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Effect of microheterogeneous environments of CTAB, Triton X-100, and Tween 20 on the oxidative degradation of D-fructose by nanoparticles of MnO₂

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Abstract

The kinetics of the oxidative degradation of D-fructose by nanoparticles of MnO₂ has been studied in dilute sulfuric acid medium and also in the presence of surfactants of cetyl trimethyl ammonium bromide (CTAB), Triton X-100 (TX-100), and Tween 20. Amorphous nanoparticles of MnO2 in the form of spherical particulates of size 50-200 nm, as detected by a transmission electron microscope, have been found to exist, supported on two-dimensional gum acacia sheets. The reaction is first order in MnO₂ but complex order with respect to fructose and H⁺. The reaction is inhibited due to adsorption of reaction products on the surface of MnO₂ nanoparticles. The reaction takes place through an intermediate complex formation between β -D-fructopyranose and protonated MnO₂. A one-step two-electron transfer reaction ultimately leads to the formation of an aldonic acid and formic acid. The entropy of activation plays the key role for the reaction in the absence of surfactants. In the surfactant-mediated reaction, partitioning of both the reactants takes place between the aqueous and micellar pseudophases and reaction occurs following Berezin's model. Binding of fructose with the surfactants in the Stern/palisade layer takes place through the ion-dipole interaction and H-bonding while protonated MnO₂ remains at the outer side of the Stern/palisade layer within the micelle. Both the enthalpy and entropy changes associated with the fructose-water interaction, fructose-micelle interaction, and micelle-water interaction finally control the fructose-micelle binding.

KEYWORDS

Berezin model, fructose, kinetics, MnO2 nanoparticles, surfactant effects

1 | INTRODUCTION

Over the past few decades, a great deal of work has been undertaken to explore the mechanistic pathways for the oxidation of both inorganic^{1–3} and organic^{4–11} substrates by permanganate in acidic and alkaline media. However, the +4 oxidation state of manganese has received less attention until now, due to its solubility problem There are reports^{12,13} on the preparation of colloidal MnO₂ by the reduction of KMnO₄ with sodium thiosulfate under neutral conditions. Such form of colloidal manganese dioxide may show better oxidizing properties owing to its having a larger specific surface. A number of kinetic studies^{14–16} on the oxidation of a few organic compounds by colloidal solution of MnO_2 have already been reported.

Carbohydrates are the structural backbone of the DNA, RNA, and nucleic acids,¹⁷ and they serve as store and source of energy in biological systems and play important roles in different nutrition processes.¹⁸ Monosaccharides are involved in carbohydrate metabolism, and the mechanisms of their oxidative degradations are of immense importance from biological point of view.^{19–21} There are a number of reports on the oxidative degradation of sugars, methylated sugars, and sugar phosphates by different oxidizing agents.^{22–25}

There is growing interest in recent times on the influence of different surfactants on the kinetics and mechanism of different reactions.^{26–33} Reaction rates are often modified owing to hydrophobic and/or electrostatic interactions between the reactant species and surfactant monomers or micelles. The oxidation of D-glucose by MnO₂ nanoparticles³⁴ in the absence and presence of different surfactants has very recently been studied. D-Glucose is an aldohexose (-CHO group in the C-1 position), whereas D-fructose is a ketohexose (-C=O group in the C-2 position). Thus the reaction centers as well as their environments are different in the two substrates. Hence, for a continuation of this study, an attempt has been made to investigate the detailed kinetics of the oxidative degradation of D-fructose by the nanoparticles of MnO₂ in the absence and presence of a cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and two nonionic surfactants Triton X-100 (TX-100) and Tween 20. An attempt has been made to account for the differences in the rate and thermodynamic parameters for the two related monosaccharides on the basis of the proposed mechanism

2 | MATERIALS AND METHODS

2.1 | Materials

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D(-)fructose (extrapure; SRL, Mumbai, India), potassium permanganate (extrapure AR; SRL, Mumbai, India), manganous sulfate monohydrate (extrapure AR; SRL, Mumbai, India), surfactants CTAB (extrapure AR; SRL, India), TX-100 (SRL, Mumbai, India), Tween 20 or polysorbate 20 (extrapure; SRL, Mumbai, India), and gum acacia (Loba Chemie, Mumbai, India) were used without purification. Water from Millipore synergy was used in all the experiments.

2.2 | Preparation of nanoparticles of MnO₂ and their characterization

The colloidal solution of MnO_2 was prepared via a comproportionation reaction between $KMnO_4$ and $MnSO_4$ as described in an earlier communication.³⁴ The absorption spectra of the colloidal solution of MnO_2 showed a large absorption band covering the UV–visible region of the spectrum with a flat maximum in the region 336–337 nm.³⁴ The kinetics of the reaction was followed by noting the absorbance at 390 nm.^{34–36}. The solution was found to obey Beer's law at this wavelength and in the studied concentration range of MnO_2 ((0.5–3.0) × 10⁻⁴ mol L⁻¹). All other chemical species in the reaction mixture showed no absorption at this wavelength. The nature of the reactant particles in the oxidant solution alone as well as in the reaction mixture was then characterized with the help of a transmission electron



FIGURE 1 TEM image of nanoparticles of MnO_2 embedded in the gum acacia cluster



FIGURE 2 TEM image of a cluster of nanoparticles of MnO_2 in the presence of fructose

microscope (TEM) (model: Tecnai G² 30ST, FEI, Hillsboro, OR, USA). The solution appeared to be homogeneous and transparent, although it contained aggregates of nanoparticles of size 50-200 nm. A bright-field TEM image (Figure 1) of such a cluster of nanoparticles of MnO₂ in the absence of fructose shows that the cluster is almost spherical in nature³⁴ and such nanoparticles were adhered on the surface of two-dimensional gum acacia sheets attaining the shape of a crumbled paper ball. The amorphous nature of the nanoparticles was confirmed by the absence of diffraction spots in the SAED (Selected Area Electron Diffraction) pattern. In the presence of fructose, the cluster gives a dense appearance (Figure 2). Therefore, it may be concluded that the oxidation of fructose by MnO₂ possibly takes place on the active surface of the nanoparticles of MnO₂ adhered to the surface of gum acacia sheets.



FIGURE 3 Surface tension measurements of CTAB solution in the absence and presence of fructose and H_2SO_4 . Plots of surface tension versus log [CTAB]: A, water; B, 0.1 mol L⁻¹ fructose; C, mixed solution (0.1 mol L⁻¹ fructose and 0.005 mol L⁻¹ H_2SO_4) [Color figure can be viewed at wileyonlinelibrary.com]

2.3 | Kinetic procedure

Appropriate quantities of H_2SO_4 , water, and fructose solution (and surfactant, if any) were taken in a glass cuvette (1.0 cm path length) and mixed thoroughly. It was then placed in the Peltier controlled thermostated cell holder of a UV–visible Shimadzu 1800 spectrophotometer. After temperature equilibration, a requisite volume of colloidal MnO_2 solution was added to start the reaction. The decreasing absorbance of the reaction mixture at 390 nm with time indicated the advancement of the reaction. Reagents other than MnO_2 did not absorb at this wavelength. The rate constants (*k* and *k'*) of the reaction were determined from the kinetic plots as described in the Results and Discussion section.

2.4 | Tensiometric measurements of critical micelle concentration

Surface tension of the three different surfactants at different concentrations was measured with the help of a Jencon (India) Du Nuoy tensiometer with a platinum ring for the measurement. The critical micelle concentration (CMC) for different surfactants in pure water as well as in the presence of fructose and H_2SO_4 was determined from the point of intersection in the plots of "surface tension" versus log[surfactant] values. Figure 3 shows three representative plots for CTAB.

2.5 | Product analysis

After completion of the reaction of fructose with MnO_2 , the reaction mixture was acidified with 4 N H_2SO_4 and then treated with the violet colored solution obtained by the addition of a few drops of phenol to a few milliliters of ferric chlo-

ride solution. Appearance of a bright yellow color indicated the formation of an aldonic acid in the oxidation product.¹¹ The presence of carboxylate anion in the reaction product was also reported in the electro-oxidation of fructose on chemically prepared MnO₂ on Pt support.³⁷ The presence of formic acid in the reaction product was confirmed by the following experiment. Three milliliters of the reaction mixture (after completion of the reaction) was mixed with 1.5 mL of 10% HgCl₂ solution and 2 mL of acetic acid-sodium acetate buffer $(pH \sim 4.2)$ on a watch glass and evaporated to dryness on a water bath. The white residue on the watch glass, after cooling, was then treated with a drop of ammonia solution when it turned black.³⁸ To see whether any intermediate lactone was formed, the reaction mixture was treated with alkaline solution of hydroxylamine and then 2% FeCl₃ and 1% HCl solution were added, but no blue coloration was obtained.²³ Possibly the intermediate lactone, which was formed in an intermediate step, was hydrolyzed to aldonic acid in a fast step.37

3 | RESULTS AND DISCUSSION

3.1 | CMC of different surfactants

With the help of tensiometric experiments, the CMC values of cationic surfactant CTAB and the nonionic surfactants TX-100 and Tween 20 in aqueous medium at 298 K were determined as 1.08×10^{-3} , 0.199×10^{-3} , and 0.050×10^{-3} mol L^{-1} , respectively. One representative plot for CTAB is shown in Figure 3. With CTAB, in the presence of fructose solution $(0.1 \text{ mol } L^{-1})$, the nature of the plot before CMC is deviated from linearity. Possibly CTAB monomers tend to aggregate with fructose molecules beyond a critical aggregation concentration (CAC) of 0.271×10^{-3} mol L⁻¹, and this became saturated or complete at the [CTAB] of 0.610×10^{-3} mol L⁻¹ known as the saturation concentration ($C_{\rm S}$). Beyond $C_{\rm S}$, the surfactant monomers began to form normal micelles while the CMC value increased to 1.156×10^{-3} mol L⁻¹ compared to the value in pure water (Figure 3). This type of aggregation between substrate and surfactant monomer possibly indicated a weak interaction between fructose molecules and CTAB monomers.³⁴ In the presence of a mixed solution (0.1 mol L^{-1} fructose and 0.005 mol L^{-1} H₂SO₄), the plot again showed some curvature but the CMC value again decreased to 0.955 $\times 10^{-3}$ mol L⁻¹ (Figure 3), which was slightly lower than that of CTAB in pure water. For TX-100, the nature of the tensiometric plots in the presence of 0.1 mol L^{-1} fructose and in the presence of a mixed solution remained unchanged, but the CMC value first increased to 0.212×10^{-3} mol L⁻¹ and then it again decreased to 0.169×10^{-3} mol L⁻¹, respectively. For Tween 20, the nature of the tensiometric plots remained unchanged, but the CMC value first decreased to 0.034 \times 10^{-3} mol L⁻¹ in the presence of 0.1 mol L⁻¹ fructose and then

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FIGURE 4 Plots of A_t/A_0 versus time for the oxidation of fructose by MnO₂ at 293 K. [H⁺] = 0.01 mol L⁻¹, [MnO₂] = 1.0 × 10⁻³ mol L⁻¹, 10² [Fruc] (mol L⁻¹): a, 2.5; b, 5.0; c, 7.5; d, 10.0; e, 12.5; f, 17.5; g, 25.0 [Color figure can be viewed at wileyonlinelibrary.com]

further decreased to 0.031×10^{-3} mol L⁻¹ in the presence of a mixed solution.

3.2 | Evaluation of the rate constant from time-dependent absorption studies

The experiments were carried out under the pseudo–firstorder condition such that $[MnO_2] \ll [fructose]$. The plots of log A_t versus time at different initial fructose concentrations were nonlinear. Instead, a plot of A_t/A_0 (where A_t and A_0 represent the absorbances at time t and at the start, respectively) versus time (Figure 4) was found to obey the following empirical equation:

$$A_t/A_0 = a + b e^{-zt} \tag{1}$$

The variable parameters a, b, and z are dependent on the concentrations of reactants and different rate constants and equilibrium constants. It may be suggested that fructose molecules get adsorbed on the surface of the nanoparticles prior to oxidation by the oxidant. The adsorbed products may hinder the oxidation by the oxidant before getting completely desorbed. Based on this idea ,the rate of the reaction may be expressed in the form

$$v = -\frac{d(c-x)}{dt} = v_f - v_i = k(c-x) - k'x$$
(2)

where v_f and v_i are the rates of forward reaction and inhibition, respectively, *c* is the initial concentration of MnO₂ nanoparticles, and *x* gives the concentration of MnO₂ that has been reduced at time *t*. Here, *k* is a pseudo–first-order rate constant that involves different rate constants and equilibrium

constants involved in the reaction steps as well as the concentrations of the reactants and k' is a rate constant related to the adsorption of the products and the term (k'x) gives the rate of inhibition.

As explained in an earlier communication,³⁴ the relation between A_t/A_0 and time will be

$$\frac{A_t}{A_0} = \frac{k'}{k+k'} + \frac{k}{k+k'}e^{-(k+k')t}$$
(3)

Therefore, a plot of A_t/A_0 versus time was expected to produce an exponential graph and the experimental results were analyzed with the help of a nonlinear fitting and the values of k and k' were evaluated.

3.3 | Dependence of the reaction rate on [MnO₂] and [D-fructose]

The dependence of the rate constant k on the MnO₂ concentration was determined by varying the initial [MnO₂] ((0.5–3.0) × 10⁻⁴ mol L⁻¹) at 298 K while [D-fructose] and [H⁺] were kept constant at 0.1 and 0.01 mol L⁻¹, respectively. The rate constant (10³k s⁻¹) were found to be 5.53, 3.91, 3.64, 3.42, 3.15, and 2.64 at MnO₂ concentrations of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0×10^{-4} mol L⁻¹, respectively. Thus increasing [MnO₂] showed an inhibiting effect on the reaction rate. The flocculation of the nanoparticles at higher concentrations might decrease the effective surface area, thereby resulting in a decrease in the value of k.³⁶

At a fixed temperature and constant $[MnO_2]$ and $[H^+]$, an increase in the concentration of fructose ((2.5–25.0) \times 10^{-2} mol L⁻¹) increased both the values of k and k' (Table 1). Such studies were carried out at different acidities (0.01-0.04 mol L^{-1}) and different temperatures (293–308 K). It may be noted here that k is directly related to the actual reaction steps associated with the oxidation of fructose. Hence, k will be dependent on the concentration of fructose. At a particular acidity and temperature, a plot of k versus [Fruc] was found to be nonlinear. On the other hand, a linear plot with a positive slope and positive intercept was obtained when k^{-1} was plotted against [Fruc]⁻¹ (Figure 5). At a particular temperature, the slopes of such double reciprocal plots at four different acidities were plotted against $[H^+]^{-1}$ when a straight line was obtained (Figure 6). The values of k_d , K_1 , and K_2 (Equation 10) at four different temperatures were determined from such straight-line plots (Figure 6) at those temperatures, and such values were found to increase with an increase in temperature.

3.4 | Dependence of the reaction rate on [H⁺]

A number of experiments for the variation of $[H^+]$ (0.01– 0.04 mol L⁻¹) were performed where at a constant temperature, [MnO₂] and [H⁺], the fructose concentration was altered

TABLE 1 Dependence of reaction rate constants on the fructose concentration at different temperatures

| | 293 K | | 298 K | | 303 K | | 308 K | |
|--|------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------|-------------------------------|-------------------|-------------------------------|
| 10^{2} [Fructose] (mol L ⁻¹) | $10^{3}k$ (s ⁻¹) | $10^{3}k'$ (s ⁻¹) | $10^{3}k$ (s ⁻¹) | $10^{3}k'$ (s ⁻¹) | $10^3 k (s^{-1})$ | $10^{3}k'$ (s ⁻¹) | $10^3 k (s^{-1})$ | $10^{3}k'$ (s ⁻¹) |
| 2.5 | 2.14 | 1.28 | 2.98 | 2.01 | 3.61 | 2.27 | 4.41 | 2.4 |
| 5.0 | 3.22 | 1.73 | 4.61 | 2.23 | 5.48 | 2.46 | 7.03 | 4.1 |
| 7.5 | 3.93 | 1.74 | 5.33 | 2.68 | 6.10 | 2.69 | 7.72 | 4.91 |
| 10.0 | 4.49 | 1.95 | 6.44 | 3.34 | 6.82 | 4.01 | 8.51 | 5.29 |
| 12.5 | 5.12 | 2.33 | 7.04 | 3.62 | 8.02 | 4.36 | 9.81 | 6.32 |
| 17.5 | 5.62 | 2.63 | 8.05 | 3.86 | 9.24 | 4.91 | 11.30 | 6.52 |
| 25.0 | 7.11 | 3.21 | 8.72 | 4.52 | 10.47 | 5.32 | 12.91 | 7.01 |
| $[MnO_2] = 1.0 \times 10^{-4} \text{ mol L}$ | $L^{-1}; [H^+] = 0.0$ | 4 mol L^{-1} . | | | | | | |



FIGURE 5 Variation of rate constant (*k*) with the fructose concentration. Plots of k^{-1} versus [Fruc]⁻¹ at different temperatures. [H⁺] = 0.02 mol L⁻¹ and [MnO₂] = 1.0×10^{-4} mol L⁻¹ [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 6 Dependence of slope on $[H^+]$. Plots of slope ({1+ $K_1[H^+]$ }/{ $k_d K_1K_2 [H^+]$ }) versus $[H^+]^{-1}$ at four different temperatures [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 Variation of rate constant (*k*) with acid concentration. Plots of k^{-1} versus $[H^+]^{-1}$ at different temperatures. $[MnO_2] = 1.0 \times 10^{-4} \text{ mol } L^{-1}$ and $[Fruc] = 0.1 \text{ mol } L^{-1}$ [Color figure can be viewed at wileyonlinelibrary.com]

$$(MnO_2)_n + H^+ \xrightarrow{K_1} MnO(OH)^+$$

 $(MnO_2)_{n-1}$ (fast)

$$\begin{array}{c} \operatorname{MnO(OH)^{*}}_{\vdots} \\ (\operatorname{MnO}_{2})_{n-1} \end{array} + \operatorname{Fruc} \underbrace{\begin{array}{c} K_{2} \\ \vdots \\ (\operatorname{MnO}_{2})_{n-1} \end{array}} \end{array} \xrightarrow{\operatorname{MnO(OH)^{+} \cdots \cdot \operatorname{Fruc}}_{\vdots} (\operatorname{fast}) \end{array}$$
(fast)

SCHEME 1 Oxidative degradation of fructose occurring through different reaction steps

in the range $(2.5-25.0) \times 10^{-2}$ mol L⁻¹. An increase in [H⁺] enhanced the reaction rate. At a particular temperature and a fixed [Fruc], a plot of k^{-1} versus [H⁺]⁻¹ produced a straight line (Figure 7). Different rate constants and equilibrium constants (Scheme 1) were then evaluated from the slopes and intercepts of these plots.

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TABLE 2 Equilibrium constants and activation parameters for the oxidation of glucose and fructose

| Substrate | K ₁ (298 K) | K ₂ (298 K) | ΔH^{\neq} (kJ mol ⁻¹) | $\Delta S^{\neq} (\mathbf{J} \mathbf{K}^{-1} \mathbf{mol}^{-1})$ | ΔG^{\neq} (kJ mol ⁻¹) | Reference |
|-----------|------------------------|------------------------|---|--|---|--------------|
| Glucose | 108 | 15.6 | 20.7 ± 2.2 | -223 ± 18 | 87.7 ± 3.2 | 34 |
| Fructose | 141 | 37.9 | 17 ± 3 | -230 ± 18 | 85.5 ± 2.9 | Present work |

3.5 | Dependence on temperature

An increase in temperature increased the values of k_d , K_1 , and K_2 . The enthalpy of activation ($\Delta H^{\#}$) and the entropy of activation ($\Delta S^{\#}$) for the rate-limiting step (Scheme 1) were calculated from the linear plot of $\ln(k_d/T)$ versus 1/T using the Eyring equation:

$$\ln\left(\frac{k_{\rm d}}{T}\right) = \left[\ln\left(\frac{k_{\rm B}}{h}\right) + \frac{\Delta S^{\#}}{R}\right] \frac{\Delta H^{\#}}{RT} \tag{4}$$

where $k_{\rm B}$ and *h* are Boltzmann constant and Planck constant, respectively, and the values are presented in Table 2. Also the enthalpy changes $(\Delta H_1^{0}, \Delta H_2^{0})$ and entropy changes $(\Delta S_1^{0}, \Delta S_2^{0})$ for the protonation of MnO₂ and for the intermediate complex formation step (Scheme 1), respectively, were determined from the linear plots of ln K_1 versus 1/*T* and ln K_2 versus 1/*T* using the following relations:

$$\ln K = \frac{\Delta H^0}{R} \frac{1}{T} + \text{constant}$$
(5)

$$\Delta G^0 = -RT \ln K \text{ and } \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$
(6)

The values of ΔH_1^0 and ΔH_2^0 are 13 ± 4 and 28 ± 3 kJ mol⁻¹ and of ΔS_1^0 and ΔS_2^0 are 86 ± 15 and 123 ± 9 J K⁻¹ mol⁻¹, respectively.

3.6 | Reaction in the presence of surfactants

The reaction was further studied in the presence of two nonionic surfactants TX-100 and Tween 20 and a cationic surfactant CTAB. It may be noted that the stability of the colloidal solution of MnO₂ increases with decreasing acidity. Moreover, addition of electrolytes has been found to affect the size and shape of the micelles as well as the CMC. For these reasons, the kinetic study in the presence of surfactants was carried out at comparatively much lower acidities.^{34,36,39} In case of CTAB, in the premicellar region there was first a negligible increase and then the rate constant (k_w) decreased until near the CMC there appeared again a hump and then the rate constant decreased gradually in the postmicellar region (Figure 8). Thus it appears that inhibition occurs both before and after CMC for CTAB. In case of each of TX-100 and Tween 20, there was at first a decrease in the value of k_w in the premicellar region, showing small inhibition, and then the value of k_w increased passing through a maximum at the CMC and then falls gradually, indicating clear inhibition in the postmicellar region. For both the nonionic surfactants, the small cat-



FIGURE 8 Variation of pseudo–first-order rate constant (k_{Ψ}) with [CTAB] and temperature. [H⁺] = 0.001 mol L⁻¹, [MnO₂] = 1.0 × 10⁻⁴ mol L⁻¹, and [Fruc] = 0.1 mol L⁻¹ [Color figure can be viewed at wileyonlinelibrary.com]

alytic part just before the CMC may be due to the reorganization of the surfactant monomers to form micellar aggregates and consequent interaction with the reactant molecules.

3.7 | Mechanism of oxidaion in the absence of surfactants

The reaction rate increases with increasing [H⁺], indicating that either fructose or MnO_2 may be protonated. But at this low concentration of H⁺, protonation of fructose is expected to be negligible.¹⁰ Thus it is quite plausible that in a fast preequilibrium, the protonation of MnO_2 takes place. Again, on the basis of the Lineweaver–Burk type linear plot of 1/k against 1/[Fruc], it may be proposed that fructose and protonated MnO_2 react in a fast step to form an intermediate complex followed by its decomposition in a slow rate-determining step³⁴ to form products (Scheme 1).

Based on the above scheme of reaction, the forward reaction rate for the reduction of MnO_2 is given by

$$v_f = \frac{k_{\rm d} K_1 K_2 \left[{\rm H}^+ \right] \left[{\rm Fruc} \right]}{1 + K_1 \left[{\rm H}^+ \right] + K_1 K_2 \left[{\rm H}^+ \right] \left[{\rm Fruc} \right]} \left[{\rm MnO}_2 \right] \tag{7}$$

Comparing Equations 2 and 7, the pseudo–first-order rate constant is as follows:

$$k = \frac{k_{\rm d}K_1K_2 \,[{\rm H}^+] \,[{\rm Fruc}]}{1 + K_1 \,[{\rm H}^+] + K_1K_2 \,[{\rm H}^+] \,[{\rm Fruc}]}$$
(8)



SCHEME 2 Mechanistic path of the redox reaction showing different steps

The relation may be rearranged to

$$\frac{1}{k} = \frac{1}{k_{\rm d}} + \frac{1 + K_1 \left[{\rm H}^+ \right]}{k_{\rm d} K_1 K_2 \left[{\rm H}^+ \right] \left[{\rm Fruc} \right]} \tag{9}$$

Thus Equation 9 corroborates the double reciprocal linear plots of k^{-1} versus [Fruc]⁻¹ at different temperatures and different acidities (Figure 5). The values of k_d at different temperatures were evaluated from the intercepts of such plots. From four sets of similar experiments at four different [H⁺], the slopes $(\{1 + K_1[H^+]\}/\{k_d K_1K_2 [H^+]\})$ of such straight lines were evaluated and plotted against 1/ [H⁺] (Figure 6). As expected from the relation, a straight-line plot resulted at each temperature. From the slope and intercept of these plots (Figure 6), the values of K_1 and K_2 at four different temperatures were determined by using the earlier obtained value of $k_{\rm d}$ at those temperatures. The values of $k_{\rm d}$ at a particular temperature obtained at four different acidities were found to be in agreement with each other. Thus at a temperature of 298 K. the straight-line plots of 1/k versus 1/[Fruc] for $[H^+]$ at 0.01, 0.02, 0.03, and 0.04 mol L⁻¹ yielded the values of k_d to be 5.05, 4.90, 5.36, and 5.46, respectively. Equation 8 may also be rearranged as

$$k^{-1} = \left\{ \left(1 + K_2 [\text{Fruc}] \right) / \left(k_d K_2 [\text{Fruc}] \right) \right\} + \left\{ 1 / \left(k_d K_1 K_2 [\text{Fruc}] \right) \right\} [\text{H}^+]^{-1}$$
(10)

The above relation justifies the linear plot of k^{-1} versus $[H^+]^{-1}$ (Figure 7). Moreover, the intercept from such plots were found to be 279, 225, 185, and 163 at 293, 298, 303, and 308 K, respectively, whereas the calculated values of {(1 + K_2 [Fruc]) / ($k_d K_2$ [Fruc])} were 292, 246, 203, and 178. The values were found to agree to a good extent.

D-Fructose is known to exist in an equilibrium mixture of pyranoid (58%) and furanoid (42%) forms.⁴⁰ Of these two forms, only the pyranose form is known to participate in the oxidation process.⁴¹ Again between the two conformers, the β -D-fructopyranose is reported to be much more reactive than the α -anomer.⁴¹ Therefore, it may be suggested that the equatorial –OH of β -D-fructopyranose combines with the protonated form of MnO₂ to form an intermediate complex, which disproportionates in a rate-limiting two-electron transfer step (Scheme 2) to produce a lactone and a hydroxymethyl carbocation. The lactone is hydrolyzed in a fast step to the aldonic acid (five membered). The unstable carbocation, on reaction with water, is fast converted to formaldehyde, which is oxidized to formic acid.^{42,43}

A similar type of two-electron transfer oxidation of fructose was observed in the reaction with N-bromoacetamide⁴² in an acid medium. The fact that one-electron transfer step did not intervene in the present reaction is further supported by the absence of polymerization within the reaction mixture in the presence of 15%(v/v) acrylonitrile.^{23,32} It may be noted that Mn(III) shows an absorption peak at 470 nm.³⁶ Keeping this in mind, time-resolved spectra of the reaction mixture were taken in the range 350-550 nm. But no increase in absorbance at 470 nm was observed during the reaction, indicating that Mn(III) was not formed as an intermediate. This further confirmed that one-electron transfer reaction did not take place. The enthalpy of activation for the rate-determining step was found to be low, which may be ascribed to the enhanced oxidizing power of MnO₂ owing to its nanoscale structures. Such low values of the enthalpy of activation have earlier been reported.^{34,44} On the contrary, for the present reaction the entropy of activation was found to be highly negative (-230 \pm 18 J K⁻¹ mol⁻¹), which might be due to the formation of a cyclic complex (Scheme 2). At this point, it will be worthwhile to compare the rates of oxidation of glucose³⁴ and fructose by the same oxidant as well as their different activation parameters and equilibrium constants. The rate of oxidative degradation of fructose is much faster than that of glucose. However, their enthalpies and entropies of activation are very near to each other and their Gibbs energies of activation ($\Delta G^{\#}$) are almost similar (Table 2). Thus the faster rate of fructose oxidation cannot be explained simply on the basis of activation parameters. But if one examines the values of equilibrium constants (K_2) for complex formation (Scheme 1), it becomes evident that the value is much higher for fructose than that for glucose (Table 2). The much greater value of K_2 for fructose may be ascribed to the fact that the environments at the reaction centers are different in the two cases. In case of glucose,³⁴ the intermediate complex is formed through the -OH group associated with C-1 carbon and thus the H atom in the axial position of C-1 is incapable of forming any Hbond with MnO₂. But in fructose the reaction center is C-2, the –OH group and in the axial position –CH₂OH group (C-1) are capable of forming H-bonding with residual MnO₂ and thus the intermediate complex formation is favored in case of fructose, resulting in a higher concentration of the complex (Scheme 1), thereby making the reaction rate faster than that of glucose. In addition, the enthalpy of activation for fructose degradation is slightly less than that of glucose.

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3.8 | The role of microheterogeneous environments in affecting the reaction rate

In the presence of surfactants, hydrophobic and electrostatic interactions occur between the reactants and the surfactant monomers/aggregates, which may either favor or restrict the movement of the attacking reagent and thus the rate of the reaction is either enhanced or retarded.^{26,45–49} For all the three surfactants, there is an initial decrease of the reaction rate with an increase in [surfactant]. There may be the iondipole interaction between the positively charged head group of CTAB and the oxygen atom of the polar -OH groups of the fructose molecule. In case of TX-100 and Tween 20, there may be interaction between the -OH groups of fructose and the polar oxyethylene groups and the -OH groups of the surfactant monomers through H-bonding. Such interactions may lead to the formation of small aggregates, called premicelles,^{45–51} which may either sterically or entropically inhibit the approach of the oxidant, thus decreasing the reaction rate. It is evident from Figure 8 that there is either a hump or a maximum near the CMC when both the reactants become associated with the micelle and come in the vicinity of each other, and beyond this point k_{w} decreases slowly with further increase of [surfactant], possibly due to lowering of concentrations of both the reactants within the micelle (known as Aqueous pseudophase



SCHEME 3 Berezin model showing reaction occurring in both aqueous and micellar pseudophases

dilution effect). Berezin et al.⁵² proposed that a normal reaction might occur in the aqueous pseudophase and simultaneously both the reactants get solubilized in the micellar pseudophase and then react (Scheme 3).

According to Berezin's model⁵² (Scheme 3), the pseudofirst-order rate constant (k_{ψ}) at surfactant concentrations above CMC will be

$$k_{\psi} = \frac{k_{\rm W} + k_{\rm M} K_{\rm F} K_{\rm O} (C_{\rm surf} - \rm CMC)^2}{\left[1 + K_{\rm F} (C_{\rm surf} - \rm CMC)\right] \left[1 + K_{\rm O} (C_{\rm surf} - \rm CMC)\right]}$$
(11)

where C_{surf} is the surfactant concentration, k_{w} and k_{M} are the pseudo–first-order rate constants in aqueous and micellar pseudophases, respectively, and K_{F} and K_{O} are the binding constants of fructose and oxidant MnO₂, respectively, with the surfactant. Considering the weak interactions between the micelles and the reactants and also the very low concentrations of the surfactants present, Equation 11 may be simplified to Equation 12 as described in our earlier works:^{32,34}

$$k_{\psi}^{-1} = k_{\rm W}^{-1} + (K_{\rm F} + K_{\rm O}) k_{\rm W}^{-1} (C_{\rm surf} - \rm CMC)$$
 (12)

The relation (12) justifies the linear plots of k_{ψ}^{-1} versus $(C_{\text{surf}} - \text{CMC})$ at four different temperatures for all the three surfactants (Figure 9). The values of $k_{\rm W}$ at four different temperatures were obtained from the intercepts of these straight lines. The values were found to corroborate with the experimental values of the pseudo-first-order rate constants (k) at the respective temperatures in aqueous medium where no surfactant was present. Moreover, at these four temperatures, the values of $(K_{\rm F} + K_{\rm O})$ were evaluated (Table 3) from the slopes and intercepts of these straight lines in Figure 9. The values of standard enthalpy changes (ΔH^0) associated with the two equilibria (Scheme 3) are -42.2 ± 1.5 , -19.9 ± 3.5 and -27.8 \pm 0.6 kJ mol⁻¹, respectively, for CTAB, TX-100 and Tween 20. The standard entropy change (ΔS^0) values are -87 ± 1 , -28 ± 12 , and $-38 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ for CTAB, TX-100, and Tween 20, respectively.



FIGURE 9 Plots of k_{Ψ}^{-1} versus ($C_{\text{surf}} - \text{CMC}$) in the post-CMC region for CTAB. [H⁺] = 0.001 mol L⁻¹, [MnO₂] = 1.0×10^{-4} mol l⁻¹, and [Fruc] = $0.1 \text{ mol } \text{L}^{-1}$ [Color figure can be viewed at wileyonlinelibrary.com]

Similar to our earlier discussion,³⁴ it may be assumed that protonated MnO_2 , through ion–ion or ion–dipole interaction, will reside at the outer region of the Stern layer, while the fructose molecule, having a number of –OH groups in its structure, will be interacting with the CTAB molecules through

TABLE 3 Values of $K_{\rm F} + K_{\rm O}$ for different surfactants at different temperatures

| $K_{\rm F} + K_{\rm O}$ | | | |
|-------------------------|--|--|--|
| СТАВ | TX-100 | Tween 20 | |
| 890 | 125 | 999 | |
| 681 | 117 | 820 | |
| 493 | 102 | 677 | |
| 388 | 84 | 575 | |
| | K _F + K _O CTAB 890 681 493 388 | K _F + K _O CTAB TX-100 890 125 681 117 493 102 388 84 | |

ion-dipole interactions and possibly resides in the Stern layer (Scheme 4). In case of TX-100 and Tween 20, the interaction between substrate and surfactant molecules occur through Hbonding. As explained in case of glucose³⁴, $K_{\rm F}$ will predominate in the value of $(K_{\rm F} + K_{\rm O})$ and hence the enthalpy change (ΔH^0) will actually stand for the fructose–micelle binding. It is plausible that the fructose-micelle interaction is stronger than fructose-water interaction and consequently when fructose is transferred from the aqueous pseudophase to the micellar pseudophase, the resultant ΔH^0 values are negative.³⁴ One -OH group and nine to ten polyoxyethylene groups are present in the molecule of TX-100, and these groups are hydrophilic in nature. When fructose binds with TX-100, the structure formation leads to a decrease in entropy, whereas release of water molecules surrounding fructose results in an increase in entropy. Possibly the decrease in entropy is greater



SCHEME 4 Possible interaction between reactants and CTAB micelles involving intermolecular H-bonding [Color figure can be viewed at wileyonlinelibrary.com] than the increase in entropy, the resultant ΔS^0 becomes negative. On the other hand, Tween 20 contains three –OH groups and 20 polyoxyethylene groups in its molecule and hence its interaction with fructose will be much greater than the interaction of TX-100 with fructose. This factor accounts for the higher negative values of both ΔH^0 and ΔS^0 in case of Tween 20. This stronger interaction with Tween 20 is justified by the higher value of $(K_{\rm F} + K_{\rm O})$ for Tween 20 over TX-100 (Table 3). Therefore, it may be concluded that both the enthalpy changes and the entropy changes associated with the fructose–water interaction, fructose–micelle interaction, and micelle–water interaction finally control the binding of fructose with the micelle.

4 | CONCLUSIONS

Nanoparticles of MnO2 are found to be present in the colloidal solution of MnO₂ and these nanoparticles remain adhered to two dimensional gum acacia sheets as spherical particulates of size 50-200 nm. The oxidation of fructose takes place on the active surface of the nanoparticles of MnO₂ adhered on to the surface of gum acacia sheets and occurs through an intermediate complex formation between β -D-fructopyranose and protonated MnO₂. The complex disproportionates in a twoelectron transfer step to form a lactone and a hydroxymethyl carbocation, which are ultimately converted to an aldonic acid and formic acid, respectively. The reaction appears to be controlled by the entropy of activation. Intermediate complex formation between carbohydrate and protonated MnO₂ is more favored in case of fructose than glucose leading to a higher rate of oxidation for fructose than glucose. For the reaction in the presence of different microenvironments, iondipole interactions play a major role in the binding of fructose with CTAB, whereas H-bonding or dipole-dipole interactions are mainly responsible for Tween 20 and TX-100. Both the enthalpy and entropy changes involved in different interactions ultimately control the binding of fructose with the micelle.

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