



Base-catalyzed oxidation of some sulfated macromolecules: Kinetics and mechanism of formation of intermediate complexes of short-lived manganate (VI) and/or hypomanganate (V) during oxidation of iota- and lambda-carrageenan polysaccharides by alkaline permanganate

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ABSTRACT

The kinetics of formation of intermediate complexes during the oxidation of iota- and lambda-carrageenan sulfated polysaccharides (CAR) as natural polymers by alkaline permanganate at pH's ≥ 12 have been investigated using a conventional spectrophotometer. The reactions showed first-order dependences in permanganate and fractional-first-order kinetics with respect to carrageenans concentration. Kinetic and spectrophotometric evidences revealed the formation of intermediate complexes involving green manganate (VI) and/or blue hypomanganate (V) short-lived transient species. The influence of pH on the oxidation rates indicated that the formation of complexes is base-catalyzed. The kinetic parameters have been evaluated and mechanisms consistent with the experimental results are discussed.

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1. Introduction

Carrageenans (CAR) are major structural red algae sulfated polysaccharides consisting of alternating 1,3 linked β -D-galactopyranose and 1,4 linked α -D-galactopyranose units of linear block copolymer structures [1–5].

In recent years, the literature survey contains a considerable amount of work on the kinetics of oxidation of macromolecules containing secondary alcoholic groups in particularly polysaccharides by permanganate ion in alkaline solutions [6–14]. It reported that the oxidation processes in those redox systems are proceeded by two distinct stages throughout the entire courses of reactions. The first stage was relatively fast which correspond to the formation of detectable intermediate complexes involving short-lived green manganate (VI) and/or blue hypomanganate (V) transient species. As those intermediates build up, slow decay of the intermediates

takes place to give rise to keto-derivatives as oxidation products, in the second stage. However, it appears that no attempt has been yet done with respect to the oxidation of carrageenans as sulfated polysaccharides containing both primary and secondary alcohols by this oxidant. One possible reason may be attributed to the kinetic complexity, which may not allow a mechanistic conclusion.

Therefore, it would be of interest to undertake the present work of oxidation of iota- and lambda-carrageenans as sulfated polysaccharides by this oxidant as part of a series of investigations on the oxidation of macromolecules by permanganate ion [6–14]. Eventhough, evidences for the formation of short-lived detectable intermediates manganate ($\text{Mn}^{\text{VI}}\text{O}_4^{2-}$) and/or hypomanganate ($\text{Mn}^{\text{V}}\text{O}_4^{3-}$) transient species during the oxidation of carrageenans have been reported by us previously [14]. Therefore, the present work aims to present the detailed kinetics and mechanisms of the oxidation of some carrageenans as sulfated polysaccharides by alkaline permanganate as well as to compare the results obtained with that previously reported [6–14]. In addition, the results obtained may shed some light on the nature of interaction of sulfated polysaccharides in aqueous solutions.

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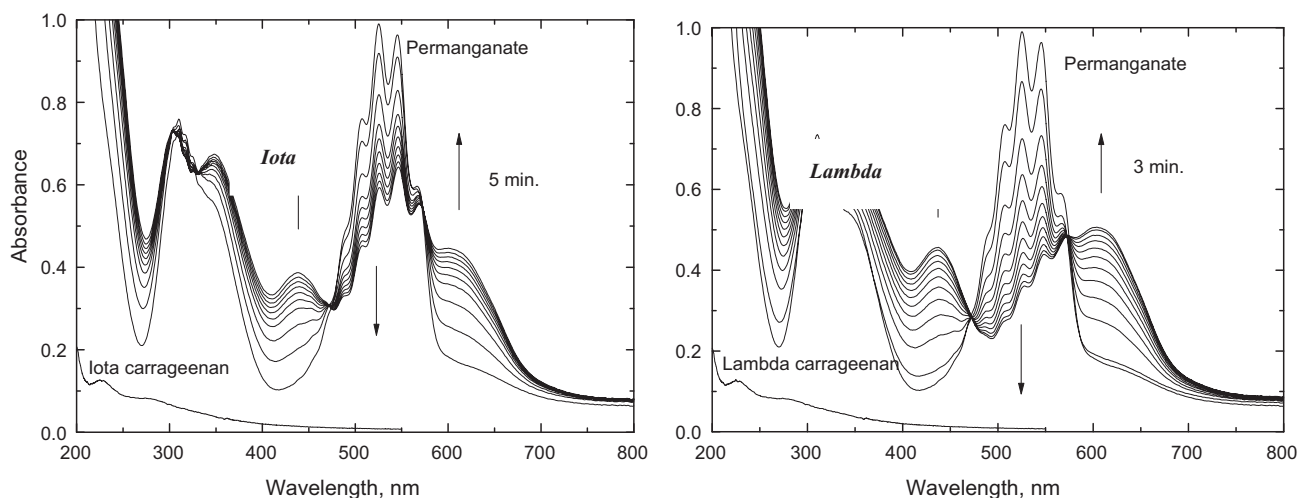


Fig. 1. Spectral changes (200–800 nm) during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; $[\text{OH}^-] = 3 \times 10^{-2}$ $l = 0.2 \text{ mol dm}^{-3}$ at 30°C .

2. Experimental

2.1. Material

Doubly distilled water was redistilled from alkaline permanganate and degassed by bubbling through nitrogen, boiling and cooling under atmosphere [15].

Stock solutions of CAR were prepared by stepwise addition of the reagents (Fluka chemical products) to deionized 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 described elsewhere [15,16]. Then, the stock solution was stored in a dark bottle away from light and restandardized spectrophotometrically before each run.

All other reagents were of analytical grade and were prepared by dissolving the requisite amount of the analytical reagent in doubly distilled water.

2.2. Kinetic measurements

Preliminary experiments indicated that, oxidation of the present reactions are of such rates that can be monitored using conven-

tional spectrophotometric techniques. The kinetic measurements were conducted under pseudo-first-order conditions where the carrageenan solutions were present in a large excess over that of permanganate concentration at constant ionic strengths of 0.2 mol dm^{-3} (in case of LCAR) and 0.5 mol dm^{-3} (in case of ICAR), respectively using NaClO_4 as an inert electrolyte. The absorbance measurements were made in a thermostated cell compartment at the desired temperature on a Shimadzu UV-2101/3101 PC automatic scanning spectrophotometer fitted with a program controller using cells of pathlength 1 cm.

The measurements were performed where permanganate was added either immediately or after a 30 min elapsed to the alkaline substrate solution in order to allow possible deprotonation. The results obtained indicated the fast deprotonation of the substrates by the alkali prior to the rate-determining step. However, some reactions were carried out under second-order conditions of $[\text{CAR}] \geq [\text{MnO}_4^-]$ in order to check the producibility of the data obtained from the pseudo-first-order kinetics. The results obtained were found to be in good agreement with each other within the experimental errors indicating the reproducibility of the measurements. The procedure for measurements was the same as described elsewhere [15]. The spectral changes during these redox reactions are shown in Figs. 1 and 2

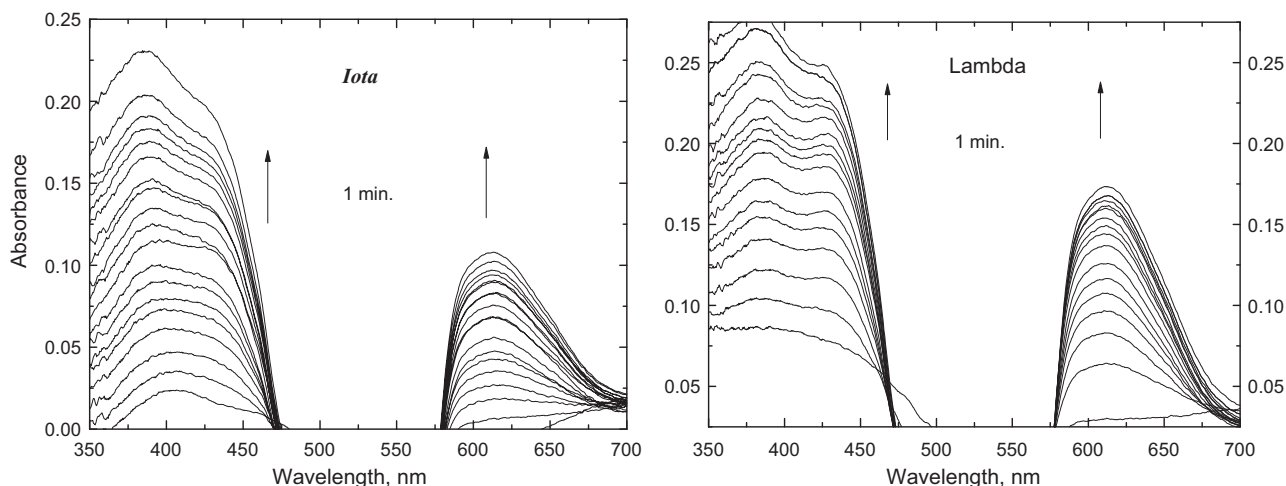


Fig. 2. Spectral changes (350–700 nm) during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; $[\text{OH}^-] = 3 \times 10^{-2}$, $l = 0.2 \text{ mol dm}^{-3}$ at 30°C . Reference cell (MnO_4^- and OH^- of the same reaction mixture concentration).

2.3. Polymerization test

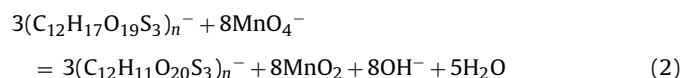
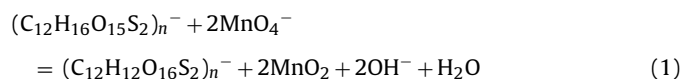
The possibility of formation of free-radicals was examined by adding acrylonitrile to the partially oxidized reaction mixture. No polymerization was found indicating that these oxidation reactions probably do not proceed via free-radical mechanisms.

3. Results

3.1. Stoichiometry

Due to the complexity of oxidation of CAR by permanganate ion as a result of formation of $[\text{CAR-Mn}^{\text{VI}}\text{O}_4^{2-}]$ and/or $[\text{CAR-Mn}^{\text{V}}\text{O}_4^{3-}]$ intermediate complexes, it is worth for determining the stoichiometric coefficients of the reactants in the overall reactions. Since manganate (VI) is well known to disproportionate at pH's <11 [17], the stoichiometry of these redox reactions were determined above pH's 12 where manganate (VI) is known to be stable and tends to accumulate as the reactions progressed [18,19].

Reaction mixtures containing different initial concentrations of the reactants were mixed together at pH's above 12 and were equilibrated in dark. The unreacted $[\text{MnO}_4^-]$ was estimated periodically until it reached a constant value, i.e. completion of the reaction. Stoichiometric ratios of $([\text{MnO}_4^-]_{\text{consumed}}/[\text{CAR}]_0)$ were found to be 2.0 ± 0.1 and 2.7 ± 0.1 mol for iota- and lambda-carrageenans, respectively. No specific method was available for the determination of carrageenans. This result conforms to the following stoichiometric equations



where $(\text{C}_{12}\text{H}_{16}\text{O}_{15}\text{S}_2)_n^-$ and $(\text{C}_{12}\text{H}_{17}\text{O}_{19}\text{S}_3)_n^-$ are iota- and lambda-carrageenans and $(\text{C}_{12}\text{H}_{12}\text{O}_{16}\text{S}_2)_n^-$ and $(\text{C}_{12}\text{H}_{11}\text{O}_{20}\text{S}_3)_n^-$ are the corresponding keto-acid oxidation derivatives, respectively. The products were identified by IR spectroscopy and elemental analysis as described earlier [20–22] and are going to be published later.

When these oxidation reactions have been carried out in nitrogen atmosphere in order to decide whether permanganate ion or dissolved oxygen is the reactive oxidizing agent at the final stages, the same keto-acid derivatives were obtained as final products. This means that the keto-aldehyde intermediate derivatives formed are oxidized by permanganate ion rather than by the dissolved oxygen at the final stage of oxidation.

3.2. Dependence of reaction rates on $[\text{MnO}_4^-]$ and $[\text{CAR}]$

Preliminary experiments indicated that the oxidation of iota- and lambda-carrageenans by alkaline permanganate proceeds via formation of detectable intermediate complexes,



followed by slow decay of these intermediates to give rise to the reaction products



As is shown by the spectral changes in Fig. 1, a gradual disappearance of MnO_4^- at $\lambda = 525$ nm, its absorption maximum, with a simultaneous growth of new absorbance intermediates at wavelengths of 606, 435, 350 and 315 nm. These spectral changes of the reaction mixtures were provided by repetitive spectral scans of the

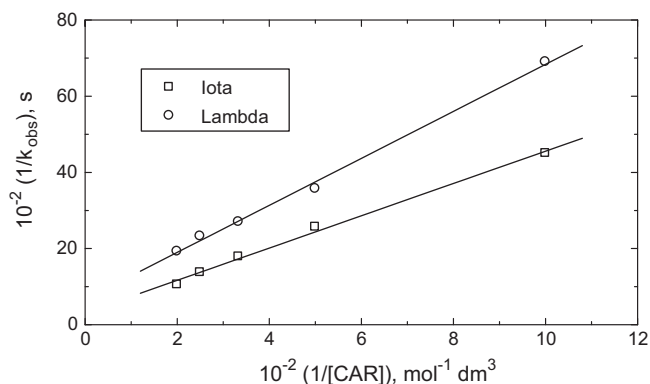


Fig. 3. Plots of $1/k_{\text{obs}}$ vs. $1/[\text{CAR}]$ during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. Iota: $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{OH}^-] = 0.05$, $I = 0.5 \text{ mol dm}^{-3}$ at 20°C ; lambda: $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{OH}^-] = 0.02$, $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

reactions at suitable time intervals. The reaction rates can be traced by following either the decay of permanganate ($\lambda = 525$ nm) or the formation of intermediates ($\lambda = 606$ nm) where no interference from other reagents is observed. Identical rate constants within experimental errors were obtained indicating that the reactions are first-order with respect to the permanganate concentration. The first-order dependences were confirmed not only by the linearity of the pseudo-first-order plots, but also by the independence of these rate constants on the different initial concentration of permanganate ion varying from 2×10^{-4} to $8 \times 10^{-4} \text{ mol dm}^{-3}$ in a number of steps at constant concentration of all other reagents. The observed first-order rate constants (k_{obs}) were calculated from the gradients of such plots using the least-square method.

Again, fractional first-order dependences in carrageenans concentration were observed. Plots of $1/k_{\text{obs}}$ against $1/[\text{CAR}]$ were found to be linear with positive intercepts on $1/k_{\text{obs}}$ axes. This linearity agrees with the Michaelis–Menten kinetics [23] for the formation of intermediate complexes. Typical plots are shown in Fig. 3.

3.3. Dependence of reaction rates on $[\text{OH}^-]$

The rates of formation of the intermediate complexes were determined at different pH's and constant ionic strength. The results indicated that these redox reactions were base-catalyzed (Table 1). Linear first-order dependences were obtained on plotting k_{obs} against $[\text{OH}^-]$ as shown in Fig. 4.

3.4. Dependence of reaction rates on ionic strength

In order to get more insight concerning the reactive species which play the main role in the intermediates formation, kinetic runs were performed at constant pH as the NaClO_4 concentration was increased. The values of pseudo-first-order rate constants of formation, k_{obs} , were found to increase with increasing the ionic

Table 1

The observed first-order rate constants during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenan by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; iota: $I = 0.5 \text{ mol dm}^{-3}$ at 20°C ; lambda: $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

| | $[\text{OH}^-]$ (mol dm ⁻³) | 0.03 | 0.05 | 0.10 | 0.20 | 0.30 |
|--------|---|------|------|------|------|------|
| iota | $k_{\text{obs}} (\times 10^3 \text{ s}^{-1})$ | 0.25 | 0.45 | 0.73 | 1.18 | 1.78 |
| Lambda | $[\text{OH}^-]$ (mol dm ⁻³) | 0.01 | 0.02 | 0.03 | 0.04 | 0.05 |
| | $k_{\text{obs}} (\times 10^3 \text{ s}^{-1})$ | 0.22 | 0.43 | 0.61 | 0.76 | 1.05 |

Experimental error $\pm 3\%$.

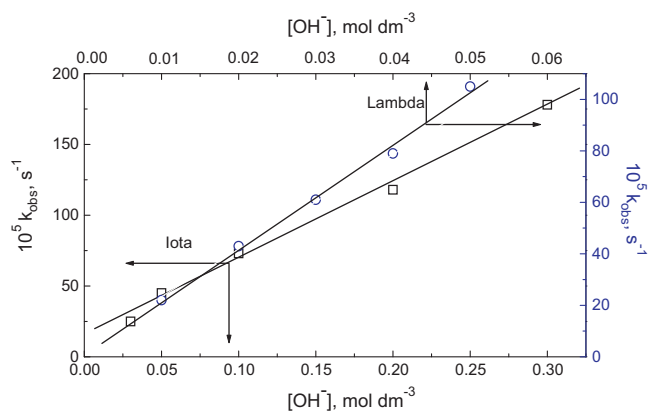


Fig. 4. Plots of k_{obs} vs. $[\text{OH}^-]$ during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; iota: $I = 0.5 \text{ mol dm}^{-3}$ at 20°C ; lambda: $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

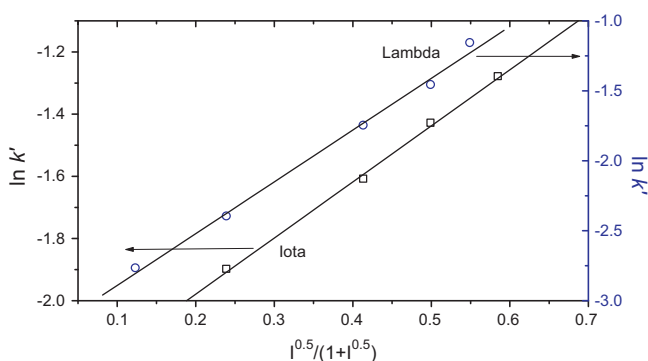


Fig. 5. Extended Brønsted–Debye–Hückel plots during the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; iota: $[\text{OH}^-] = 0.05 \text{ mol dm}^{-3}$ at 20°C ; lambda: $[\text{OH}^-] = 0.02 \text{ mol dm}^{-3}$ at 25°C .

strength. Good linear plots of extended Brønsted–Debye–Hückel relationships ($\ln k_{\text{obs}}$ vs. $I^{0.5}/(1+I^{0.5})$ or $\ln k_{\text{obs}}$ vs. $I^{0.5}$) with positive slopes were observed. Typical plots are shown in Fig. 5.

3.5. Dependence of reaction rates on temperature

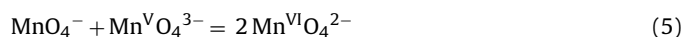
To evaluate the kinetic parameters for these redox reactions, the rates of formation were estimated at various temperatures and constants of pH and ionic strength. The kinetic parameters were calculated by the method of least-squares using Eyring and Arrhenius relationships.

4. Discussion

Carrageenans are water-soluble sulfated polysaccharides which form viscous colloidal solutions. These solutions are of hydrophilic sol nature owing to the presence of both $-\text{OH}$ and $-\text{OSO}_3^-$ moieties which have a high tendency to interact with water. In aqueous solutions, swelling (orientation) of the spherical or coiled colloids transfer them to structures of linear block copolymer nature. Therefore, an interface between CAR macromolecules and water is formed via $-\text{OH}$ and $-\text{OSO}_3^-$ groups [12]. During the oxidation of such substrates by alkaline permanganate, the CAR macromolecule is converted into the intermediate complexes which can be monitored spectrophotometrically.

As is shown in Figs. 1 and 2, a wealth of information revealing the formation of intermediate complexes involving short-lived

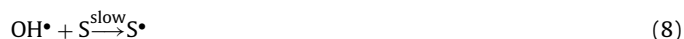
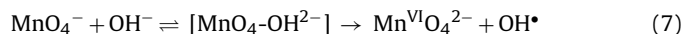
Mn^{VI} and/or Mn^{V} is observed. The absorption band corresponding to MnO_4^- at 525 nm is gradually decreased with a simultaneous increase in the height of the 606 nm peak is observed. This indicates that permanganate oxidant reacts with iota- or lambda-carrageenan via the formation of detectable green $[\text{CAR}-\text{Mn}^{\text{VI}}\text{O}_4^{2-}]$ and/or blue $[\text{CAR}-\text{Mn}^{\text{V}}\text{O}_4^{3-}]$ intermediate complexes which exhibit the absorption bands appearing at 606 nm. It is well known that manganate (VI) possesses an absorption band at this wavelength [24–26]. This in turn may confirm the presence of the more stable Mn^{VI} intermediate rather than the less stable Mn^{V} transient species. At this wavelength, the absorption of MnO_4^- is much weaker, thus the detection of $\text{Mn}^{\text{VI}}\text{O}_4^{2-}$ was not difficult. Again, the non-accumulation of hypomanganate (V) intermediate at its absorption maximum around 700 nm can be explained by its extremely short life-time [24,27–31] which disappeared by one of the following reactions



The disproportionation process defined by Eq. (6) is autocatalyzed by the presence of Mn^{IV} formed.

On the other hand, the naked-eye observation on the change in color of the solution mixture as the reaction proceeded from purple-pink ($\text{Mn}^{\text{VII}}\text{O}_4^-$), to blue ($\text{Mn}^{\text{V}}\text{O}_4^{3-}$), to green ($\text{Mn}^{\text{VI}}\text{O}_4^{2-}$), to yellow (Mn^{IV}), may suggest the formation of the hypomanganate (V) intermediate at the first stage of the oxidation process. Again, the interconversion of MnO_4^- to both $\text{Mn}^{\text{VI}}\text{O}_4^{2-}$ and $\text{Mn}^{\text{V}}\text{O}_4^{3-}$ was manifested from isobestic points at the absorption maxima of 580 and 475 nm, respectively. The yellow color which persists even after completion of reactions confirms the formation of soluble colloidal Mn^{IV} . The latter may be coagulated by aging to give MnO_2 precipitate. These observations encourage us to perform numerous careful attempts in order to detect hypomanganate (V) spectrophotometrically. Our keen trials have been met with success. The formation of intermediate complexes involving Mn^{V} transient species was detected at wavelengths around 738–745 nm using a conventional spectrophotometer for the first time. The spectral changes and characteristics of hypomanganate (V) are reported elsewhere [14].

It is reported [32–34] that oxidation of some organic substrates by permanganate ion in strong alkaline media may proceed by the hydroxyl free-radical, OH^\bullet , generated in the following equilibrium



where S and S^\bullet are the substrate and substrate radical, respectively.

The negative result of polymerization test can be considered as evidence against the proposal of such free-radical mechanism for oxidation of carrageenans by alkaline permanganate. Again, if the present oxidation reactions obeyed the above free-radical mechanism, the reaction kinetics should not show first-order dependences in permanganate or hydroxyl ion concentration, therefore, such free-radical mechanism was excluded.

On the other hand, the base-catalysis observed for the reaction rates in the formation of the intermediate complexes may suggest the fast deprotonation of carrageenan substrates by the alkali prior to the rate-determining steps in order to form the reactive alkoxides as follows

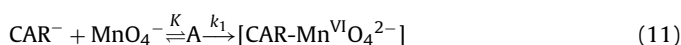


where CAR and CAR^- denote the carrageenans and their alkoxide forms, respectively and K is the corresponding deprotonation con-

stant. This suggestion was found to be in good agreement with that proposed for alcohols when oxidized by alkaline permanganate where the reactive enolate forms [35,36] were formed by the deprotonation of alcohols prior to the rate-determining steps.

Again, the observed first-order dependences in $[\text{OH}^-]$ may suggest that, at least, one reaction-path involving OH^- is present in the rate-determining steps. Furthermore, the ionic strength dependences of the rate constants lie far outside the Debye–Hückel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on the ionic strength [37]. The results obtained are qualitatively indicating the charges involved [38,39].

In view of the foregoing aspects and the experimental observations, the most suitable reaction mechanism which may be suggested involves a fast deprotonation of carrageenan substrate by alkali to form the corresponding alkoxide, followed by the attack of permanganate ion on the alkoxide to form a reactive transient species (A) prior to the formation of $[\text{CAR-Mn}^{\text{VI}}\text{O}_4^{2-}]$ in the rate-determining step



Also, the formed $\text{Mn}^{\text{VI}}\text{O}_4^{2-}$ is capable to oxidize the formed alkoxide ion, but the reaction is several orders of magnitude slower than permanganate oxidation owing to its lower reactivity [40] and, hence, would not influence the kinetics of the initial reaction.

The rate of disappearance of the permanganate ion or the formation of the intermediate complex can be expressed by the following rate-law equation

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = + \frac{d[\text{CAR-Mn}^{\text{VI}}\text{O}_4^{2-}]}{dt} = k_1[\text{MnO}_4^-][\text{CAR}^-] \quad (12)$$

Assuming the steady-state approximation of the reactive species (A), the change in the apparent rate constant of the formation of the complex with the change in the substrate and hydroxyl ion concentrations can be written as follows

$$\text{Rate} = \frac{k_1 K K_1 [\text{OH}^-] [\text{MnO}_4^-] [\text{CAR}]_{\text{T}}}{1 + K [\text{OH}^-] + K K_1 [\text{OH}^-] [\text{MnO}_4^-]} \quad (13)$$

where $[\text{CAR}]_{\text{T}}$ is the analytical total concentration of either iota- or lambda-carrageenan. When the carrageenan substrate is present in a large excess over that of MnO_4^- concentration, the rate-law can be expressed by Eq. (14)

$$\text{Rate} = k_{\text{obs}} [\text{MnO}_4^-] \quad (14)$$

Comparing Eqs. (13) and (14), the following relationship is obtained

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K [\text{OH}^-]}{k_1 K [\text{OH}^-]} \right) \frac{1}{[\text{CAR}]_{\text{T}}} + K' \quad (15)$$

The rate expression defined by Eq. (15) requires that plot of $1/k_{\text{obs}}$ vs. $1/[\text{CAR}]$ at constant pH to be linear with positive intercept on $1/k_{\text{obs}}$ axis. The experimental observations satisfied this requirement as shown in Michaelis–Menten plots (Fig. 3). Again, plots of $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ at constant $[\text{CAR}]$ should be linear as is experimentally observed. The relatively small intercepts observed in Fig. 3 lead us to simplify Eqs. (15) and (16)

$$\frac{1}{k'} \frac{[\text{CAR}]_{\text{T}}}{k_{\text{obs}}} = \left(\frac{[\text{OH}^-]^{-1}}{k'_1} + \frac{1}{k''_1} \right) \quad (16)$$

where $k'_1 = k_1 K_1 K$, $k''_1 = k_1 K$ and k' is the second-order rate constant ($k_{\text{obs}}/[\text{KAR}]$). Plots of $1/k'$ against $1/[\text{OH}^-]$, at various temperatures, gave good straight lines (Figs. 6 and 7) from whose slopes and intercepts, the values of the apparent rate constants (k'_1 and k''_1) and the deprotonation constant (K) can be evaluated. These values were

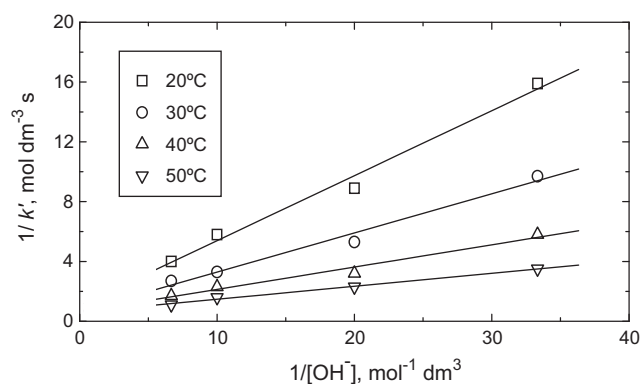


Fig. 6. Plots of $1/k'$ vs. $1/[\text{OH}^-]$ during the formation of the intermediate complex in the oxidation of iota-carrageenan by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{ICAR}] = 4 \times 10^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$.

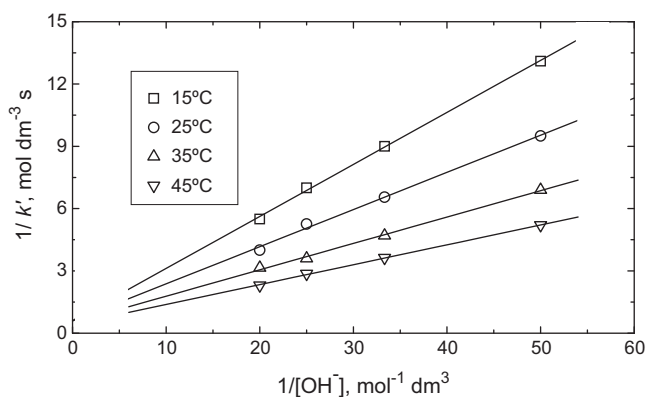


Fig. 7. Plots of $1/k'$ vs. $1/[\text{OH}^-]$ during the formation of the intermediate complex in the oxidation of lambda-carrageenan by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{LCAR}] = 4 \times 10^{-3}$ and $I = 0.2 \text{ mol dm}^{-3}$.

calculated using the least-square method and are summarized in Table 2. The calculated values of the deprotonation constant (K) were found to be of the same order of magnitude to that obtained for other oxidation reactions of polysaccharides by alkaline permanganate [6,9,11,13]. This result may confirm the validity of the proposed mechanism.

Unfortunately, the values of the rate constants of the elementary reaction k_1 could not be calculated because of the non-availability of the formation constants K_1 . Some attempts have been made to calculate the formation constants from the experimental data but the results were not encouraged. Therefore, the calculated values of

Table 2

Values of k'_1 , k''_1 and K for the formation of the intermediate complexes in the oxidation of iota- and lambda-carrageenans by alkaline permanganate at different temperatures. $[\text{MnO}_4^-] = 4 \times 10^{-4}$; $[\text{CAR}] = 4 \times 10^{-3}$; iota: $[\text{OH}^-] = 0.05$, $I = 0.5 \text{ mol dm}^{-3}$; lambda: $[\text{OH}^-] = 0.02$, $I = 0.2 \text{ mol dm}^{-3}$.

| Carrageenan | Constant | Temperature ($^{\circ}\text{C}$) | | | |
|-------------|---|------------------------------------|-------------|-------------|-------------|
| | | 20 | 30 | 40 | 50 |
| iota | k'_1 ($\text{dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$) | 2.61 | 3.84 | 5.58 | 7.69 |
| | k''_1 ($\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) | 1.11 | 1.32 | 1.56 | 1.88 |
| | K ($\text{dm}^3 \text{ mol}^{-1}$) | 2.35 | 2.91 | 3.58 | 4.09 |
| | | Temperature ($^{\circ}\text{C}$) | | | |
| | | 15 | 25 | 35 | 45 |
| Lambda | k'_1 , $\text{dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$ | 3.71 | 5.41 | 7.85 | 10.51 |
| | k''_1 , $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ | 1.55 | 1.72 | 2.02 | 2.32 |
| | K , $\text{dm}^3 \text{ mol}^{-1}$ | 2.39 | 3.14 | 3.89 | 4.52 |

Table 3

Activation parameters of k'_1 , k''_1 and k_1 in the oxidation of iota- and lambda-carrageenans by alkaline permanganate. $[\text{MnO}_4^-] = 4 \times 10^{-4}$, $[\text{CAR}] = 4 \times 10^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$ for iota and 0.2 mol dm^{-3} for lambda.

| Carrageenan | Rate constant | Parameter | | | | |
|-------------|---------------|---|--|--|--------------------------------|---|
| | | ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$) | ΔH^\ddagger (kJ mol^{-1}) | ΔG^\ddagger (kJ mol^{-1}) | E_a (kJ mol^{-1}) | A ($\text{mol}^{-1} \text{s}^{-1}$) |
| Iota | k'_1 | -148.32 | 25.91 | 70.11 | 24.17 | 1.56×10^7 |
| | k''_1 | -205.77 | 11.18 | 72.45 | 13.73 | 3.21×10^4 |
| | k_1 | -153.23 | 31.03 | 77.69 | 40.01 | 1.53×10^6 |
| Lambda | k'_1 | -149.65 | 24.17 | 68.77 | 29.06 | 5.03×10^5 |
| | k''_1 | -213.67 | 7.91 | 71.58 | 10.43 | 0.36×10^2 |
| | k_1 | -163.20 | 24.50 | 78.33 | 25.88 | 5.12×10^3 |

Table 4

Values of kinetic parameters for the intermediate formation (k') in the oxidation of some macromolecules by alkaline permanganate.

| Macromolecule | ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$) | ΔH^\ddagger (kJ mol^{-1}) | $\Delta G^\ddagger_{25^\circ\text{C}}$ (kJ mol^{-1}) | References |
|-------------------------|---|--|---|------------|
| Alginate | -63.39 | 54.51 | 73.40 | [6] |
| Poly(vinyl alcohol) | -47.67 | 58.93 | 73.13 | [8] |
| Carboxymethyl cellulose | -138.20 | 33.68 | 74.80 | [12] |
| Methyl cellulose | -220.40 | 9.93 | 75.61 | [13] |
| Pectate | -38.58 | 60.35 | 71.85 | [10] |
| Kappa-carrageenan | -182.99 | 18.17 | 72.70 | [14] |
| Iota-carrageenan | -153.23 | 31.03 | 77.69 | This work |
| Lambda-carrageenan | -163.20 | 24.50 | 78.33 | This work |

Experimental error 4%.

k'_1 and k''_1 are considered to be the products of the apparent rate constants, the deprotonation constants and the formation constants, respectively.

The activation parameters of the apparent rate constants (k'_1 and k''_1) and second-order rate constant (k') were calculated from the temperature dependence of the rate constants using the method of least-squares and are listed in Table 2. The large negative values observed for ΔS^\ddagger may confirm the compactness of the intermediate manganate (VI) complex formed.

Again, the positive values of both ΔH^\ddagger and ΔG^\ddagger indicate the endothermic formation of the intermediates and its non-spontaneity, respectively. This evidence accords with the suggested transition states which may confirm the formation of the intermediate complexes via inner-sphere electron transfer mechanism. This mechanism is supported by the proposition made by Stewart and co-workers [24,41] for ionic transition states in oxidation of many organic substrates by permanganate ion. They reported that the entropy of activation tends to be more positive for reactions of outer-sphere mechanisms, whereas it is more negative for reactions of inner-sphere type. Therefore, such an agreement may be considered as an evidence to support the formation of intermediate complexes of inner-sphere nature for electron transfer processes in the cited redox reactions. The small frequency factors in Table 3 may indicate the strictly compact formed intermediate complex [42] in particularly for $[\text{LCAR-Mn}^{\text{VI}}\text{O}_4^{2-}]$ complex. Moreover, the large negative entropy of activations, ΔS^\ddagger , are revealing these strictly compact formed complexes which are accompanied by the observed low values of frequencies.

The activation parameters for oxidation reactions of some macromolecules with alkaline permanganate having negative entropies of activation are summarized in Table 4. Leffler and Grunwald [43] have pointed out that many reactions show an isokinetic relationship $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$. As is shown in Fig. 8, a plot of ΔH^\ddagger against ΔS^\ddagger of the second-order rate constants (k') for some reactions of macromolecules involving MnO_4^- as an oxidant is fairly linear with $\alpha = 74 \text{ kJ mol}^{-1}$ and $\beta = 288 \text{ K}$. This linearity indicates that the kinetics of oxidations of these macromolecules may follow similar reaction mechanisms. Also, the β value obtained is significant and reflects the high reactivity of these macromolecules [44]. Also, plots of ΔH^\ddagger vs. ΔS^\ddagger for the apparent rate constants (k'_1 or k_1)

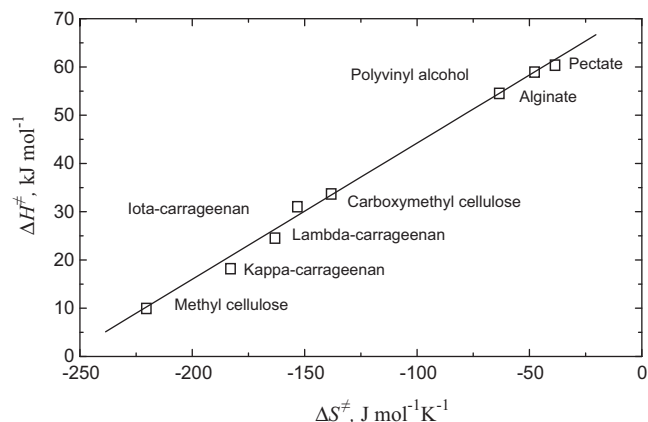
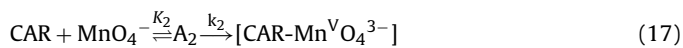
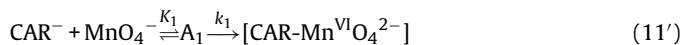


Fig. 8. Isokinetic plot, ΔH^\ddagger vs. ΔS^\ddagger , for the intermediate formation (k_1) in the oxidation of some polysaccharides by alkaline permanganate.

for these oxidation reactions were found to be linear confirming such a similarity between the reaction mechanisms in these redox systems.

Furthermore, an alternative reaction mechanism based on the presence of two competitive reactions in the rate-determining step, could be suggested as follows



In a similar manner to the derivation of the previous mechanism, a rate-law expression defined by Eq. (18) may be deduced

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K[\text{OH}^-]}{k_1 K K_1 [\text{OH}^-] + k_2 K_2} \right) \frac{1}{[\text{CAR}]_{\text{T}}} + K'' \quad (18)$$

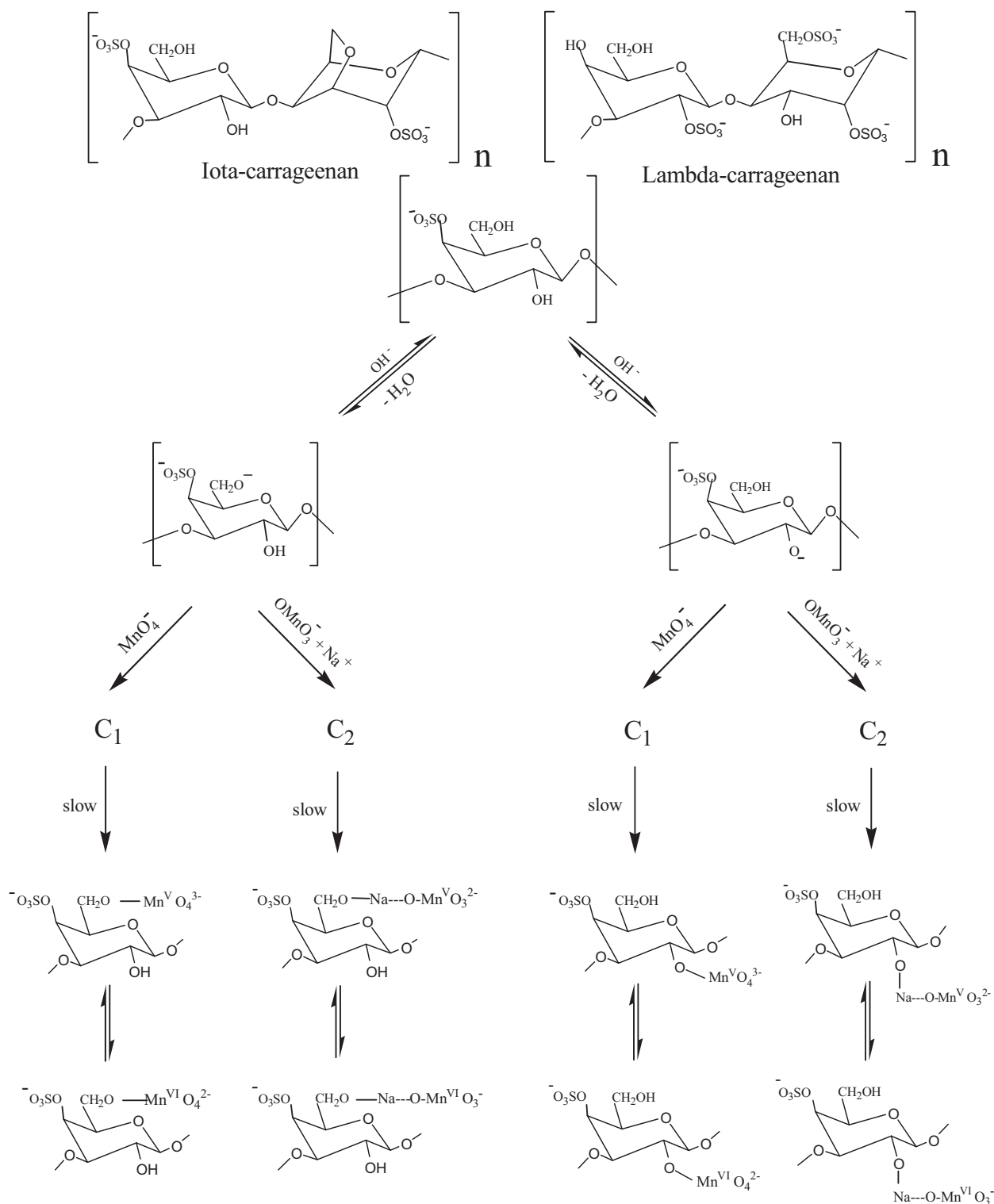
According to Eq. (18), plots of $1/k_{\text{obs}}$ vs. $1/[\text{CAR}]$ at constant pH should be linear with positive intercept on $1/k_{\text{obs}}$ axis as is experimentally observed (Fig. 3). The small intercepts observed in Fig. 3 along with the assumption that $K[\text{OH}^-] \ll 1$, may lead us to recast

the relationship (18) to (19)

$$\frac{[\text{CAR}]_T}{k_{\text{obs}}} = k' = k'_1[\text{OH}^-] + k'_2 \quad (19)$$

where $k' = k_1K_1K$ and $k'_2 = k_2K_2$, respectively. It is worth noting that plots of k' against $[\text{OH}^-]$ of Eq. (19) were linear with positive intercepts on k' axis which indicative to the deduced rate equation (19) confirming the alternative mechanism. From the calculated val-

Formation



Scheme 1. Mechanism of oxidation of carrageenans by alkaline permanganate.

ues of k'_1 and k'_2 , it was found that the k'_1 values were larger than that of k'_2 values for at least 10^2 orders of magnitude. This result may confirm that reaction (17) is the sole reactive species in the rate-determining step and, hence, supports the former reaction mechanism.

The detail kinetics for the decay of the intermediate complexes defined by Eq. (4) ($[\text{CAR-Mn}^{\text{VI}}\text{O}_4^{2-}]$ and/or $[\text{CAR-Mn}^{\text{V}}\text{O}_4^{3-}]$) are in progress for publishing later.

In view of the kinetic interpretations and the experimental observations, a tentative reaction mechanism in good consistent with the experimental results for the formation of the intermediates can be illustrated in Scheme 1.

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