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Synthesis of Novel Diketoacid Carragenans as Coordination Biopolymeric Chealting Agent Precursor by Oxidation of Kappa-Carrageenan Polysaccharide by Alkaline Permanganate

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Keywords

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Diketoacid derivative of kappa-carrageenan (KCAR) was synthesized as an oxidation product of oxidation of KCAR with potassium permanganate in alkaline solution at pH's > 12 with a yield of 96.2%. The chemical structure of the coordination biopolymer macromolecule (DKA-KCAR) has been elucidated by elemental analysis and IR spectroscopy. The product has a high efficiency for removal of toxic heavy metal cations from the contaminated matters in environment. Suggested models for chelation were presented. A tentative reaction mechanism consistent with the experimental results for oxidation is suggested.

Introduction

Permanganate ion is a strong oxidant, which has been used for oxidation of most organic [1-8] and inorganic [9-11] substrates. Again, Hassan and coworkers were studied the kinetics of oxidation of some macromolecules containing secondary alcoholic groups either natural [12-14] or synthetic [15] polymers by alkaline permanganate at pH's > 12. They reported that oxidation of secondary alcoholic groups was led to formation of the corresponding keto-derivatives in alginates [16] pectates [17] and carboxymethyl cellulose [18] as biopolymer precursors. However, a little attention has been focused to the oxidation of macromolecules in particularly sulfated polysaccharides that containing both primary and secondary alcohols by this oxidant

[19]. This fact may be attributed to the complexity of the reaction kinetics which may not allow a mechanistic conclusion.

Kappa-carrageenan (KCAR) is a water-soluble polysaccharide of linear block copolymer structure builds up of sulfated D-galactans extracted from algae. It is characterized by an alternating disaccharide units $(1 \rightarrow 3)$ linked β -D-galactose- 4-sulfate and $(1 \rightarrow 4)$ linked 3, 6 anhydro-α-D-galactose [20-23].

Therefore, the present work of permanganate oxidation of kappa-carrageenan as a natural polymer containing both primary and secondary alcoholic groups is of greet significant to gain further information on the nature of the products as well as the interaction of this macromolecule in aqueous alkaline solutions with a special sight on the influence of the nature of the functional groups on the mechanistics and kinetics in this redox system. In addition, this work aims to synthesize ketoacid derivatives as biopolymer precursors. These biopolymers could be used to encapsulate, protect and deliver bioactive or functional components such as minerals, peptides, proteins, enzymes, drugs, lipids or dietary fibers. The mono- or diketoacid derivatives formed as final oxidation products would useful as precursors for synthesis of new biopolymers as selective biochelating agents for polyvalent cations forming ionotropic gels. These gels would be useful as conductors, selective cation sieves, semi- permeable membranes, biocatalysts and cation exchange resins.

Experimental Methods

All materials employed in the present study were of analytical grade. Bidistilled water was used in all preparations. Kappa-carrageenan employed in the present study (Fluka) was used without further purification.

Preparation of Diketoacid Kappa-Carrageenan (DKA-KCAR)

Kappa-carrageenan powder (5 g) was dissolved in 350 cm^3 of deionized water whose pH was previously adjusted to pH $\geq$ 12 using sodium hydroxide. This process was performed by stepwise addition of the powder KCAR to the solution while stirring rapidly and continuously to avoid the formation of aggregates. A 150 cm^3 solution containing 3.87 g of potassium permanganate and 4.07 g of sodium fluoride was then added stepwise over 2 h to the KCAR solution. The reaction mixture was stirred for 48 h at room temperature, the formed MnF_4 was filtered off, and the solution was concentrated to one-fifth of the original solution using a rotary evaporator. A portion of this concentrated solution was acidified using dilute acetic acid to a pH of ca. 5-6. The resultant solution dried under vacuum, and then subjected to elemental analysis and IR spectroscopy.

IR-Spectra

The IR-spectra were scanned on a Pyc Unicum Sp 3100 spectrophotometer using the KBr disc technique (4000-200 cm^{-1}). *ANAL*: Diketoacid kappa-carrageenan (DKA-KCAR) $C_{12}H_{11}O_{13}S$ (395): Calcd (found): C, 36.45 (36.10); H, 2.78 (2.63). IR: 3420 (OH of COOH group); 1795-1730 (broad) (C=O of -diketone); 1634 (C=O of COOH, γ_{as} OCO); 1413 (C = O of COOH, γs OCO) and 1258 cm^{-1} (C — O — C of KCAR) [24].

2,4-Dinitrophenyl Hydrazone Derivative

ANAL: $C_{24}H_{19}O_{19}N_8S$ (755): Calcd (found): C, 38.15 (38.11); H, 2.52 (2.55); N, 14.83 (14.75). IR: 3390 (OH of COOH group); 3310 (NH of hydrazone); 1680 (C=N of hydrazone); 1200 (C — O — C of KCAR).

Dioxime Derivative

ANAL: C18H7O13N2S (491): Calcd (found): C, 43.99 (43.97); H, 1.43 (1.45); N, 5.70 (5.63). IR: 3300 (OH of COOH and oxime); 1670 (C=N); 1595 (C=O of COOH); 1225 (C — O — C of KCAR).

The diketoacid derivative was also identified by elemental analysis and IR spectral data as described elsewhere [16-18].

Polymerization Test

The possibility of formation of free radicals was examined by adding acrylonitrile to the partially oxidized reaction mixture.

Under the experimental conditions of $[MnO_4^-] = 4.90 \times 10^{-2}$, $[KCAR] = 2.45 \times 10^{-2}$, $[OH^-] = 4.0 \times 10^{-2}$ and $[acrylonitrile] = 5 \times 10^{-5}$ mol dm^{-3} at 25°C, no polymerization was observed indicating that the oxidation reaction probably does not proceed via a free–radical intervention mechanism.
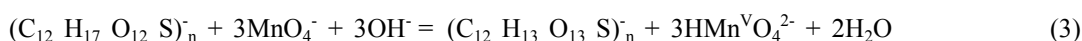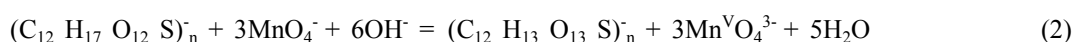
Results and Discussion

The stoichiometry of oxidation of kappa-carrageenan by potassium conforms the following stoichiometric equation,

$$3(C_{12}H_{17}O_{12}S)^-_n + 8MnO_4^- = 3(C_{12}H_{11}O_{13}S)^-_n + 8MnO_2 + 8OH^- + 5H_2O \tag{1}$$
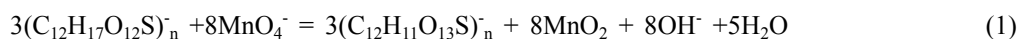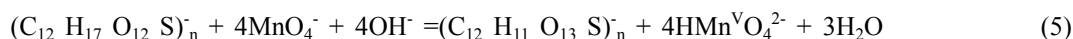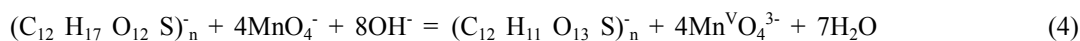
It was reported that the formation of mono- or diketo-derivatives for oxidation of polysaccharides containing two secondary alcoholic groups by alkaline permanganate depends on the molar ratio of reactants as well as the pH of the medium [12, 16]. The influence of the molar concentration of the oxidant and the pH of the medium on the oxidation product may be expressed as follow:

Monoketo derivatives

$$(C_{12}H_{17}O_{12}S)^-_n + 3MnO_4^- + 6OH^- = (C_{12}H_{13}O_{13}S)^-_n + 3Mn^VO_4^{3-} + 5H_2O \tag{2}$$

$$(C_{12}H_{17}O_{12}S)^-_n + 3MnO_4^- + 3OH^- = (C_{12}H_{13}O_{13}S)^-_n + 3HMn^VO_4^{2-} + 2H_2O \tag{3}$$

Diketo derivatives

$$(C_{12}H_{17}O_{12}S)^-_n + 4MnO_4^- + 8OH^- = (C_{12}H_{11}O_{13}S)^-_n + 4Mn^VO_4^{3-} + 7H_2O \tag{4}$$

$$(C_{12}H_{17}O_{12}S)^-_n + 4MnO_4^- + 4OH^- = (C_{12}H_{11}O_{13}S)^-_n + 4HMn^VO_4^{2-} + 3H_2O \tag{5}$$

where $(C_{12}H_{17}O_{12}S)^-_n$, $(C_{12}H_{13}O_{13}S)^-_n$ and $(C_{12}H_{11}O_{13}S)^-_n$ denote kappa-carrageenan and its corresponding monoketoacid and diketoacid derivatives, respectively. Elemental analysis and spectral data can identify these ketoderivatives.

Some experiments were performed in nitrogen atmosphere in order to check the participation of the dissolved oxygen into the solvent media on the oxidation process. Analysis of the oxidation product indicated that diketoacid derivative is formed in either the presence or absence of oxygen. This result may reveal that the permanganate ion, but not dissolved oxygen is the responsible for oxididation of the formed aldehyde to its corresponding acid in the last slow stage.

Under our experimental conditions, the diketoacid kappa-carrageenan (Eq. 5) was found to be in good agreement with the experimental results obtained. This diketoacid derivative gave satisfactory elemental analysis and broad IR absorption bands at 1690-1650 cm^{-1} (broad) that characterize the carbonyl group of α-diketone [25]. The enhancement of the absorption band of the OH group in the IR spectra indicated the complete oxidation of both OH groups in KCAR to the corresponding ketone. This product was also reacted with 2,4-dinitrophenyl hydrazine and hydroxylamine to afford the corresponding bis-2,4-dinitrophenyl hydrazone and dioxime derivatives, which gave satisfactory elemental analysis and spectroscopic data as shown in Figure 1. The yield was 96.2%.
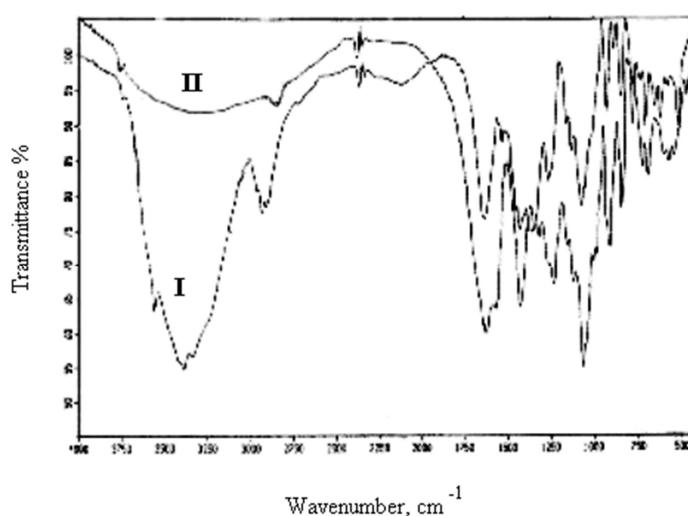

Figure 1. FTIR Spectra of Kappa-Carrageenan (I) and Diketo-Acid Derivative (II).

The oxidation of KCAR by alkaline permanganate was found to occur stepwise through two distinct stages. The first step was relatively fast which corresponds to the formation of detectable coordination biopolymeric intermediate complex [KCAR-Mn^{VI}O$_4^{2-}$] and/or [KCAR-Mn^{V}O$_4^{3-}$] involving green manganate (VI) and/or blue hypo- manganate(V) transient species [26, 27]. As this intermediate builds up, a slow decay takes place for the intermediate complex to give rise to the products in the slow second stage [28].

The observed pseudo first-order rate constants of oxidation of KCAR by alkaline permanganate were found to be 0.083 s^{-1} and 0.015 s^{-1} for the formation and decomposition processes of the intermediate complex, respectively, at [MnO$_4^-$]= 4x10^{-4}, [KCAR]=4x10^{-3}, [OH$^-$]=5x10^{-2} and I=0.1 mol dm^{-3} at 40°C [27, 28].

A tentative reaction mechanism for the oxidation process has been suggested, itinvolves the removal of protons from KCAR by alkali to give the corresponding alkoxide forms, followed by the attack of MnO$_4^-$ to alkoxide centers to form intermediate complexes. This attack is facilitated by the polarization of Mn-O bond [29] or the presence of Na$^+$ cations that tend to reduce the net charge of the intermediate. As the intermediate builds up, it further deprotonates prior to the rate-determining step of the second stage, followed by a slow decomposition process to give the final product.

An alternative reaction mechanism for the oxidation of kappa-carrageenan by alkaline permanganate may be suggested. It involves a fast deprotonation of the substrate prior to the rate-determining step, followed by the attack of the MnO$_4^-$ oxidant to the H-C bond [30, 31] of the alcoholic groups to form a further intermediate complex involving green manganite (VI) transient species through the initial fast stage. Then the later formed intermediate is slowly decomposed to give rise to the final oxidation product at the final stage of reaction.

This latter mechanism reveals the absence of the hydroxide ion dependence of the observed rate constants which is opposite to our experimental observations of the remarkable dependency of the rate constants on [OH$^-$] in the slow decomposition stage. Again, the assumption based on the hydride abstraction is not easy acceptable from mechanistic points of view since the abstraction of hydride might occur just as well or even easier from a neutral molecule; whereas the –CH bond in the negatively charged molecule anion does not seem more loosened than in the neutral molecule [32]. Accordingly, the alternative mechanism that corresponds to the formation of that latter intermediate complex is excluded. Moreover, under our experimental conditions used, Eqs. (2) and (3) can be neglected.

Similar reaction mechanisms for oxidation of some macromolecules by this oxidant in alkaline solutions have been reported elsewhere [11-18].

The ability of the diketo-acid carrageenan product for chelation with some metal cations of monovalent metal ions such as Ag(I) and divalent metal ions such as Ca(II), Sr(II), Ba(II), Cd(II) and Pb(II) has been examined. The experimental results indicated its high affinity for chelation. Some suggested models of chelation are shown in Scheme I.
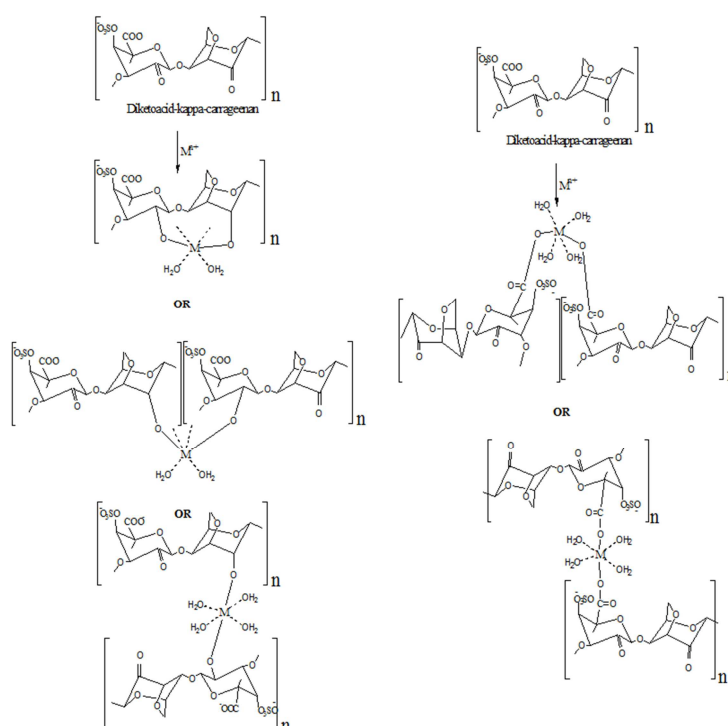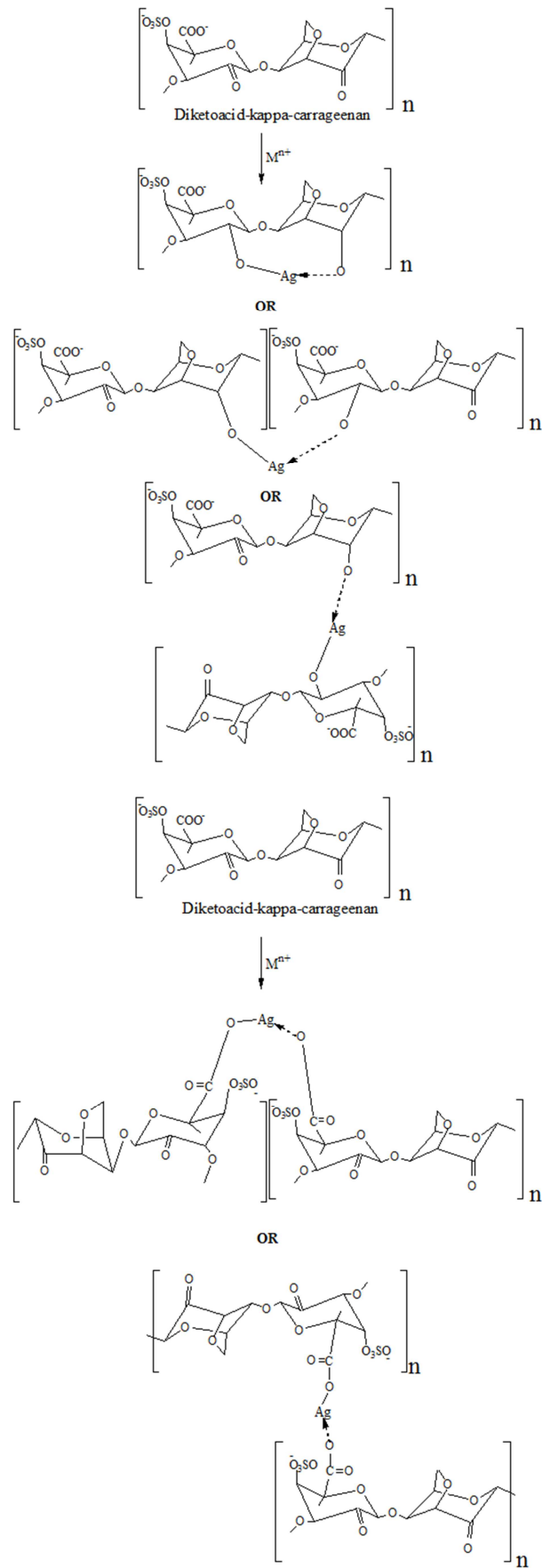
Scheme I. *Some suggested models of chelation between Diketoacid-Kappa carrageenan with some metal cations.* ∎

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