

Cerium(IV) oxidations of sulfated polysaccharides in aqueous perchlorate solutions: A kinetic and mechanistic approach

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Received: 28 November 2015, Revised: 30 January 2016 and Accepted: 24 March 2016

ABSTRACT

The kinetics of oxidation of iota- and lambda-carrageenans as sulfated polysaccharides by cerium(IV) was studied spectrophotometrically in aqueous perchlorate solutions at a fixed ionic strength of 2.0 mol dm⁻³ and a temperature of 25 °C. The reactions showed a first order dependence on [Ce^{IV}], whereas the orders with respect to each carrageenan concentration were less than unity. The reactions exhibited fractional-first order kinetics with respect to [H⁺]. Increasing ionic strength increased the oxidation rates. The oxidation products of carrageenans were characterized by elemental analysis and IR spectra as their diketo-acid derivatives. The oxidation products were found to have high tendencies to form coordination polymer complexes with some metal cations such as Ba^{II}, Cd^{II}, Pb^{II} and Ag^I. Kinetic evidences for the formation of 1:1 complexes were revealed. Plausible mechanistic scheme for cerium(IV) oxidations of carrageenans were proposed. The activation parameters with respect to the slow step of the reactions were evaluated and discussed. The rate laws have been derived and the reaction constants involved in the different steps of the mechanisms were calculated. The activation parameters associated with the rate-determining step of the mechanism along with thermodynamic quantities of the equilibrium constants were computed and discussed. Copyright © 2016 VBRI Press.

Keywords: Carrageenans; cerium(IV); oxidation; kinetics; mechanism.

Introduction

Carrageenans (CAR) are water-soluble sulfated polysaccharides extracted from seaweeds [1]. They are very important hydrocolloids having a large list of industrial applications. Carrageenans are valuable gelling agents employed in food applications to improve food texture, gelation, stability and viscosity. Secondary advantage includes improved palatability and appearance. They are used in both milk and water systems. In medical and pharmaceutical uses, a discovery is that carrageenans even in very great dilution act as an anticoagulant of blood. Despite the potential applications of different types of carrageenans biopolymers in various fields, these biopolymers are frequently subjected to the action of the oxidizing agents and their activities depend largely in their redox behaviour. A literature review showed a lack of information about the kinetics of oxidations of such significant macromolecules [2-8]. This may be attributed to the complexity of the oxidation kinetics of these substrates since they contain both primary and secondary alcoholic groups in their macromolecular chains.

Cerium(IV) is one of the most powerful one-equivalent oxidants in acid media which has been employed in various kinetic and mechanistic studies [9-19]. The oxidizing potentialities of Ce^{IV} in sulfuric acid solutions have conclusively been established [9-14]. Nevertheless, the oxidant has rarely been employed in perchloric acid

solutions [15-18], probably due to presence of dimers and polymers of Ce^{IV} species in these solutions. However, the oxidations by Ce^{IV} in perchloric acid proceed much faster than those in sulfuric acid.

Owing to the forgoing points, the title reactions have been investigated in order to establish the optimum conditions for oxidations of such polysaccharides by Ce^{IV} in perchlorate solutions, to examine the effect of the substrate structure and to elucidate a plausible oxidation reactions mechanism.

Experimental

Materials

Iota- and lambda-carrageenans (ICAR & LCAR) were Fluka reagents and were used without further purification. Stock solutions of ICAR and LCAR were prepared by stepwise addition of the samples (BDH) in double distilled water with rapid and continuous stirring to avoid formation of lumpy aggregates. A fresh solution of Ce^{IV} was prepared by dissolving ceric ammonium sulfate in a 1.0 mol dm⁻³ sulfuric acid solution, diluted with double distilled water and kept for overnight. Concentration of Ce^{IV} was determined by titrating against standard ferrous ammonium sulfate solution and by spectrophotometry. The solution of Ce^{IV} was stored in a dark glass bottle and was used after 24 h, since the hydrolysis is negligible small or ruled out

after 12 h of preparation [20]. Solutions of other reagent were prepared by dissolving the requisite amounts of the samples in doubly distilled water.

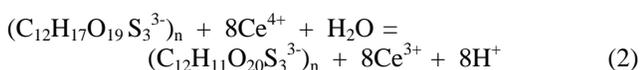
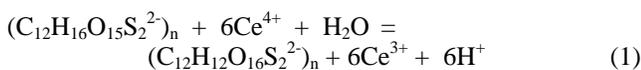
Kinetic measurements

The kinetic measurements were performed under pseudo-first order kinetics where the carrageenan substrates (CAR) were presented in large excesses relative to Ce^{IV} . The reactions were followed spectrophotometrically by tracing the disappearance of cerium(IV) absorbance at its maximum absorption wavelength, $\lambda_{max} = 315$ nm, whereas the other constituents of the reactions did not absorb significantly at this wavelength. The absorbance measurements were performed on Shimadzu UV-2101/3101 double-beam spectrophotometer. First order plots of $\ln(\text{absorbance})$ versus time were found to be linear up to about 70 % of the reactions completion and the observed first order rate constants (k_{obs}) were calculated as the gradients of such plots. Average values of at least two independent runs of the rate constants were taken for the analysis. The runs were reproducible to within ± 4 %. Some kinetic runs were performed after bubbling purified nitrogen and compared with those taken under air. The results were found to be the same suggesting that the dissolved oxygen did not have any effect on the oxidation rates. The orders of the reactions with respect to each reactant were determined from the slopes of $\log k_{obs}$ versus $\log(\text{concentration})$ plots by varying the concentrations of the substrates and perchloric acid, in turn, while keeping other conditions constant.

Results

Stoichiometry and product identification

Different reaction mixtures of the carrageenans and cerium(IV) were equilibrated in 1.0 mol dm^{-3} perchlorate solutions at constant ionic strength of 2.0 mol dm^{-3} . The unreacted $[Ce^{IV}]$ was estimated periodically until it reached a constant value, i.e. completion of the oxidation reactions. The obtained results conform the following stoichiometric equations,



where, $(C_{12}H_{16}O_{15}S_2^2-)_n$ and $(C_{12}H_{17}O_{19}S_3^3-)_n$ are iota- and lambda-carrageenans and $(C_{12}H_{12}O_{16}S_2^2-)_n$ and $(C_{12}H_{11}O_{20}S_3^3-)_n$ are the corresponding keto-acid oxidation derivatives, respectively. The products were identified by the spectral data and elementary analysis as described elsewhere [21-23]. On the other hand, the oxidation products were found to have high tendencies for chelation with some metal cations such as Ba^{II} , Cd^{II} , Pb^{II} and Ag^I where the original substrates (ICAR and LCAR) have been failed.

Spectral changes

The spectral changes during the oxidation of ICAR and LCAR by Ce^{IV} in perchlorate solutions are shown in

Fig. 1(a) and (b), respectively. In all cases, the scanned spectra indicated gradual decay of Ce^{IV} band at its absorption maximum with time as a result of its reduction to $Ce(III)$ oxidation product.

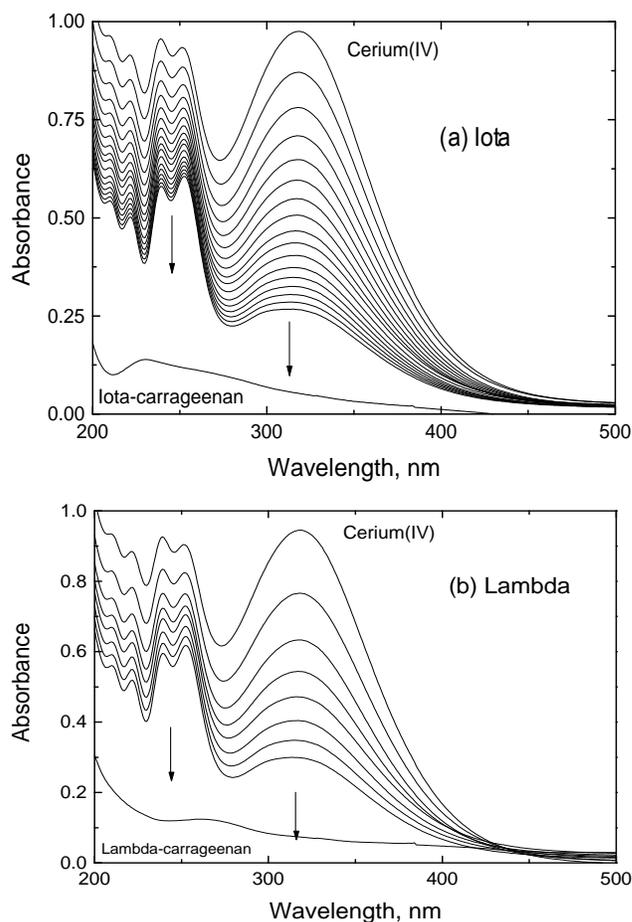


Fig. 1. (a, b). Spectral changes during the oxidation of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[Ce^{IV}] = 2.0 \times 10^{-4}$, $[H^+] = 1.0$, $[CAR] = 2.0 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C . Scan time intervals = 5 min.

Reaction-time curves

Plots of $\ln(\text{absorbance})$ versus time were straight lines up to about 70 % and then deviate from linearity. This deviation may be resulting from the interference of Ce^{III} oxidation product. Again, some results have been calculated as the gradients of absorbance versus time plots at the initial stages of the reactions. The results were found to be reproducible to each other. Therefore, values of the observed first order rate constants, k_{obs} , were used in the present study.

Dependence of the oxidation rates on $[Ce^{IV}]$

The oxidant Ce^{IV} was varied in all reactions in the range of $(1.0 - 6.0) \times 10^{-4} \text{ mol dm}^{-3}$ at fixed carrageenans concentration, ionic strength and temperature. The non-significant variation of the observed-first order rate constants at various initial concentrations of Ce^{IV} (Table 1) indicates that the reactions order with respect to Ce^{IV} was unity. The first order kinetics was also confirmed by the linearity of the plots of $\ln(\text{absorbance})$ versus time.

Dependence of the oxidation rates on [CAR]

The observed rate constants (k_{obs}) were measured at different initial concentrations of both ICAR and LCAR substrates while other variables were kept constant. It was found that increasing [CAR] increased the rates as listed in **Table 1**. The plots of k_{obs} versus [CAR] were linear with positive intercepts (**Fig. 2**) confirming the fractional-first order dependences with respect to the substrates concentration.

Table 1. Effects of variation of $[\text{Ce}^{\text{IV}}]$, [CAR], $[\text{H}^+]$ and ionic strength, I , on the observed first order rate constants (k_{obs}) in the oxidation of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions at 25 °C.

$10^4 [\text{Ce}^{\text{IV}}]$ (mol dm ⁻³)	$10^3 [\text{CAR}]$ (mol dm ⁻³)	$[\text{H}^+]$ (mol dm ⁻³)	I (mol dm ⁻³)	$10^5 k_{\text{obs}}$ (s ⁻¹)	
				Iota	Lambda
1.0	2.0	1.0	2.0	21.9	38.4
2.0	2.0	1.0	2.0	22.3	39.7
3.0	2.0	1.0	2.0	23.1	37.9
4.0	2.0	1.0	2.0	20.7	40.1
6.0	2.0	1.0	2.0	23.5	40.6
2.0	1.0	1.0	2.0	15.2	29.7
2.0	2.0	1.0	2.0	22.3	39.7
2.0	4.0	1.0	2.0	30.1	51.0
2.0	8.0	1.0	2.0	44.7	70.6
2.0	12.0	1.0	2.0	58.0	89.2
2.0	2.0	0.75	2.0	17.3	33.4
2.0	2.0	1.00	2.0	22.3	39.7
2.0	2.0	1.25	2.0	26.3	48.9
2.0	2.0	1.50	2.0	31.3	55.6
2.0	2.0	1.75	2.0	36.9	62.5
2.0	2.0	1.0	2.0	22.3	39.7
2.0	2.0	1.0	2.5	24.1	41.9
2.0	2.0	1.0	3.0	25.5	43.1
2.0	2.0	1.0	3.5	27.0	45.9
2.0	2.0	1.0	4.0	28.8	47.7

Experimental error \pm 4%

Dependence of the oxidation rates on $[\text{H}^+]$

To explore the effect of hydrogen ion concentration on the oxidation rates of both carrageenans, kinetic runs were carried out by varying $[\text{HClO}_4]$ in the range of 0.75 - 1.75 mol dm⁻³ while maintaining other variables constant. The data listed in **Table 1** indicated that the increase in $[\text{H}^+]$ increased the oxidation rates of the carrageenans. The plots of k_{obs} versus $[\text{H}^+]$ were also linear with positive slopes (**Fig. 3**) confirming the fractional-first order kinetics with respect to $[\text{H}^+]$.

Dependence of the oxidation rates on the ionic strength

At constant concentrations of the reactants and with other conditions constant, the ionic strength was varied between 2.0 and 4.0 mol dm⁻³ by addition of sodium perchlorate as an inert electrolyte. The results indicated that the observed rate constants increased with increasing the ionic strength (**Table 1**) and the Debye-Huckel plots were linear with positive slopes as shown in **Fig. 4**.

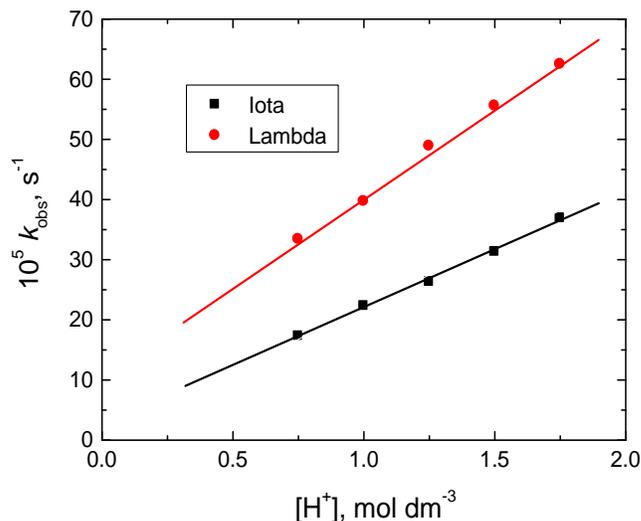


Fig. 2. Plots of k_{obs} versus $[\text{H}^+]$ in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[\text{Ce}^{\text{IV}}] = 2.0 \times 10^{-4}$, $[\text{CAR}] = 2.0 \times 10^{-3}$ and $I = 2.0$ mol dm⁻³ at 25 °C.

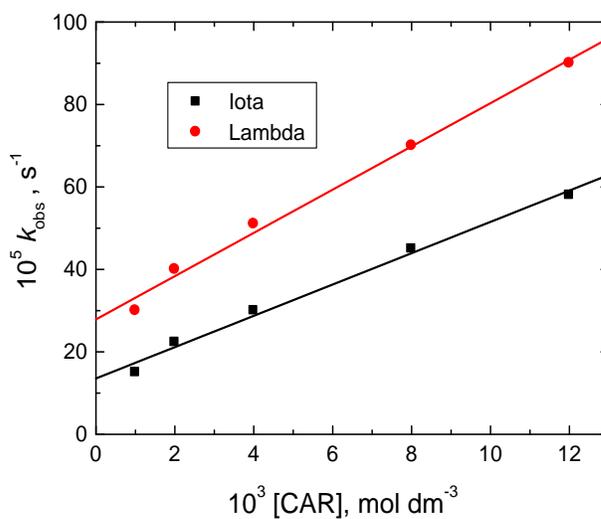


Fig. 3. Plots of k_{obs} versus [CAR] in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[\text{Ce}^{\text{IV}}] = 2.0 \times 10^{-4}$, $[\text{H}^+] = 1.0$ and $I = 2.0$ mol dm⁻³ at 25 °C.

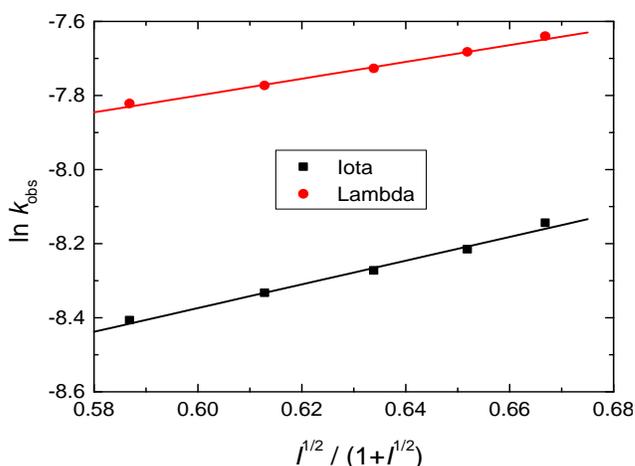


Fig. 4. Debye-Huckel plots for the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[\text{Ce}^{\text{IV}}] = 2.0 \times 10^{-4}$, $[\text{H}^+] = 1.0$ and $[\text{CAR}] = 2.0 \times 10^{-3}$ mol dm⁻³ at 25 °C.

Test for free radicals intervention

The possibility of free radicals intervention was examined by polymerization test. The reaction mixtures, to which known quantities of acrylonitrile were added, were kept in inert atmosphere for about 6 h at room temperature. When the reaction mixtures were diluted with methanol, progressive white precipitates were formed suggesting intervention of free radicals in the present oxidation reactions. When the experiments were repeated in the absence of the carrageenans under similar conditions, the tests were negative. This indicates that the reactions were routed through free radical paths.

Discussion

It is reported [24] that cerium(IV) species in perchloric acid exists mainly in the form of monomeric species Ce^{4+} and $Ce(OH)^{3+}$ and partially in the form of dimeric species $Ce-O-Ce^{6+}$ and $Ce-O-CeOH^{3+}$. However, spectrophotometric studies [25, 26] showed that the hydrated form, Ce^{4+} , is the predominant species at $[H^+] \geq 1.0 \text{ mol dm}^{-3}$ up to the concentration of $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ of $[Ce^{IV}]$, whereas $Ce(OH)^{3+}$ and dimers are the more predominant at $[H^+] < 0.7 \text{ mol dm}^{-3}$. Therefore, under our experimental conditions of $[H^+] > 0.7 \text{ mol dm}^{-3}$, Ce^{4+} may be regarded as the kinetically active species of cerium(IV).

The observed small deviation of $\ln(\text{absorbance})$ versus time plots may be attributed to either the interference of Ce^{III} oxidation product and/or the aggregation of the helices into the network junctions of the macromolecular chains. The influence of addition of Ce^{III} could not be tested owing to the observed turbidity during the progress of oxidation reactions. This may be explained by a possible complexation occurs between the oxidation products and Ce^{III} species leading to sol-gel transformation phenomenon.

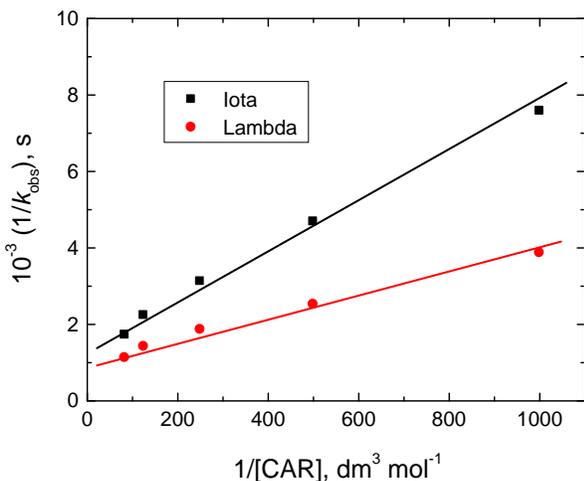
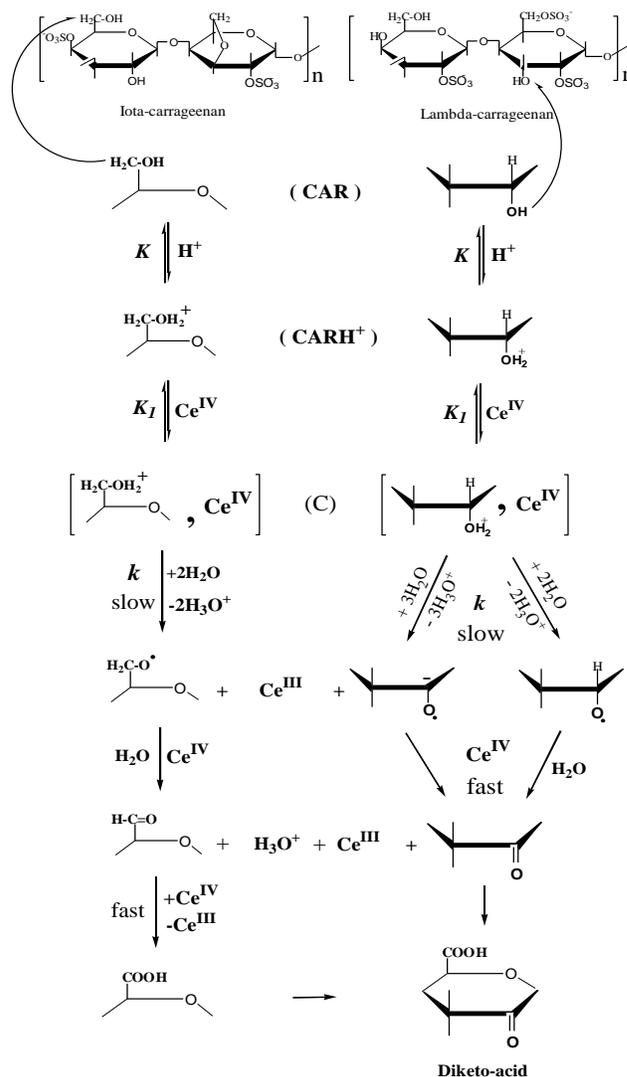


Fig. 5. Plots of $1/k_{\text{obs}}$ versus $1/[CAR]$ in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[Ce^{IV}] = 2.0 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25°C .

The reactions of iota- and lambda-carrageenans with Ce^{IV} in perchlorate solutions exhibited first order dependence with respect to $[Ce^{IV}]$, less than unit order each with respect to $[H^+]$ and $[CAR]$. The observed increase in the rate constant with increasing the hydrogen ion concentration with less than unit orders in $[H^+]$ may be an

indication of the protonation of carrageenans in the first step to form more reactive species of the reductants. Also, the fractional-first order kinetics with respect to carrageenans concentration presumably due to formation of complexes between the kinetically active Ce^{IV} species (Ce^{4+}) and the protonated substrates ($CARH^+$) prior to the slow (rate-determining) step. Complexes formation was proved kinetically by the non-zero intercepts of the plots of $1/k_{\text{obs}}$ versus $1/[CAR]$ [27] as shown in **Fig. 5**. Furthermore, increasing the oxidation rates with the increase in ionic strength indicates that the reactions have been occurred between two similarly charged ions [28, 29] i.e., between Ce^{4+} and $CARH^+$. The formed complexes are slowly decomposed in the slow step leading to formation of free radicals derived from the reductant substrates (CAR^\cdot) in addition to Ce^{III} . The formed substrates radicals are rapidly oxidized by the oxidant leading to the final oxidation products as illustrated in **Scheme 1**. Such Scheme represents two suggested paths, the first one shows the oxidation of primary alcoholic group to the corresponding acid form, whereas the second one refers to the oxidation of secondary alcoholic group to the corresponding ketone form.



Scheme 1. Mechanism of oxidations of iota- and lambda-carrageenans by Ce^{IV} in perchlorate solutions.

The suggested mechanism leads to the following rate-law expression,

$$\text{Rate} = \frac{kK_1[\text{Ce}^{\text{IV}}][\text{CAR}][\text{H}^+]}{1 + K[\text{H}^+] + KK_1[\text{CAR}][\text{H}^+]} \quad (3)$$

This rate law is consistent with all the observed orders with respect to the different species.

Under pseudo-first order condition, the rate law can be expressed by Eq. (4),

$$\text{Rate} = \frac{-d[\text{Ce}^{\text{IV}}]}{dt} = k_{\text{obs}}[\text{Ce}^{\text{IV}}] \quad (4)$$

Comparing Eqs. (3) and (4), the following relationship is obtained,

$$k_{\text{obs}} = \frac{kK_1[\text{CAR}][\text{H}^+]}{1 + K[\text{H}^+] + KK_1[\text{CAR}][\text{H}^+]} \quad (5)$$

Eq. (5) can be verified by rearranging it to the following equation,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1 + K[\text{H}^+]}{kK_1[\text{H}^+]} \right) \frac{1}{[\text{CAR}]} + \frac{1}{k} \quad (6)$$

Equation (6) requires that plots of $1/k_{\text{obs}}$ versus $1/[\text{CAR}]$ at constant $[\text{H}^+]$ to be linear with positive intercepts on $1/k_{\text{obs}}$ axes as was experimentally observed (Fig. 5). Again, at constant $[\text{CAR}]$, plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ gave good straight lines with positive intercepts on $1/k_{\text{obs}}$ axes as shown in Fig. 6. From the intercepts of these plots, the values of the rate constants of the slow step (k) in the oxidations mechanism of iota- and lambda-carrageenans by cerium(IV) could be evaluated and were found to be 7.71×10^{-4} and $11.13 \times 10^{-4} \text{ s}^{-1}$, respectively, at 25 °C.

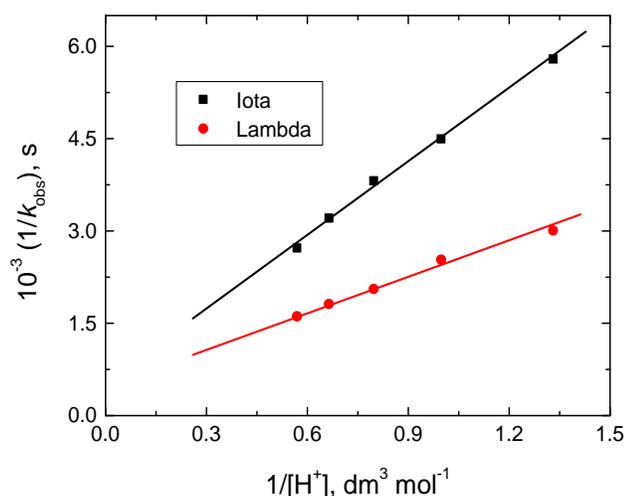


Fig. 6. Plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[\text{Ce}^{\text{IV}}] = 2.0 \times 10^{-4}$, $[\text{CAR}] = 2.0 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$ at 25 °C.

The small intercepts observed in Fig. 5 may lead us to simplify Eq. (6) to Eq. (7) which is considered to be the suitable rate-law expression of oxidation of CAR by Ce^{IV} oxidant,

$$\frac{[\text{CAR}]}{k_{\text{obs}}} = \frac{1}{k'[\text{H}^+]} + \frac{1}{k''} \quad (7)$$

where, k' and k'' are the apparent rate constants and are equal to kK_1 and k , respectively.

According to Eq. (7), plots of $[\text{CAR}]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ gave good straight lines with positive intercepts on $[\text{CAR}]/k_{\text{obs}}$ axes as shown in Fig. 7(a, b), from whose slopes and intercepts, the values of the apparent rate constants (k' and k'') and the protonation constant (K) can be evaluated. These values were calculated by least-squares method.

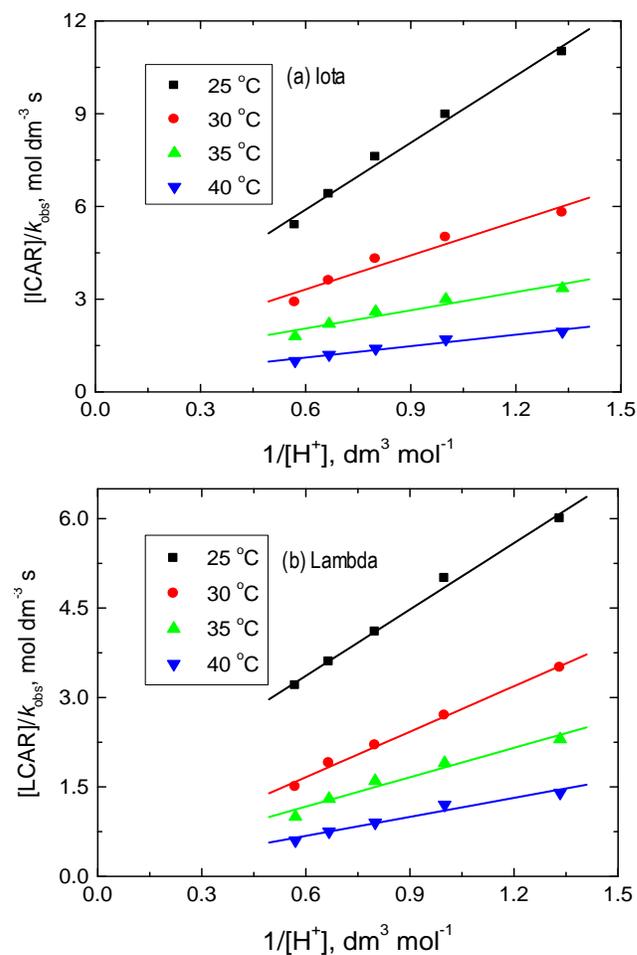


Fig. 7. Plot of $[\text{CAR}]/k_{\text{obs}}$ versus $1/[\text{H}^+]$ in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions. $[\text{Ce}^{\text{IV}}] = 2.0 \times 10^{-4}$, $[\text{CAR}] = 2.0 \times 10^{-3}$ and $I = 2.0 \text{ mol dm}^{-3}$.

The values of the protonation constants of iota- and lambda-carrageenans and their corresponding thermodynamic parameters are listed in Table 2. Also, the values of the activation parameters of the apparent rate constants (k' and k'') were calculated from the temperature-dependence of the rate constants by least-squares method

using Eyring and Arrhenius equations. These values are listed in **Table 3**.

Table 2. Values of the protonation constants (K) at different temperatures and their thermodynamic parameters in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions.

CAR	Temperature ($^{\circ}$ C)			
	25	30	35	40
Iota	0.13	0.1	0.06	0.03
Lambda	0.17	0.13	0.10	0.08
Parameter	ΔH° kJ mol $^{-1}$	ΔS° J mol $^{-1}$ K $^{-1}$	ΔG°_{298} kJ mol $^{-1}$	
Iota	-31.62	-89.16	+5.05	
Lambda	-40.45	-150.70	+4.46	

Experimental error \pm 3%

Table 3. Activation parameters of the apparent rate constants in the oxidations of iota- and lambda-carrageenans by cerium(IV) in perchlorate solutions.

CAR	Rate constant	ΔS^{\ddagger} J mol $^{-1}$ K $^{-1}$	ΔH^{\ddagger} kJ mol $^{-1}$	Parameter		$10^{-4} A$ mol $^{-1}$ s $^{-1}$
				ΔG^{\ddagger} kJ mol $^{-1}$	E_a^{\ddagger} kJ mol $^{-1}$	
Iota	k'	-3.82	81.89	78.42	86.63	1.66x10 14
	k''	+280.60	157.30	67.89	163.12	2.97x10 24
Lambda	k'	-6.64	74.38	76.38	76.94	7.84x10 12
	k''	+140.75	113.89	71.59	115.90	3.12x10 20

Experimental error \pm 4%

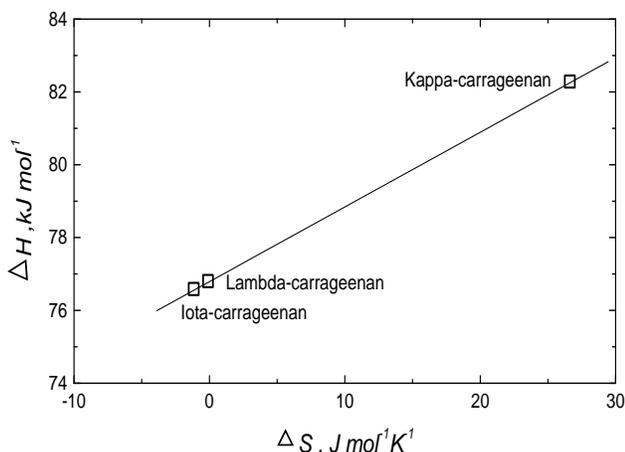


Fig. 8. Exner isokinetic plot (ΔH^{\ddagger} vs. ΔS^{\ddagger}) for the oxidations of carrageenans by cerium(IV) in perchlorate solutions.

Furthermore, the activation parameters of the second-order rate constants (k_2) for oxidation of iota- and lambda-carrageenans by cerium(IV) along with those reported for oxidations of such polysaccharides by other oxidants in aqueous perchlorate solutions are listed in **Table 4**.

Leffler and Grunwald [30] have pointed out that many

Table 4. Activation parameters of the second-order rate constants (k_2) in the oxidations of iota- and lambda-carrageenans by various oxidants in perchlorate solutions.

CAR	Oxidant	ΔH^{\ddagger} kJ mol $^{-1}$	ΔS^{\ddagger} J mol $^{-1}$ K $^{-1}$	Parameter ΔG^{\ddagger} kJ mol $^{-1}$	E_a^{\ddagger} kJ mol $^{-1}$	$10^{-4} A$ mol $^{-1}$ s $^{-1}$	Conditions		Reference
							$[H^+]$ mol dm $^{-3}$	I mol dm $^{-3}$	
Iota	MnO $_4^-$	49.57	-79.27	78.74	52.30	3.20x10 6	2.0	2.0	8
	CrO $_4^{2-}$	59.69	-77.65	83.60	62.32	1.57x10 9	3.0	4.0	Submitted
	Ce IV	76.56	-1.11	76.89	84.78	7.89x10 13	1.0	2.0	This work
Lambda	MnO $_4^-$	57.62	-47.49	79.82	60.13	7.29x10 9	2.0	2.0	8
	CrO $_4^{2-}$	40.16	-121.13	77.47	42.76	8.21x10 9	3.0	4.0	Submitted
	Ce IV	76.77	-0.05	76.78	79.26	1.69x10 13	1.0	2.0	This work

reactions show an isokinetic linear relationship, $\Delta H^{\ddagger} = \alpha + \beta \Delta S^{\ddagger}$. **Fig. 8** shows that a plot of ΔH^{\ddagger} against ΔS^{\ddagger} for the second-order rate constants, listed in **Table 4**, of the redox reactions involving cerium(IV) as an oxidant with kappa-[5], iota- and lambda-carrageenans is fairly linear. This linearity indicates that the kinetics of oxidations of such carrageenans by cerium(IV) may follow similar reaction mechanism. Also, the obtained β value (76.79 kJ mol $^{-1}$) is significant and reflects the high reactivity of these macromolecules. Also, plots of ΔH^{\ddagger} vs. ΔS^{\ddagger} for the apparent rate constants (k_1' or k_1'') in these oxidation reactions were found to be linear (Figure not shown) confirming the similarity between the reaction mechanisms in these redox systems.

Conclusion

The kinetics of oxidation of iota- and lambda-carrageenans by cerium(IV) was studied in aqueous perchlorate solutions. The change in the structure of carrageenans polysaccharides was found to have no influence on the mechanism of oxidation, but it affects the rate of oxidation which were found to be lambda > iota.

Reference

- Davidson, L.L.; Handbook of Water-Soluble Gums and Resins", McGraw-Hill, New York, Chapter 5, **1980**. DOI: [10.1007/978-1-4615-6385-3](https://doi.org/10.1007/978-1-4615-6385-3)
- Zaafarany, I.A.; Khairou, K.S.; Hassan, R.M; *J. Mol. Cat.*, **2009**, *302*, 112. DOI: [10.1016/j.molcata.2008.12.005](https://doi.org/10.1016/j.molcata.2008.12.005)
- Ahmed, G.A.; Fawzy, A.; Hassan, R.M; *Carbohydr. Res.*, **2007**, *342*, 1382. DOI: [10.1016/j.carres.2007.03.022](https://doi.org/10.1016/j.carres.2007.03.022)
- Hassan, R.M.; Fawzy, A.; Ahmed, G.A.; Zaafarany, I.A.; Asghar, B.S.; Khairou, K.S; *J. Mol. Cat. A*, **2009**, *309*, 95. DOI: [10.1016/j.molcata.2009.05.005](https://doi.org/10.1016/j.molcata.2009.05.005)
- Hassan, R.M.; Alaraifi, A.; Fawzy, A.; Zaafarany, I.A.; Khairou, K.S.; Ikeda, Y.; Takagi, H.D; *J. Mol. Cat. A*, **2010**, *332*, 138. DOI: [10.1016/j.molcata.2010.09.009](https://doi.org/10.1016/j.molcata.2010.09.009)
- Zaafarany, I.A.; Fawzy, A.; Ahmed, G. A.; Ibrahim, S.A.; Hassan, R.M.; Takagi, H.D; *Carbohydr. Res.*, **2010**, *345*, 1588. DOI: [10.1016/j.carres.2010.04.013](https://doi.org/10.1016/j.carres.2010.04.013)
- Hassan, R.M.; Fawzy, A.; Alarifi, A.; Ahmed, G.A.; Zaafarany, I.A.; Takagi, H.D; *J. Mol. Cat. A*, **2011**, *335*, 38. DOI: [10.1016/j.molcata.2010.11.011](https://doi.org/10.1016/j.molcata.2010.11.011)
- Hassan, R.M.; Fawzy, A.; Ahmed, G.A. Zaafarany, I.A.; Asghar, B.H.; Takagi, H.D.; Ikeda, Y; *Carbohydr. Res.*, **2011**, *346*, 2260. DOI: [10.1016/j.carres.2011.07.018](https://doi.org/10.1016/j.carres.2011.07.018)
- Fawzy, A; *Carbohydr. Polym.* **2016**, *138*, 356. DOI: [10.1016/j.carbpol.2015.10.076](https://doi.org/10.1016/j.carbpol.2015.10.076)
- Mathur, S.; Yadav, M.B.; Devra, V; *J. Phys. Chem. Biophys.*, **2013**, *3*, 5. DOI: [10.4172/2161-0398.1000128](https://doi.org/10.4172/2161-0398.1000128)
- Thabaj, K.A.; Chimatarad, S.A.; Nandibewoor, S.T; *Transition Met. Chem.*, **2006**, *31*, 186. DOI: [10.1007/s11243-005-6366-3](https://doi.org/10.1007/s11243-005-6366-3)

12. Bolattin, M.; Meti, M.; Nandibewoor, S.T.; Chimatadar, S.A; *J. Solution Chem.*, **2015**, *44*, 152.
DOI: [10.1007/s10953-015-0292-6](https://doi.org/10.1007/s10953-015-0292-6)
13. Das, A.K.; Islam, M.; Bayen, R; *Int. J. Chem. Kinet.*, **2008**, *40*, 445.
DOI: [10.1002/kin.20332](https://doi.org/10.1002/kin.20332)
14. Sumathi, T.; Shanmugasundaram, P.; Chandramohan, G; *J. Saudi Chem. Soc.*, **2013**, *17*, 223.
DOI: [10.1016/j.jscs.2011.03.011](https://doi.org/10.1016/j.jscs.2011.03.011)
15. Naik, D.V.; Byadagi, K.S.; Nandibewoor, S.T.; Chimatadar, S.A; *Monatsh. Chem.*, **2013**, *144*, 1307.
DOI: [10.1007/s00706-013-1005-8](https://doi.org/10.1007/s00706-013-1005-8)
16. Byadagi, K.S.; Naik, D.V.; Savanur, A.P.; Nandibewoor, S.T.; Chimatadar S.A; *React. Kinet. Mech. Catal.*, **2010**, *99*, 53.
DOI: [10.1007/s11144-009-0113-2](https://doi.org/10.1007/s11144-009-0113-2)
17. Jattinagoudar, L.N.; Byadagi, K.S.; Nandibewoor, S.T.; Chimatadar, S.A; *Synth. React. Inorg. Met. Org. Nano Met. Chem.*, **2015**, *45*, 1138.
DOI: [10.1080/15533174.2013.862684](https://doi.org/10.1080/15533174.2013.862684)
18. Khan, F.; Kushwaha U.; Singh, A.K; *J. Chem. Pharm. Res.*, **2012**, *4*, 3715.
DOI: [org/10.4314/tjpr.v13i7.4](https://doi.org/10.4314/tjpr.v13i7.4)
19. Datt, N.; Nagori, R.R.; Mehrotra, R.N; *Can. J. Chem.*, **1986**, *64*, 19.
DOI: [10.1139/v86-005](https://doi.org/10.1139/v86-005)
20. Hardwick, J.J.; Roberston, E; *Can. J. Chem.*, **1951**, *29*, 818.
DOI: [10.1139/v51-094](https://doi.org/10.1139/v51-094)
21. Hassan, R.M.; Abd-Allah, M.A.; El-Zohary, M.F; *J. Appl. Polym. Sci.*, **1993**, *47*, 1649.
DOI: [10.1002/app.1993.070470912](https://doi.org/10.1002/app.1993.070470912)
22. Hassan, R.M.; Abd-Allah, M.A; *J. Mat. Chem.*, **1992**, *2*, 609.
DOI: [10.1039/JM9920200609](https://doi.org/10.1039/JM9920200609)
23. Khairou, K.S.; Hassan, R.M.; Shaker, M.A; *J. Appl. Polym. Sci.*, **2002**, *85*, 1019.
DOI: [10.1002/app.10523](https://doi.org/10.1002/app.10523)
24. Dikshitulu, L.S.A.; Vani, P.; Rao V.H; *J. Inorg. Nucl. Chem.*, **1981**, *43*, 1261.
DOI: [10.1016/0022-1902\(81\)80028-0](https://doi.org/10.1016/0022-1902(81)80028-0)
25. Offiner, H.G; Skoog, D.A; *Anal. Chem.*, **1966**, *38*, 1520.
DOI: [10.1021/ac60243a015](https://doi.org/10.1021/ac60243a015)
26. Amzad, Z.; McAuely; *J. Chem. Soc. Dalton Trans.*, **1974**, 511.
DOI: [10.1039/DT9740000511](https://doi.org/10.1039/DT9740000511)
27. Michaelis, L.; Menten, M.L; *Biochemische Zeitschrift*, **1913**, *49*, 333.
DOI: [10.1093/database/bar009](https://doi.org/10.1093/database/bar009)
28. Laidler, K; *Chemical Kinetics*; McGraw-Hill, New York, **1965**.
DOI: [doi/abs/10.1021/j150488a018](https://doi.org/doi/abs/10.1021/j150488a018)
29. Frost, A.A.; Person, R.G; *Kinetics and Mechanism*. New Delhi: Wiley Eastern, **1973**.
DOI: [abs/10.1021/j100820a601](https://doi.org/abs/10.1021/j100820a601)
30. Leffler, J.; Grunwald, E; *Rates Equilibria of Organic Reactions*", Wiley, New York, **1963**.
DOI: [pdfplus/10.1021/ed041p407.1](https://doi.org/pdfplus/10.1021/ed041p407.1)

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