

# Orientation on the Mechanistics of Electron-Transfer on Oxidation of Chondroitin-4-Sulfate as Sustainable Sulfated Polysaccharide by Permanganate Ion in Aqueous Perchlorate Solutions

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**Abstract:** A spectrophotometric investigation of oxidation of chondroitin-4-sulfate (CS) as a sustainable and biodegradable sulfated macromolecule by oxyanion permanganate ion as multi-equivalent oxidant in acid perchlorate solutions at a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$  has been studied. The experimental results on the influence of the concentration of the reactants the reaction rates revealed first-order dependence in  $\text{MnO}_4^-$ , fractional second-order in  $[\text{CS}]$  and fractional first-order with respect to the hydrogen ion concentration. The hydrogen acid concentration dependence of the rate constants indicated that the oxidation rates were increased with increasing the acid concentration which means that the oxidation reaction is of acid-catalyzed nature. The oxidation of all other polysaccharides by this oxidant in acidic solutions indicated that the oxidation processes were proceeding throughout two distinct stages. The first stage was relatively slow, followed by a more fast reaction in the second stage. The addition of  $\text{Mn}^{2+}$  and  $\text{F}^-$  ions to the reaction mixtures indicated that the  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$  as the reduced forms of permanganate were the reactive species in the second fast stage. Here, neither formation of  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$  transient species nor presence of two stages in the oxidation reaction were detected in the oxidation process, and this result was found to be on contrary to that observed for oxidation of all other polysaccharides by this oxidant. Formation of 1:2 coordination biopolymer intermediate complexes prior to the rate-determining step was revealed, kinetically. Identification of the oxidation product revealed the formation of keto-acid as derivative precursor of CS oxidation. This product was identified by formation of 2,4-dinitrophenylhydrazone and dioxime as wells as by the bands at frequencies  $3430 \text{ cm}^{-1}$  (OH of COOH group);  $1760\text{--}1730 \text{ cm}^{-1}$  (broad) for C=O of diketone;  $1639 \text{ cm}^{-1}$  of  $\nu_{\text{as}}$ , OCO;  $1418 \text{ cm}^{-1}$  of  $\nu_{\text{s}}$  OCO and  $1338 \text{ cm}^{-1}$  of C–O–C, respectively, in the FTIR spectra. Two-electron transfer process of inner-sphere nature in the slowest step has been suggested. A tentative reaction mechanism in terms of the kinetic parameters have been suggested and discussed.

**Keywords:** Chondroitin-4-sulfate; permanganate; oxidation; electron-transfer; kinetics; mechanisms



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## 1 Introduction

Recently, polysaccharides including chondroitin-4-sulfate as sustainable, biodegradable and hydrophilicity macromolecule have received much attention owing to its potential applications in technological industry such as biopharmaceutical in drug delivery [1, 2], biomedical industries [3], cleaning up industrial wastes [4-6], biocatalysts [7] and corrosion inhibition [8-10].

The kinetics of oxidation of some sulfated macromolecules such as carrageenans [11, 12] and chondroitin-4-sulfate [13] have been investigated in alkaline permanganate in more details and discussed previously. However, the oxidation of polysaccharides including sulfated carrageenans has been investigated in acidic permanganate [14-19], no attention was paid to the oxidation of chondroitin-4-sulfate by this oxidant in acidic solutions up till now. Pseudo first-order plots of oxidation of polysaccharides in acidic solutions showed two distinct separate stages of sigmoidal inverted S-shapes curves named induction and auto-acceleration periods. The initial rates were relatively slow at the early stages, followed by an increase in the oxidation rates over longer time periods. Formation of coordination biopolymer intermediate complexes in both two stages was revealed, kinetically. Again, added salts such as  $Mn^{2+}$  to the reaction mixtures indicated that both formed  $Mn^{3+}$  and/or  $Mn^{4+}$  as transient species of reduced permanganate play the important role in the reaction kinetics of oxidation.

Preliminary experiments on the oxidation of chondroitin-4-sulfate polysaccharide by acidic permanganate was found to be much surprising where the oxidation process indicated the absence of such two stages or the formation of  $Mn^{3+}$  and  $Mn^{4+}$  as transient species during the reaction course. This behavior was quite different from that observed for the oxidation of other polysaccharides by this oxidant [14-19].

In view of the above discrepancies and our interest in the kinetics of oxidation of polysaccharides by various oxidants [20-25], the present work oxidation of CS by acidic permanganate seems to be of great importance and merits an investigation with the aims of shedding some light on the nature of electron-transfer and transition states in the rate-determining step and to compare the results obtained with that reported earlier for oxidation of other polysaccharides by this oxidant [14-19]. Again, a comparison of the kinetic parameters for oxidation of CS and other polysaccharides in acidic media by this oxidant is presented and discussed. This work may enhance the elucidation of a suitable reaction mechanism of oxidation of such alcoholic macromolecules in acidic solutions. Again, a novel ketoacid-chondroitin coordination biopolymer chelating agent was synthesized as a precursor derivative of oxidation.

## 2 Experimental

### 2.1 Materials

All materials used were of analytical grade. Doubly distilled water was redistilled from alkaline permanganate and degassed by bubbling through nitrogen, boiling and cooling under atmosphere [26].

Stock solutions of chondroitin-4-sulfate (ICN Biomedicals, Inc.) were prepared by stepwise addition of the reagent powder to doubly-distilled water whilst rapidly stirring the solution to avoid the formation of aggregates, which swell with difficulty.

A stock solution of  $KMnO_4$  was prepared and standardized by the conventional methods as described elsewhere [26, 27]. Then, the stock solution was stored in a dark bottle away from light to avoid photoreduction and was re-standardized spectrophotometrically before each run.

All other reagents were prepared by dissolving the requisite amounts of the sample in doubly distilled water.

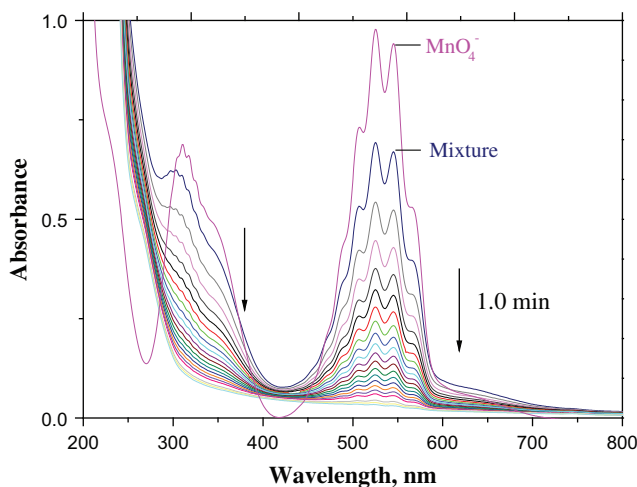
The ionic strength was controlled by addition of  $NaClO_4$  as a non-complexing agent. The temperature was controlled within  $0.05^\circ C$ .

## 2.2 Kinetic Measurements

Absorbance – time plots showed that the initial part (~7–10%) was too fast to be followed by the conventional spectrophotometer used. Therefore, the cited kinetic measurements were concerned with the remained part (~90–93%) of the reaction completion. Pseudo-first-order conditions in the presence of a large excess of [CS] over that of permanganate concentration was applied in all kinetic measurements. Sodium perchlorate, NaClO<sub>4</sub>, as an inert electrolyte was used to maintain the ionic strength constant. The measurements of absorbance changes were made in a thermostated cell compartment at the desired temperature on a Shimadzu UV-2101 double-beam spectrophotometer using cells of path length 1 cm.

Some experimental runs have been carried out in nitrogen atmosphere in order to decide whether permanganate ion or dissolved oxygen is the reactive oxidizing agent for oxidation of the formed aldehyde to its corresponding acid at the final stage. The same product was obtained in both two cases. This means that the dissolved oxygen has no influence on the oxidation process.

The procedure of measurements was the same as described elsewhere [26–28]. The spectral changes during the oxidation reaction are shown in Fig. 1.



**Figure 1:** Spectral changes (200–800 nm) in the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous HClO<sub>4</sub> during the reaction progression. [MnO<sub>4</sub><sup>-</sup>] = 4.0 × 10<sup>-4</sup>, [CS] = 3.0 × 10<sup>-2</sup>, [H<sup>+</sup>] = 1.0 and I = 2.0 mol dm<sup>-3</sup> at 25°C. Scanning time intervals = 1 min

## 2.3 Polymerization Test

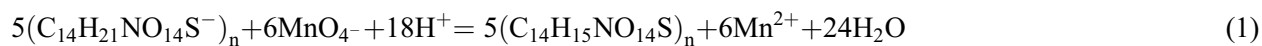
The possibility of formation of free-radicals during the progress of oxidation process was examined by adding 10% (v/v) acrylonitrile to the partially oxidized reaction mixture. The formation of a heavy white precipitate after the lapse of 15 min on warming indicating that the oxidation reaction of the present work was proceeding via free-radical intervention mechanism.

## 3 Results

### 3.1 Stoichiometry

Determination of the reaction stoichiometry is of great importance since the kinetics of this present redox reaction is different from that reported for oxidation of other sulfated polysaccharides such as carrageenans by this oxidant and seems to be of non-complementary nature by this oxidant. Reaction mixtures containing different initial concentrations of the reactants at [H<sup>+</sup>] = 1.0 and I = 2.0 mol dm<sup>-3</sup> were equilibrated in dark bottles away from light at room temperature. The unreacted [MnO<sub>4</sub><sup>-</sup>] was estimated periodically until it

reaches a constant value. A stoichiometric ratio of  $([\text{MnO}_4^-]_{\text{consumed}}/[\text{CS}]_0)$  was found to be  $1.2 \pm 0.1$  mol. This result conforms to the following stoichiometric equation

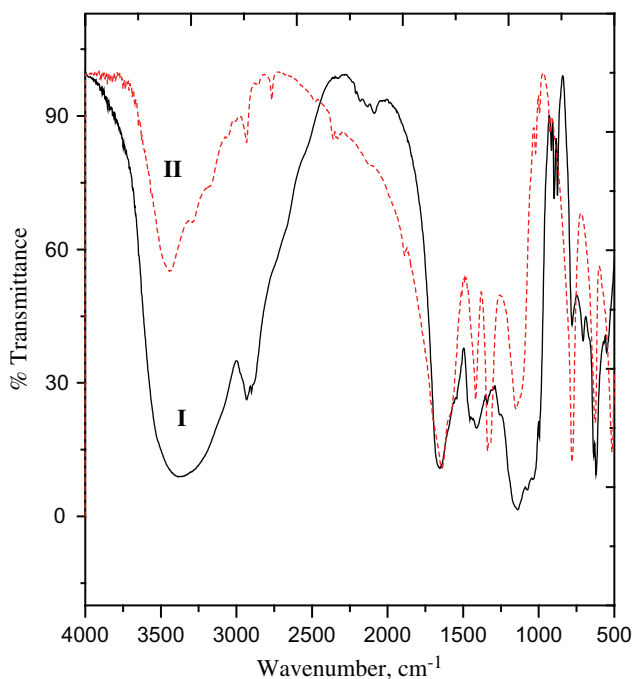


where  $(\text{C}_{14}\text{H}_{21}\text{NO}_{14}\text{S}^-)_n$  and  $(\text{C}_{14}\text{H}_{15}\text{NO}_{14}\text{S}^-)_n$  represent the chondroitin-4-sulfate and its corresponding keto-acid derivative, respectively. The products were separated by the method described elsewhere [29, 30]. The keto-acid derivatives were characterized by the formation of 2,4-dinitrophenylhydrazone and dioxime derivatives on addition of 2,4-dinitrophenylhydrazine and hydroxyl amine respectively as following analysis:

2,4-Dinitrophenyl hydrazone derivative ANAL:  $\text{C}_{26}\text{H}_{23}\text{N}_9\text{O}_{21}\text{S}$  (829): Cald (Found) : C, 37.64 (37.45); H, 2.77 (2.66); N, 15.20 (15.10).

Dioxime derivative ANAL:  $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_{15}\text{S}$  (499):Cald (Found):C, 33.67 (33.62); H, 3.41 (3.39); N, 8.42 (8.40).

Again, the product was also identified by the IR spectral bands observed at frequencies of 1760–1730  $\text{cm}^{-1}$  that characterize the carbonyl group of  $\alpha$ -diketones; 1639  $\text{cm}^{-1}$  of  $\nu_{\text{as}}$ , OCO ; 1418  $\text{cm}^{-1}$  of  $\nu_{\text{s}}$  OCO and 1338  $\text{cm}^{-1}$  of C–O–C, respectively [31]. The enhancement of the absorption band of OH group at wavelength of 1700 nm in the IR spectra of the product may indicate oxidation of OH groups present in CS monomers to its corresponding keto-forms as shown in Fig. 2.

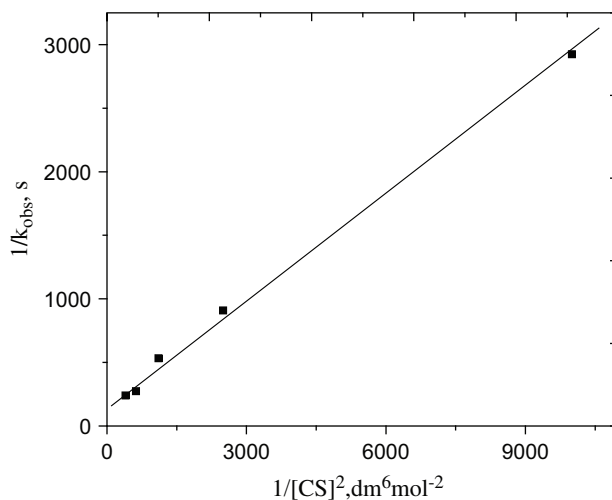


**Figure 2:** FT-IR spectra of the reactants and products; (I) chondroitin-4-sulfate; (II) ketoacid-derivative

### 3.2 Dependence of Reaction Rate on $[\text{MnO}_4^-]$ and $[\text{CS}]$

Plots of  $\ln(\text{Absorbance})$  vs. time gave good straight lines for more than two-half-lives of reaction completion indicating that the oxidation reaction is first-order in permanganate ion concentration. This dependency was confirmed not only by the pseudo first-order plots but also by the independence of the

reaction rates on various initial concentration of permanganate used ranging between  $2 \times 10^{-4}$  and  $8 \times 10^{-4}$  mol  $\text{dm}^{-3}$ . A fractional-second-order in [CS] was obtained from the plots of double logarithm of the rate constants and concentration ( $k_{obs} = [\text{CS}]^n$ ). Again, when the reciprocals rate constants,  $1/k_{obs}$  were plotted against  $1/[\text{CS}]^2$ , straight lines with positive intercept on the  $1/k_{obs}$  axis was obtained. This behavior indicates that the present redox system exhibits the Michaelis-Menten kinetics for formation of 1:2 intermediate complexes (Fig. 3). Again, the small shift in absorbance of permanganate ion to shorter UV-spectra at wavelength of 300 nm may confirm the formation of an intermediate complex prior to the rate-determining step. From the line weaver- Burk plot, the Michaelis-Menten constant ( $K_m$ ) was calculated and found to be  $5.86 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$  where the maximum rate ( $\gamma_{max}$ ) =  $4.17 \times 10^{-3} \text{ s}^{-1}$ . The large value obtained for ( $K_m$ ) may confirm the fast formation of the intermediate complex prior to the rate-determining step.



**Figure 3:** Reciprocal Michaelis-Menten plot for the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$   $[\text{H}^+] = 1.0$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$

### 3.3 Dependence of Reaction Rate on $[\text{H}^+]$

Kinetic measurements were performed in  $\text{HClO}_4$ - $\text{NaClO}_4$  solutions with different  $[\text{H}^+]$  and constant ionic strength and temperature to clarify the influence of  $[\text{H}^+]$  on the reaction rates as well as to elucidate a suitable reaction mechanism. An increase in the acid concentration was found to accelerate the oxidation rates. This means that the oxidation reaction is acid-catalyzed (Tab. 1). Fractional first-order dependence with respect to  $[\text{H}^+]$  was observed ( $\ln k_{obs} - \ln [\text{H}^+]$  plots).

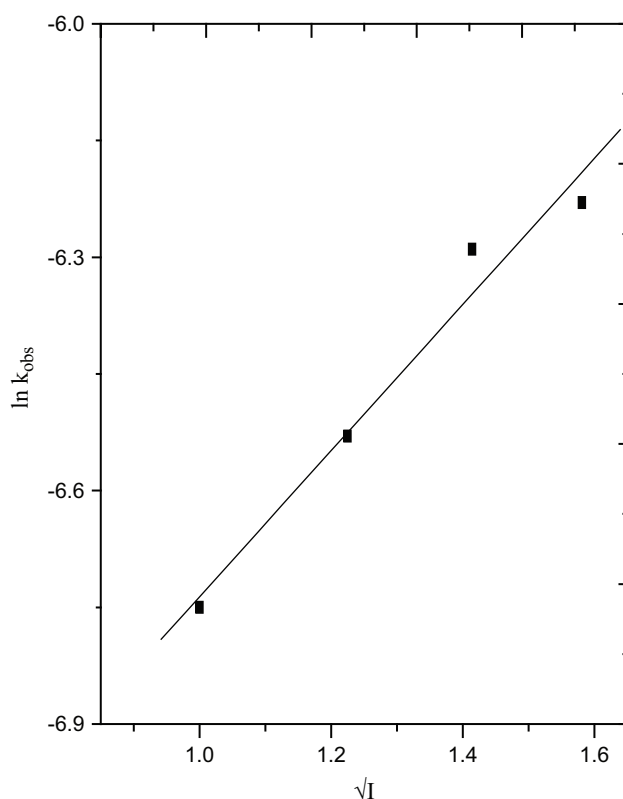
**Table 1:** Dependence of pseudo-first order of the rate constants ( $k_{obs}$ ) on  $[\text{H}^+]$  and [CS] reactants in the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$  and  $I = 2.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$

$[\text{H}^+]^a$	$10^3 k_{obs}, \text{s}^{-1}$	$10^2 [\text{CS}]^b, \text{mol dm}^{-3}$	$10^3 k_{obs}, \text{s}^{-1}$
1.0	1.96	1.0	0.342
2.0	2.92	5.0	4.17

Notes: Experimental error  $\pm 4\%$ . a:  $[\text{CS}] = 3 \times 10^{-2} \text{ mol dm}^{-3}$ ; b:  $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ .

### 3.4 Dependence of Reaction Rate on Ionic Strength

In order to shed some lights on the reactive species in the rate-determining step, kinetic runs were performed at constant  $[H^+] = 1.0 \text{ mol dm}^{-3}$  as the  $\text{NaClO}_4$  concentration was increased to  $2.5 \text{ mol dm}^{-3}$ . The value of  $k_{obs}$  was found to increase with increasing the ionic strength as shown in Fig. 4. This result indicated the catalytic salt effect which was supported by the linearity of the Debye–Hückel relationship ( $\ln k_{obs}$  vs.  $I^{0.5}$  plot). The ionic strength dependence is qualitatively as expected when considering the charges involved despite the used ionic strength was far from the applied Debye–Hückel range [32, 33]. This means that the oxidation reaction may occur between a cation and a neutral molecule.



**Figure 4:** Ionic strength dependency of the rate constants in the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous perchlorate solutions.  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{CS}] = 3.0 \times 10^{-2}$ ,  $[H^+] = 1.0 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$

### 3.5 Dependence of Reaction Rate on Added Salts

The influence of  $\text{Mn}^{2+}$  on the rate of reaction should be examined since it is one of the oxidation products. It is reported [34, 35] that acidified permanganate ion is reduced by  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  as transient species according to the Eq. (2),



If the intermediate manganese ions,  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$ , are the reactive oxidizing species, the addition of  $\text{Mn}^{2+}$  should cause an acceleration of the reaction rate. Similarly, the addition of  $\text{F}^-$  ions should retard the reaction if the intermediate manganese ions are mainly the responsible species for oxidation, but should cause no significant change if  $\text{MnO}_4^-$  ions are the principal oxidizing entities [35].

Addition of either  $[\text{Mn}^{2+}]$  or  $[\text{F}^-]$  ions to the reaction mixtures, was found to have no appreciable changes of the reaction rates under our experimental conditions. This negative result may indicate the absence of formation of either  $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$  as transient-species intermediates throughout the oxidation reaction. This result is opposite to that observed in the oxidation of other carbohydrates by this oxidant [14-19].

#### 4 Discussion

Although, a considerable amount of work has been reported on the kinetics of oxidation of organic and inorganic substrates as well as the alcoholic macromolecules by permanganate ion as a multi-equivalent oxidant in acidic solutions, some unanswered questions concerning the mechanisms of oxidation in terms of the nature of electron-transfer process and the transition states in the rate-determining steps still remain not completely understood [36]. A question of basic interest may arise here, is whether the transfer of electrons, proceeds through successive one-electron transfer process  $\text{Mn}^{\text{VII}} \rightarrow \text{Mn}^{\text{VI}} \rightarrow \text{Mn}^{\text{V}}$  in a sequence or by simultaneous two-electron changes  $\text{Mn}^{\text{VII}} \rightarrow \text{Mn}^{\text{V}} \rightarrow \text{Mn}^{\text{III}}$  in a single step. In addition, is whether the mechanism of electron-transfer process exhibits outer-sphere or inner-sphere nature. These difficulties may arise from the reactions complexity with respect to the formation of unstable intermediates through the passage of manganese ion from heptavalent to divalent state in acidic solutions. Therefore, a variety of reaction mechanisms has been suggested for oxidation of various substrates by this oxidant. Some of these reactions tend to proceed by the formation of ion pairs [26] and intermediate complexes of inner-sphere nature through free-radicals [18, 27, 37] or without free-radical intervention [38]. Other reactions were proceeding through outer-sphere mechanisms in the absence of free-radical intervention [39].

In view of the above discrepancies of the kinetic results in comparison to that reported for other polysaccharides oxidized by this oxidant, the most suitable reaction mechanism which may be suggested for oxidation of CS by permanganate ion involves the protonation of both reactants to give the more reactive permanganic acid ( $\text{HMnO}_4$ ) and alkoxonium ion ( $\text{CSH}^+$ ), respectively,



where  $K$  and  $K_1$  are the protonation constants of permanganate ion and CS substrate, respectively. This suggestion was based on the observed hydrogen ion dependence of the reaction rates. Again, the dependence of the observed pseudo first-order rate constants on  $[\text{CS}]$  which obeys the Michaelis-Menten kinetics (Fig. 3) may suggest the formation of 1:2 coordination biopolymeric intermediate complexes. This means that the protonated substrate ( $\text{CSH}^+$ ) is rapidly attacked by  $\text{HMnO}_4$  oxidant to form a coordination biopolymer intermediate complex ( $\text{C}_1$ )



This intermediate complex ( $\text{C}_1$ ) picks up a further protonated substrate molecule to give further intermediate complex ( $\text{C}_2$ ) with subtraction of hydronium ions prior to the rate-determining step as follows



where  $K_2$  and  $K_3$  are the formation constants of the complexes  $\text{C}_1$  and  $\text{C}_2$ , respectively. Then, the formed complex ( $\text{C}_2$ ) is slowly decomposed in the rate-determining step to give the substrate radical ( $\text{C}_2^\cdot$ ) and  $\text{Mn}^{\text{V}}$  as initial oxidation products.





A formed substrate radical is rapidly oxidized by picking up either further oxidant molecule or the formed  $Mn^V$  in Step (7) to give rise to the final oxidation products.



The change of the rate constants with the change in the hydrogen ion and CS substrate concentrations may be expressed by the following rate-law,

$$\text{Rate} = \frac{kKK_1K_2K_3[H^+][CS]_T^2[OX]}{1+K_1[H^+]+KK_1K_2[H^+][OX]([H^+]+K_3[OX])} \quad (9)$$

where  $[CS]_T$  is the analytical total concentration of CS substrate.

Under our experimental conditions in the presence of a large excess of  $[CS]$  over that of the oxidant, the rate-law expression is,

$$\text{Rate} = k_{obs}[OX] \quad (10)$$

where  $k_{obs}$  is the observed pseudo first-order rate constant and  $[OX]$  represents to the permanganate ion oxidant.

On comparison of Eqs. (9) and (10) and rearrangement, one concludes that,

$$\frac{1}{k_{obs}} = \left( \frac{[H^+]}{k_aKK_1K_2K_3} + \frac{1}{k_aKK_2K_3} \right) \frac{1}{[CS]^2} + *K' \quad (11)$$

$$*K' = \frac{[OX]}{k_a[CS]^2} \left( \frac{1}{K_3} + \frac{1}{KK_1K_2[H^+]} \right)$$

According to Eq. (11), at constant  $[H^+]$  a plot of  $1/k_{obs}$  against  $1/[CS]^2_T$  should be linear with positive intercept on  $1/k_{obs}$  axis. The experimental results satisfied this requirement as shown in Michaelis-Menten plot (Fig. 3). Again, a plot of  $1/k_{obs}$  versus  $1/[H^+]$  at constant  $[CS]_T$  gave good straight lines with positive intercepts on  $1/k_{obs}$  axis.

The small intercept observed in Fig. 3 may lead us to simplify Eqs. (11) to (12), which is considered as the appropriate rate-law expression for oxidation of CS by permanganate ion.

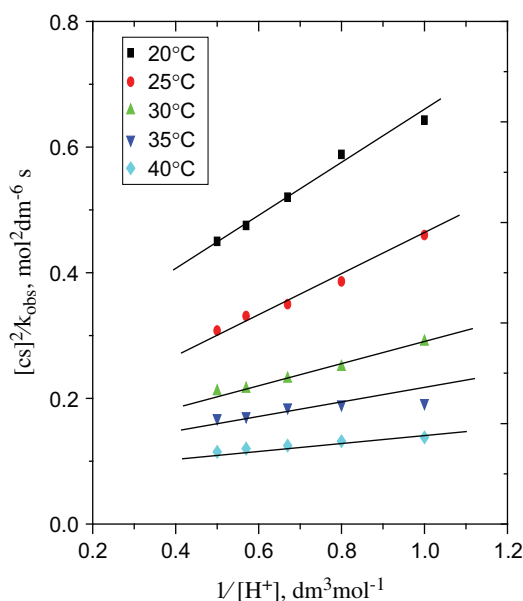
$$\frac{[CS]^2}{k_{obs}} = \frac{1}{k_n} = \left( \frac{[H^+]^{-1}}{k_a'} + \frac{1}{k_a''} \right) \quad (12)$$

where  $k_a' = k_aKK_1K_2K_3$ ,  $k_a'' = k_aKK_2K_3$  and  $k_n$  is the second-order rate constant. According to Eq. (12), a plot  $[CS]^2/k_{obs}$  against  $1/[H^+]$  gave straight lines with the positive intercepts (Fig. 5) from whose slopes and intercepts, the values of the apparent rate constants  $k_a'$  and  $k_a''$  as well as the protonation constant  $K_1$  can be evaluated. These values calculated by using the least-squares method and found to be 0.67, 0.62, and 0.51 at 25, 30, and 35°C, respectively. The calculated values of protonation constants ( $K_1$ ) were found to be in good agreement with that reported for oxidation of other polysaccharides by this oxidant elsewhere [14-19].

The negative values of entropies of activation ( $\Delta S^\ddagger$ ) observed in Tab. 2 indicates the compactness of the intermediates rather than the reactants. Again, the positive values observed for  $\Delta G^\ddagger$  may confirm the non-spontaneity of the formed intermediate complexes as was suggested by the proposed mechanism. The observed small activation energy value,  $E_a^\ddagger$  (Tab. 2), may support that the high tendency of the reaction between the neutral molecule and the positive ion as was deduced from the ionic strength dependency of the rate constants. This means that the reactants do not need much energy to bring them together in order to form the transition states of the formed complexes.

Moreover, it has been reported previously [40-44] that entropy of activation tends to be more negative for reactions of inner-sphere nature, whereas the reactions of negative  $\Delta S^\ddagger$  values proceed via an inner-sphere





**Figure 5:** Plots of  $[CS]^2/k_{obs}$  vs.  $1/[H^+]$  in the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous perchlorate solutions.  $[MnO_4^-] = 4.0 \times 10^{-4}$ ,  $[CS] = 3.0 \times 10^{-2}$ ,  $I = 2.0 \text{ mol dm}^{-3}$  at various temperatures

**Table 2:** The thermodynamic parameters of the protonation constant ( $K_1$ ) and the activation parameters of the apparent rate constants ( $k_a'$  and  $k_a''$ ) in the oxidation of chondroitin-4-sulfate by permanganate ion in aqueous perchlorate solutions

Parameters	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger_{298}$	$E_a^\ddagger$	A
Constants	$\text{kJmol}^{-1}$	$\text{Jmol}^{-1}\text{K}^{-1}$	$\text{kJmol}^{-1}$	$\text{kJmol}^{-1}$	$\text{mol}^{-1} \text{ s}^{-1}$
$k_a'$	42.21	-92.16	69.67	44.59	$2.5 \times 10^8$
$k_a''$	61.97	-22.53	68.68	64.49	$1.14 \times 10^{12}$
$^a k_n'$	57.11	-75.46	79.59	60.07	$2.30 \times 10^9$
$K_1$	$\Delta H^\circ \text{ kJmol}^{-1}$	$\Delta S^\circ_{298} \text{ Jmol}^{-1}\text{K}^{-1}$	$\Delta G^\circ_{298} \text{ kJmol}^{-1}$		
	+1.08	+0.27	+1.0		

Notes: Experimental errors  $\pm 4\%$ . a: The second-order rate constant at  $[H^+] = 1.0 \text{ mol dm}^{-3}$ .

of one- or two-electron transfer mechanism. In view of the values observed for the entropy of activations (Tab. 2), the oxidation of CS by permanganate ion is more favorable to proceed by inner-sphere path of two-electron changes rather than by outer-sphere mechanism. In this context, it should be noted that there does not appear to be any experimental confirmation of outer-sphere two-electron transfer process [19, 42].

Leffler and Grunwald suggested an isokinetic relationship between the enthalpies and entropies of activations ( $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$ ). Therefore, the activation parameters of the second-order rate constants for oxidation of some polysaccharides by permanganate ion in aqueous perchlorate solutions are summarized in Tab. 3.

However, the variation of the alcoholic substrate polysaccharide, and the nature of electron-transfer process and the transition states in the rate-determining steps, the values of activation enthalpies  $\Delta G^\ddagger$  seems to be unaltered, i.e., with the same order of magnitude. This means these redox reactions should

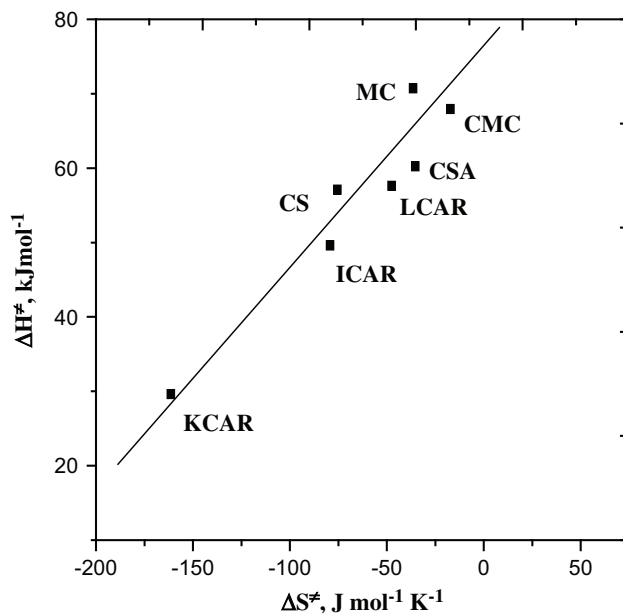
**Table 3:** The activation parameters of the second-order rate constants in the oxidation of some polysaccharides by permanganate ion in aqueous perchlorate solutions

Parameters Substrate	$\Delta H^\ddagger$ , kJmol <sup>-1</sup>	$\Delta S^\ddagger$ , Jmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G^\ddagger_{298}$ , kJmol <sup>-1</sup>	$E_a^\ddagger$ , kJmol <sup>-1</sup>	A, mol <sup>-1</sup> s <sup>-1</sup>	Ref.
<b>Chondroitin-4-Sulfate (CS)</b>	57.11	-75.46	79.59	60.07	2.30 x 10 <sup>9</sup>	This work
<b>Kappa-Carrageenan (KCAR)</b>	29.63	-161.30	77.70	32.70	8.67 x 10 <sup>12</sup>	[14]
<b>Iota-Carrageenan (ICAR)</b>	49.57	-79.27	78.74	52.30	-	[14]
<b>Lambda-Carrageenan( LCAR)</b>	57.62	-47.49	79.82	60.13	-	[14]
<b>Chitosan (CSA)</b>	60.22	-35.25	70.72	62.42	-	[17]
<b>Carboxymethyl Cellulose (CMC)</b>	67.92	-17.22	73.05	70.46	2.19 x 10 <sup>12</sup>	[18]
<b>Methyl Cellulose (MC)</b>	70.72	-36.39	81.57	73.29	2.21 x 10 <sup>11</sup>	[19]

Notes: Calculated at  $[H^+] = 1.0 \text{ mol dm}^{-3}$ ; Experimental error  $\pm 4\%$ .

have a correlation relationship. Therefore, an isokinetic plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  values of (Leffler and Grunwald [45]) gave a straight line as shown in Fig. 6. This means that the oxidation products still remains the same (keto or keto-acid derivatives depending on the nature of alcoholic groups) despite the various routes and kinetic behavior of oxidation. The activation energies,  $E_a^\ddagger$ , indicated that efficiency for transferring the reactants to overcome the energy barriers for formation of the corresponding intermediates complexes were decreased in the order  $KCAR > ICAR > CS \geq LCAR \geq CSA > CMC > MC$ , respectively. This means that the reactants needs more energy for overcome this barrier in the same order which is depending on the geometrical configuration of substrate, the positions of the OH groups, the magnitude of the charge formed on the complex and the reactive species of the reactants.

This linearity may indicate that the mechanism of electron-transfer in such oxidation reactions is similar which corresponds to the inner-sphere type. Again, the  $\beta$  value obtained (305K) is significant and may be

**Figure 6:** Isokinetic relationship ( $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$ ) of the second-order rate constants in the oxidation of some polysaccharides by permanganate ion in aqueous perchlorate solutions



considered as a deserved comment for the reactivity of these redox reactions. In view of the above kinetic interpretations and the experimental observations, a tentative reaction mechanism for oxidation of chondroitin-4-sulfate by acidic permanganate may be suggested as illustrated by [Scheme I](#).

The perturbation of the spectra change ([Fig. 1](#)) may indicate that the initial fast part of oxidation reaction is not true electron-transfer process. Therefore, the initial rapid part of oxidation may be attributed to a fast formation of an intermediate between the reactants. Again, some trials have been performed in order to detect the formation of hypomanganate (V) intermediate as transient species. Unfortunately, all attempts were unsuccessful. This failure may be attributed to the lower absorptivity of formed Mn (V) under our experimental conditions of lower reactants concentrations or the fast reaction between the formed manganese (V) and substrate radical ([Eq. \(7\)](#)) to give rise to the final oxidation products.

## 5 Conclusions

The kinetics and mechanism of oxidation of CS as a sulfated macromolecule by permanganate ion oxidant in acid perchlorate solutions at a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$ , has been studied spectrophotometrically. The experimental results of the pseudo first order plots indicated that the oxidation exhibits only one step pathway reaction; first-order in  $\text{MnO}_4^-$ , fractional second-order in [CS] and fractional first-order with respect to the hydrogen ion concentration. Acid-dependence of the reaction rates indicated that the oxidation reaction was of acid-catalyzed nature. Absence of either  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$  transient species as involvement species in the oxidation process was confirmed by the added  $\text{Mn}^{2+}$  to the reaction mixtures. Formation of 1:2 coordination biopolymer intermediate complexes prior to the rate-determining step was revealed, kinetically. These kinetic results observed here were found to be on contrary to that observed for the oxidation of other alcoholic polysaccharides by this oxidant which showed two distinct stages of S-sigmoidal curves for the pseudo first order plots. The initial stage was relatively slow (induction period), followed by a relatively fast stage (autoacceleration period which involving the  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$  as transient species) with formation of 1:1 or 1:2 intermediate complexes prior to the rate-determining steps. A tentative reaction mechanism in terms of the kinetic observations and evaluated kinetic parameters have been suggested and discussed.

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**Conflicts of Interest:** The authors declare that they have no conflicts of interest to report regarding the present study.

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