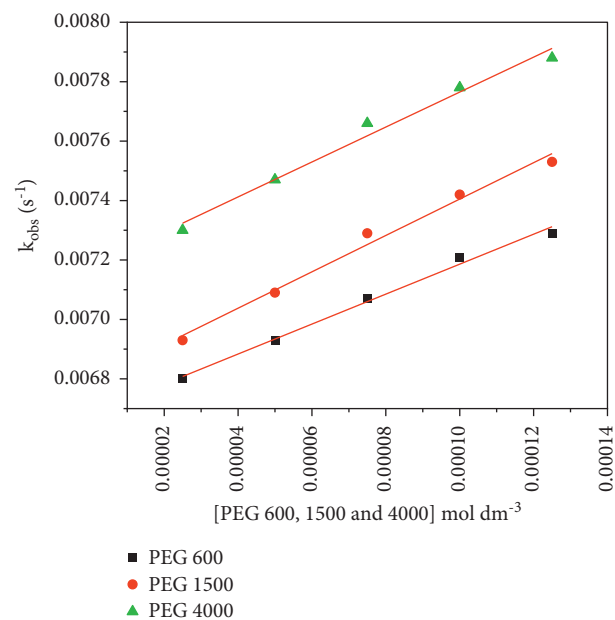
3.7. Effect of PVP. The influence of PVP on the reaction rate has been presented by the catalytic profile in Figure 6, where the k_{obs} have been plotted versus [polymer]. The impact of the existence of PVP on the rate of reactions is similar to that detected in our previous study [13]. But here, the rate increased linearly with [PVP]. Regression coefficients $r^2 \geq 0.999$, average standard deviation and error are 1.71×10^{-4} and 9.81×10^{-5}, respectively. However, the catalytic profile of PVP showed a powerful enhancement of the rate constant in comparison with the uncatalyzed oxidation of maltose, where the rate of the oxidation has been increased to 12-fold. Moreover, the influence of increasing [PVP] on the reaction rate was higher than [PEGs] under the same reaction conditions.

On the other hand, where the logarithm of $(k_{obs} - k_{kw}/k_{km} - k_{obs})$ was plotted versus log [PVP] to generate a straight line with a slope of 2.64 (Figure 3S). Moreover, the n value of PVP is greater than that that occurred in the presence of PEG; this also indicates positive cooperativity. Generally, a larger n of PVP than that of PEGs indicates an increased number of aggregations of micellar clusters and considerable stability of polymer-substrate aggregates constructed with PVP. These kinetic results supplied more rationalization for the better catalytic activity of PVP compared to that of PEGs, and this effect might be attributed to the higher polarity and chain lengths of PVP, which improve the interactions with the reactant molecules.

3.8. Effect of Surfactants. Surfactants, also called surface-active agents, are compounds with a highly polar head group and a nonpolar chain. When they are present in an aqueous medium at certain concentrations, called critical micelle concentration (CMC), they form micelles with a hydrophobic core due to the existence of polar hydrophilic and nonpolar hydrophobic moieties inside the same surfactant molecules [22]. Micelles are kinetically labile and thermodynamically stable. The kinetics of the oxidation of maltose by Ce (IV) by employing the anionic micelles of SDS, cationic micelles of CTAB, and nonionic micelles of Tween-20 have been investigated, and the results have been illustrated in the current work. Generally, the effect of the various types of surfactant micelles on the rate of reaction may take place because of electrostatic/hydrophobic and hydrogen bonds between the oxidant/reductant and the surfactant molecules to build reactive or unreactive surfactant oxidant/reductant complexes [23, 24].

3.8.1. Effect of SDS. Sodium dodecyl sulfate (SDS), which generates anionic micelles in the aqueous medium, was found to improve the reaction rates. Figure 7 shows the catalytic effect of SDS surfactant, where the k_{obs} values have been plotted versus [SDS]. Increasing the [SDS] is attached by a progressive increase in values of k_{obs}, to reach a maximum, then drop slightly and end up with an almost steady plateaued curve (average standard deviation and error are 1.73×10^{-5} and 1.00×10^{-5}, respectively). The maximum k_{obs} have emerged at 6.25×10^{-3} mol dm^{-3} [SDS], which is slightly below the CMC of SDS ($8.0 \times$
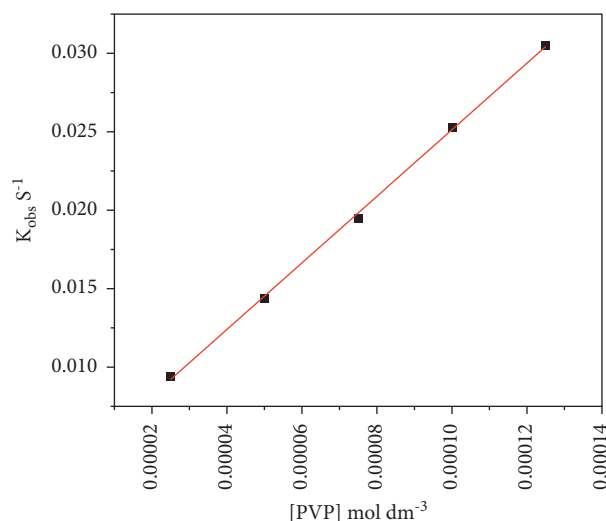

FIGURE 6: k_{obs} versus [PVP] at the following reaction conditions: [Ce (IV)] = 0.0030 mol dm^{-3}, [Maltose] = 0.030 mol dm^{-3}, and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 298 K.

10^{-3} mol dm^{-3}) [13, 25]. The higher value of k_{obs} was more than double that in the uncatalyzed redox reaction. However, the catalytic activity of SDS might be attributed to the association of a large number of active cationic charged species of Ce (IV) on the surface of the anionic micelles. Then they can penetrate the cores of the micelles to contact with the substrates, which is possible to be responsible for the catalytic effect of the anionic surfactant on the reaction rates.

In general, at very low concentrations of a surfactant, the effect of the micelles on the reaction rates has been usually interpreted by the kinetic model designed by Piszkiewicz. Hence, log $(k_{obs} - k_{kw}/k_{km} - k_{obs})$ has been plotted against log [D] in Figure 4S, which showed linearity, and the value of n could be evaluated to be 0.63, indicating negative cooperativity, which signifies the retard of the association of further molecules of the reactants via the binding of the first substrate molecule with the micelle.

3.8.2. Effect of CTAB. The catalytic profile of CTAB has exhibited various patterns. However, an increase was observed at sufficiently low concentration to reach the maximum reaction rate at [CTAB] which is also slightly lower than the measured CMC of CTAB (9.0×10^{-4}) [24]. The k_{obs} value was more than threefold that in the uncatalyzed reaction, followed by a sudden decrease in the k_{obs} at higher [CTAB] as shown in Figure 8 (average standard deviation and error are 5.77×10^{-6} and 3.33×10^{-6}, respectively). This catalytic action may be due to an increase in the reaction solution viscosity in the presence of CTAB molecules or electrostatic repulsion between the positive head group of CTAB and one of the reactive cerium (IV) ions like Ce(SO$_4$)$^{+2}$ [13, 16]. In the same context, plotting of log $(k_{obs} - k_w/k_m - k_{obs})$ against log [D] gives a straight line, and the value of n has been determined from Figure 5S to be 0.62, indicating a negative co-operatively.
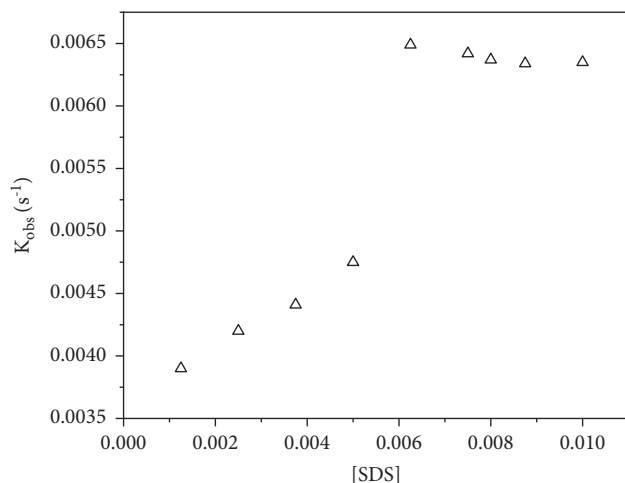
FIGURE 7: k_{obs} vs. [SDS], at the following reaction conditions: [Maltose] = 0.030 mol dm^{-3}, [Ce (IV)] = 0.0030 mol dm^{-3}, and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 293 K.

3.8.3. Effect of Tween 20.

The catalytic influence of the ionic and non-ionic nature of the surfactants on the rate of reactions is owing to the combination of hydrogen bonding and electrostatic/hydrophobic interactions between the reactant molecules [26, 27]. In the case of the existence of a nonionic surfactant in a reaction medium like Tween 20, the electrostatic interaction will be not possible. In addition, maltose and Ce (IV) species have no hydrophobicity. Consequently, hydrogen bonding will play a significant role in the catalytic action of Tween 20. Tween 20 molecules consist of a lot of oxyethylene chains, and maltose molecules contain a number ofOH groups that will facilitate strongly the formation of hydrogen bonding. Thus, the construction of the multiple hydrogen bonds between the polar polyoxyethylene chains of Tween 20 and the reactants might be responsible for the catalytic action of Tween 20 in this reaction by bringing the molecules of reactants closer together in the correct orientation.

The impact of Tween 20 as a catalyst on the reaction rate is shown graphically in Figure 9, which discloses that the rate of reaction increased with the increasing concentration of Tween 20. The k_{obs} are enhanced more than threefold in the absence of any surfactant and occurred at [Tween 20] near to its CMC (8×10^{-5}) [28]. The catalytic profile has declined slightly and ended up with an almost constant plateaued curve (average standard deviation and error are 6.02×10^{-5} and 3.48×10^{-5}, respectively). Piszkiewicz's model has been employed to interpret the catalytic effect of Tween 20. The plot of log ($k_{obs} - k_w/k_m - k_{obs}$) against log [Tween 20] was found to successfully provide a straight line with a slope of 1.1, as shown in Figure 6S. This value indicates a positive cooperative, in which the interaction of the first substrate molecule to make it easier for the association of additional surfactant molecules to catalytically productive submicellar aggregates in the whole surfactant concentration range. Under the same reaction conditions, compared with SDS and CTAB, it is found that Tween 20 is more efficient in catalyzing the oxidation of maltose by Ce (IV).
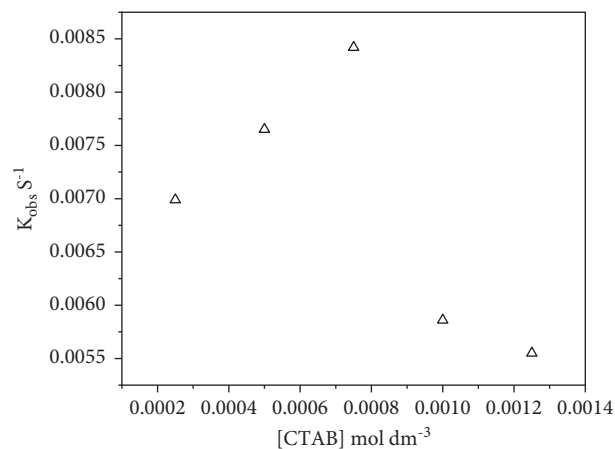

FIGURE 8: k_{obs} vs. [CTAB], at the following reaction conditions: [Maltose] = 0.030 mol dm^{-3}, [Ce (IV)] = 0.0030 mol dm^{-3}, and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 293 K.

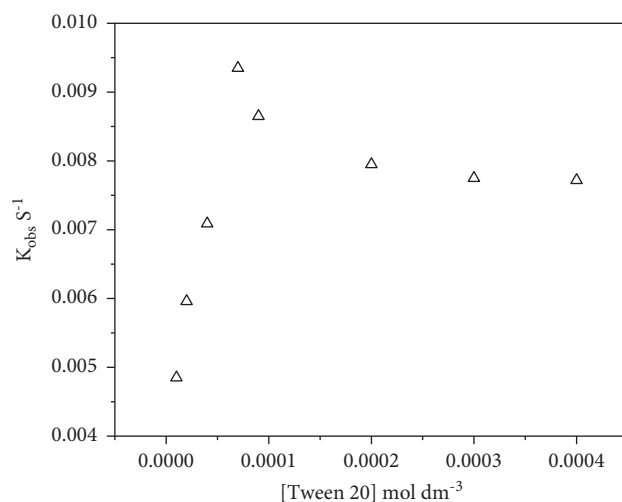FIGURE 9: k_{obs} vs. [Tween 20], at the following reaction conditions: [Maltose] = 0.030 mol dm^{-3}, [Ce (IV)] = 0.0030 mol dm^{-3}, and [H$_2$SO$_4$] = 0.40 mol dm^{-3} at 293 K.

3.8.4. Mechanism.

A suggested mechanism for the redox reaction that matches the kinetic results is shown in the subsequent steps in Scheme 3. Based on these results, the slow step takes place via the reaction of a neutral molecule of maltose and a positively charged cerium ion to form a maltose- Ce (IV) complex in the micellar core, which then decomposes to form radical intermediates. Therefore, the existence of the radicals has been proved by the reaction with acrylonitrile solution (30%). Maltose molecules react reversibly with Ce(SO$_4$)$^{+2}$ ions in the rate-determining step to build the positive complex, in which the cerium ions are interacted with the oxygen atoms of maltose by coordinated covalent bonds. The formed radical moieties reacted immediately with another Ce(SO$_4$)$^{+2}$ species to generate carbonyl groups, which have been then converted into carboxylic groups in the presence of the acid and water.

The mechanism in the polymer/surfactant medium has been carried out through the complexes constructed in the

first step of the reaction inside the core of micelles, which will make the backward return to the original reactants less possible due to the electrostatic interaction or hydrogen bonding between the reactants and the micelles. Therefore, the construction of the reactive complex will be non-reversibly. The active complex and the related intermediates, as well as the expected product are highly hydrophilic, which indicates that the following steps in the redox reaction will take place in the bulk aqueous phase.

Assuming that the first step that involves the construction of the complex is the slowest step, we can summarize the mechanism as:

$$\text{Maltose} + Ce(\text{IV}) + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} \text{Complex}, \text{Complex} \xrightarrow{k_2} P, \quad (7)$$

where P is the product, which results from fast cascades of several intermediates appear in Scheme 3.

The Overall rate of the reaction with respect to P can be expressed as:

$$\frac{dP}{dt} = k_2[\text{Complex}]. \quad (8)$$

The rate of concentration change of the complex can be written as:

$$\frac{d[\text{Complex}]}{dt} = k_1[\text{Maltose}][Ce(\text{IV})][H^+]$$
$$- k_{-1}[\text{Complex}] - k_2[\text{Complex}]. \quad (9)$$

Application of stationary state to equation (9) leads to the following equation:

$$k_1[\text{Maltose}][Ce(\text{IV})][H^+] = k_{-1}[\text{Complex}] + k_2[\text{Complex}]. \quad (10)$$

Equation (10) leads to the following equation:

$$[\text{Complex}] = \frac{k_1[\text{Maltose}][Ce(\text{IV})][H^+]}{k_{-1} + k_2}. \quad (11)$$

Put $k_m = k_{-1} + k_2/k_1$ and substitute in equation (11), we get the following equation:

$$[\text{Complex}] = \frac{[\text{Maltose}][Ce(\text{IV})][H^+]}{k_m}. \quad (12)$$

The total concentration of added cerium ions can be summed as following:

$$[Ce(\text{IV})]_t = [Ce(\text{IV})]_f + [Ce(\text{IV})]_c. \quad (13)$$

Where $[Ce(\text{IV})]_t$ is the total concentration of Ce (IV), $[Ce(\text{IV})]_f$ is the concentration of noncomplexed (free) Ce (IV), and $[Ce(\text{IV})]_c$ is the concentration of complexed) Ce (IV).

$[Ce(\text{IV})]_f = [\text{Complex}]$, therefore equation (13) is rewritten as:

$[Ce(\text{IV})]_t = [Ce(\text{IV})]_f + [\text{Complex}]$ substitution for $[Ce(\text{IV})]_f$ in equation (11).

$$[\text{Complex}] = \frac{[\text{Maltose}]([Ce(\text{IV})]_t - [\text{Complex}])[H^+]}{k_m} = \frac{[\text{Maltose}][Ce(\text{IV})]_t[H^+] - [\text{Maltose}][\text{Complex}][H^+]}{k_m}. \quad (14)$$

Solving equation (14) for [Complex] we get the following equation:

$$[\text{Complex}] = \frac{[\text{Maltose}][Ce(\text{IV})]_t[H^+]}{k_m + [\text{Maltose}][H^+]}. \quad (15)$$

Substitution for [Complex] in equation (8), the final overall rate raw is then:

$$\frac{dP}{dt} = k_2 \frac{[\text{Maltose}][Ce(\text{IV})]_t[H^+]}{k_m + [\text{Maltose}][H^+]}, \quad (16)$$

which is in agreement with the experimental findings.

4. Conclusion

The kinetics of oxidation of maltose was spectrophotometrically investigated in polymer media of polyethylene glycols (600, 1500, and 4000) and PVP, as well as micellar media of the SDS, CTAB, and Tween-20 surfactants. The reaction was found to be first-order with respect to cerium (IV), and fractional order to maltose and H^+. The presence of polymers such as PEGs and PVP has considerably enhanced the oxidation of maltose. In addition, the reaction rates have been increased in the presence of anionic micelles of SDS, cationic micelles of CTAB, and nonionic micelles of Tween 20. Notably, PVP showed a distinguished catalytic activity compared with PEGs and surfactants. We tried to use the Piszkiewicz model to explain the catalytic effect of polymer and micellar catalysis. However, depending on UV–Vis spectra, 1, 2-DNPH tests, CO_2 evolution testing, and reaction stoichiometry, which indicate the formation of a carboxylic acid product. We have also attempted to propose an acceptable mechanism. We hope this work opens up the possibility to use and kinetic study of the influence of various polyethylene glycols and polyvinylpyrrolidone as efficient catalysts in oxidation-reduction reactions.

Data Availability

The data of this work are available with the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgments

Supplementary Materials

The file of the supplementary materials contains the raw data of experiments that were part of this work (Tables (1S–14S). It also contains Figures (4S–8S) that show the applicability of the Piszkiewicz model to the catalytic behaviour of the used polymers and surfactants. (*Supplementary Materials*)

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