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NON-ISOTHERMAL DECOMPOSITION OF AL- , CR- AND FE- CROSS-LINKED TRIVALENT METAL-ALGINATE COMPLEXES

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ABSTRACT

. The thermal decomposition of Al^{III}, Cr^{III} and Fe^{III} metal-alginate complexes have been investigated thermogravimetrically using (TG) and (DTG) techniques in static air. However, the TG curves showed three stages of weight loss, the DTG curves indicated the presence of a series of thermal peaks associated with the TG curves. The thermal dehydration of the coordinated water molecules was found to occur in the first stage, whereas the decomposition of the dehydrated complexes were occurred in the second and third stages, respectively. The results revealed the formation of hydroxide, oxalate and carbonate intermediates for the cross-linked Al^{III}, Cr^{III} and Fe^{III} metal–alginate complexes, respectively, followed by decomposition of these intermediates to the corresponding metal oxides as final products. These complexes have been characterized by FTIR and chemical analysis. A tentative mechanism for decomposition has been suggested and discussed in terms of the strength of chelation and the structure geometry.

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KEY WORDS: Thermal decomposition, alginates, polysaccharides, trivalent metal ions, complexes, geometry.

INTRODUCTION

Alginate is a polyelectrolyte which consists of a binary heteropolymer consisting of 1,4 linked β-D-mannuronic and α-L-guluronic acid units in a linear block copolymer structure [1-4].

The thermal decomposition of solid materials proceeded in two directions, using either the powdered material or a single crystal. The former studies are much more extensive than the latter one. The advantages of the solid state decomposition were attributed to the destruction of the crystal lattice of the sample, the breaking and redistribution of the chemical bonds involved, the formation of the crystal lattice of the product and the diffusion process of one component or the other through the product layer for further propagation of the dissociation reactions [5].

Although, there are some reports on the thermal decomposition of some cross-linked divalent and hexavalent metal-alginate complexes [6-9], it seems that no attempt has been made with respect to alginate complexes of trivalent metal ions. Therefore, the present work is of great significance to shed some light on the thermal decomposition of these complexes as well as to gain some information on their chemical stabilities compared with that of other polyvalent metal-alginate complexes. Again, since trivalent metal-alginate complexes posses electrical properties lie in the range of semiconductors, they can be applied in some solar energy cells and electrical devices.

EXPERIMENTAL

Chemicals

All materials used were of Analar quality . Sodium-alginate (BDH) used was without further purification. Doubly distilled conductivity water was used in all preparations.

Preparation of sample Complexes

Cross-linked metal-alginate complexes in the form of granules were prepared by replacement of Na^+ counter ions of alginate macromolecule by Al^{3+} Cr^{3+} and Fe^{3+} metal ions. This process was carried out by stepwise addition of the alginate powder reagent to the electrolyte solutions of these metal ions (Ca. 1.0 M) whilst stirring the solutions vigorously in order to avoid the formation of lumpy gelatinous precipitate of metal-alginate gels which swell with difficulty. After completion of exchange processes, the metal-alginate granules formed were washed with deionized water several times, then with doubly distilled water until the washings become free-from the metal ions. The sample complexes were dried at about 105 °C under vacuum over anhydrous $CaCl_2$ or P_2O_5.

TECHNIQUES

Thermogravimetry (TG) and differential thermogravimetry (DTG) analyses were carried out using a Mettler TA 3000 thermal analyzer, the heating rate was 10 K min^{-1} in static air.

The microanalyses were performed with a microanalyzer and the analytical data of the complexes are presented in Table 1.

Infrared Spectroscopy

The FTIR spectra were recorded on a Pye Unicam Sp 3100 spectrophotometer using the KBr disc technique (4000-200 cm^{-1}) as shown in Figure 1.

Table 1: Analytical data for metal alginate complexes.

Complex	Found (%)			Calculated (%)			Formula
	C	H	M	C	H	M	
Al^{III}-alginate	35.89	4.56	4.31	35.53	4.77	4.44	$C_{18}H_{21}O_{17}Al.4H_2O$
Cr^{III}-alginate	34.33	4.55	8.24	34.12	4.58	8.21	$C_{18}H_{21}O_{17}Cr.4H_2O$
Fe^{III}-alginate	33.82	4.41	8.88	33.92	4.55	8.74.	$C_{18}H_{21}O_{17}Fe.4H_2O$

Table 2: Infrared frequencies (cm^{-1}) for sodium and metal alginate complexes.

Complex	$\upsilon_{as}OCO$	$\upsilon_{s}OCO$	υ_{OH}	$\upsilon_{M\text{--}O}$	Reference
Na-alginate	1600	1400	3500	850	6
Al^{III}-alginate	1648	1425	3490	830	This work
Cr^{III}-alginate	1637	1420	3463	810	This work
Fe^{III}-alginate	1633	1418	3448	817	This work

Table 3: The maximum decomposition (T_{max}) and the weight loss accompanying the stages of decomposition (10 K) min.

Complex	Stage	TG			Weight loss (%)	$T_{max}/^{o}C$
		$T_i/^{o}C$	$T_m/^{o}C$	$T_f/^{o}C$		
Al^{III}-alginate	1st	53	106	190	12.1	220
	2nd	190	220	340	52.7	
	3rd	340	395	453	33.1	
Cr^{III}-alginate	1st	51	104	151	11.8	207
	2nd	151	207	342	25.9	
	3rd	342	395	442	55.5	
Fe^{III}-alginate	1st	53	101	145	11.2	205
	2nd	145	205	289	38.2	
	3rd	289	293	347	43.9	

T_i : initial, T_m : medium and T_f : final

RESULTS AND DISCUSSION

The replacement of Na^+ counter ions of alginate macromolecule by polyvalent metal ions of the electrolyte solutions can be generally expressed by the following stoichiometric equation

$$\underset{\text{Sol}}{Z(Na-Alg)_n} + \underset{\text{electrolyte}}{nM^{Z+}} = \underset{\text{complex}}{(M\text{-}Alg_Z)_n} + \underset{\text{electrolyte}}{ZNa^+} \qquad (1)$$

where M denotes the metal ion and Z stands to its valency.

Any counter ions, which leave the macromolecular chains of alginate, must be compensated by an equivalent amount of other metal ions, even if the mobilities and valencies of the two counter ions are quite different [10-12]. This is the necessary demands of electroneutrality. The exchange processes for the formation of the complexes studied were found to be inherent stoichiometrically [13-16].

The infrared spectra of the present complexes have been measured and the vibration assignments of the bands are cited in Table 2. It is well known [17] that the bands correspond to the symmetry stretching vibrations of the $-OCO^-$ (υ_s) in sodium alginate lie at 1400 cm^{-1} and that of the asymmetric stretching vibrations (υ_{as}) lie at 1600 cm^{-1}. A broad band is located near 3500 cm^{-1} due to the stretching vibration of the hydrogen bond of water or the hydroxyl group. Again, the free ligand has a strong band in the 1735 cm^{-1}. As shown in Table 2, the band of the stretching vibrations of $-OCO^-$ group is shifted from 1400 cm^{-1} (υ_s) to 1418-1425 cm^{-1} whereas the band at 1600 cm^{-1} (υ_{as}) is shifted to 1633-1648 cm^{-1}, respectively. This result indicates the participitation of $-OCO^-$ groups in chelation. Again, the shift in the υ_{OH} band to lower frequencies which becomes more broader than that of sodium alginate may also indicate the sharing of OH groups in the chelation process.

Furthermore, the model structure of coordination plays an important role in the stability of these metal alginate complexes. Polyvalent metal ions tend to chelate the carboxylate and hydroxyl functional groups of alginate macromolecular chains via either intra- or intermolecular association mechanism in order to attain stable coordination geometry. This depends on the nature, valency and coordination number of the chelated metal ions. Since the divalent metal ions are chelated with two carboxylate groups and one or more pairs of hydroxyl groups of alginate macromolecular chains, the two geometrical structures (intra- and intermolecular associations) are possible in chelation. On the other hand, trivalent metal ions cross-link three carboxylate groups and one or more pairs of the hydroxyl groups depending on the coordination number of the chelated metal ion. Hence, trivalent metal ions are restricted to cross-linking via intermolecular association in their alginate complexes for geometrical reasons. The preferability of the intermolecular association for trivalent metal-alginate complexes may be explained by their tendency to decrease the bond stretching resulting from metal-oxygen bond elongation in case of intramolecular association. This association may explain the week mechanical properties of trivalent metal alginate complexes in their gel forms, in handling since the attraction forces around the metal ion will not be the same in all directions, when compared with those of divalent metal ions of equal attraction forces around the metal ion [19].

The thermal decomposition curves of the studied complexes are shown in Figure 2. The TG curves exhibit three stages of weight loss, the DTG curves indicate the presence of a series of thermal decomposition associated with the TG curves. This behaviour is quite different than that observed in case of sodium alginate macromolecule [6], and may be explained by the difference in the strength of chelation resulting from the partially ionic bonds between sodium or trivalent metal ions and the carboxylate groups as well as the presence of partially coordinate bonds between trivalent metal ions and hydroxyl groups, while these later bonds are not present in case of sodium-alginate macromolecule.

In view of the thermal decomposition, behaviour of other divalent metal-alginate complexes reported elsewhere [6-9], a suitable mechanism of thermal decomposition consistent with the experimental observations may be suggested. The weight loss observed in the first stages in the TG curves (Table 3) can be explained by the evolution of four coordinated water molecules as follows,

$$C_{18}H_{21}O_{17}M\ .\ 4H_2O \qquad\qquad C_{18}H_{21}O_{17}M\ +\ 4H_2O \qquad (2)$$

The observed weight-losses, which associated with the second stage (Table 3) may indicate the decomposition of the dehydrated complexes formed in Eq. (2) to give intermediate fragments, followed by fast decomposition of these fragments to form the corresponding hydroxide, oxalate and carbonate intermediate of metal salts for Al- , Cr- and Fe-alginate complexes respectively. Consequently, the decomposition of these dehydrated complexes can be expressed by the following equations,

$$C_{18}H_{21}O_{17}Al + X\ O_2 \xrightarrow[II]{340^{o}\ C} \xrightarrow{\text{up to } 155^{o}\ C} \text{intermediate fragments} \xrightarrow{\text{fast}} Al(OH)_3 \qquad (3)$$

$$2C_{18}H_{21}O_{17}Cr + Y\ O_2 \xrightarrow[II]{342^{o}\ C} \text{intermediate fragments} \xrightarrow{\text{fast}} Cr(C_2O_4)_3\ nH_2O \qquad (4)$$

$$2C_{18}H_{21}O_{17}Fe\ + Z\ O_2 \xrightarrow[II]{289^{o}\ C} \text{intermediate fragments} \xrightarrow{\text{fast}} Fe_2(CO_3)_3 \qquad (5)$$

where $C_{18}H_{21}O_{17}$ represent to the structural formulas of three combined monomers of alginate macromolecule that chelated to the trivalent metal ion in the respective complex. This behaviour was found to be quite similar to that observed for the thermal decomposition of some cross-linked divalent metal alginate complexes [8,9].

The observed weight-losses (Table 3) which associated with the third stage were found to be in good consistent with the decomposition of the formed intermediates $Al(OH)_3$, $Cr(C_2O_4)_3\ nH_2O$ and $Fe_2(CO_3)_3$ to give the corresponding metal oxides for Al- , Cr- and Fe-alginate complexes, respectively, as final products

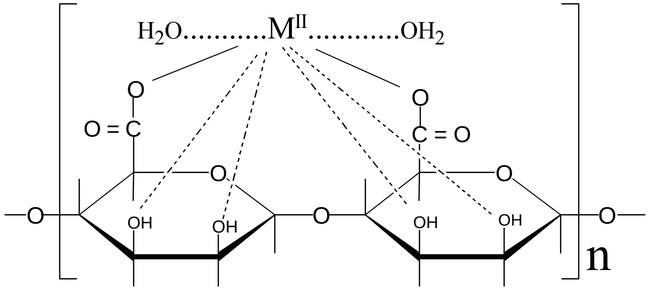
$$2Al(OH)_3 \xrightarrow{453^{o}\ C} Al_2O_3\ + 3H_2O \qquad (3)'$$

$$Cr_2(C_2O_4)_3\ .\ nH_2O + 3/2\ O_2 \xrightarrow{424^{o}\ C} Cr_2O_3\ + 6CO_3 \qquad (4)'$$

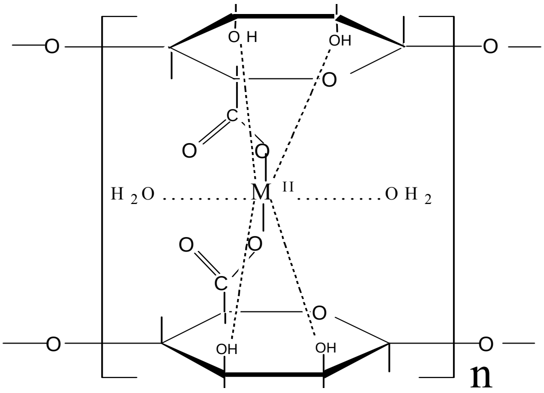
$$Fe_2(CO_3)_3 \xrightarrow{347^{o}\ C} Fe_2O_3\ + 3CO_2 \qquad (5)'$$

The values of the maximum decomposition temperature of the main process (Table 3) may reflect the stability of the metal-alginate complexes. The observed values indicate that the stability decreases in the order Al > Fe ≥ Cr – alginates. The order of stability agrees very well with the magnitude of M-O bond energies [18], i.e. the stability depends on the strength of chelation between the chelated metal ion and functional groups of alginate macromolecule.

In intramolecular association the functional groups involved in chelation are belonging to the same chain. Hence, the plane involving the chelated metal ion is parallel to the plane of alginate macromolecular chains. This configuration may be called a planar geometry. While, in intermolecular association the plane containing the metal ions is perpendicular to the plane of alginate chains and the involved functional groups are related to different chains. Here, the configuration obtained is termed a non-planar geometry [19] The two geometrical configuration are shown in Schemes I and II.

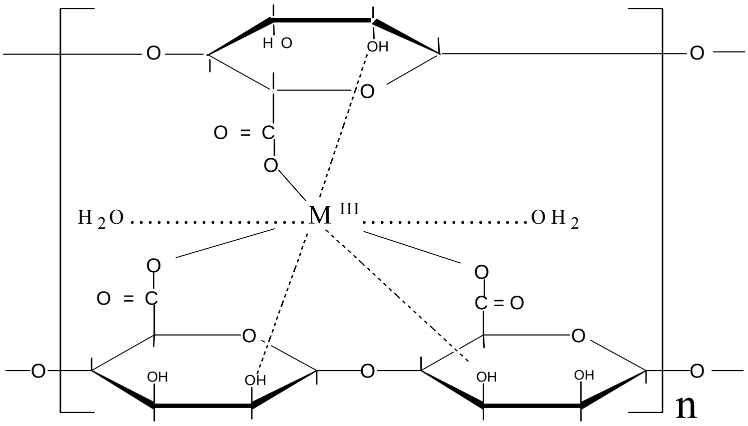


Intramolecular association



Intermolecular association

Scheme I 0 Cross-Linked Divalent Metal Ions



Intermolecular Association

Scheme II - Cross-Linked Trivalent Metal Ions

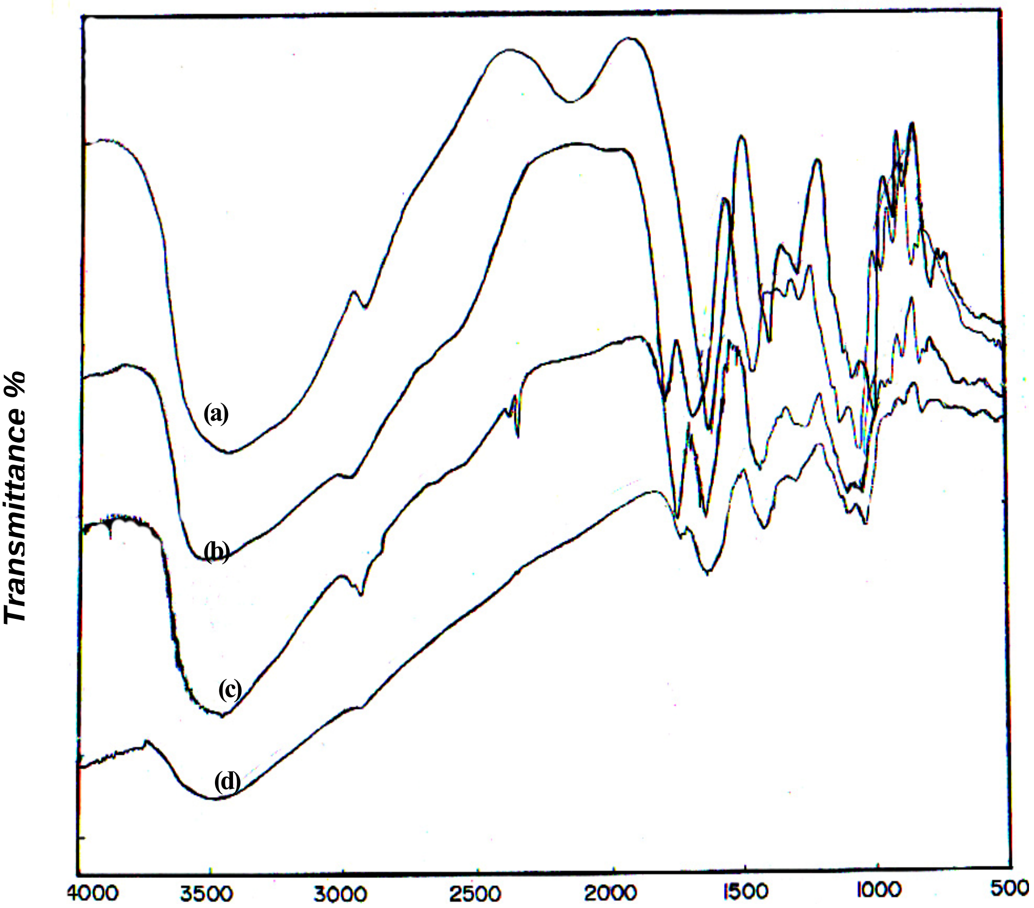
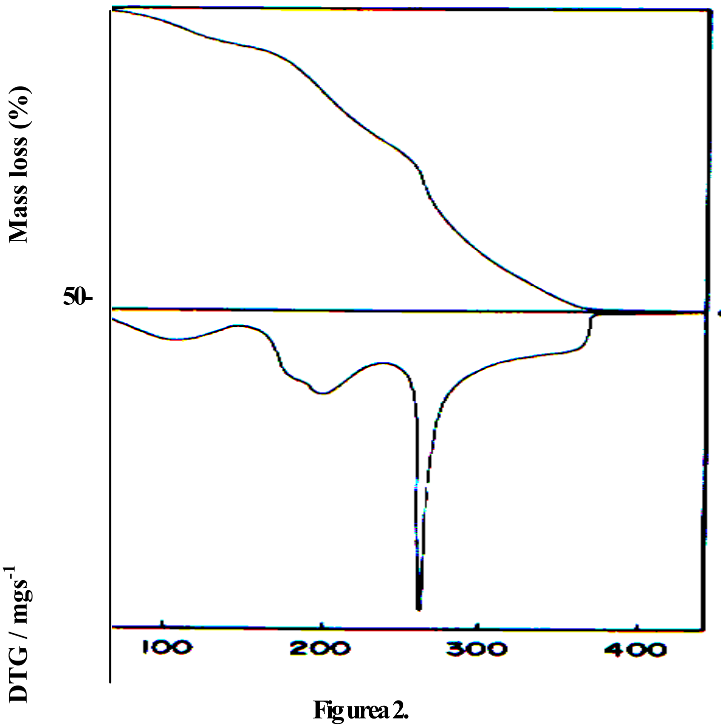


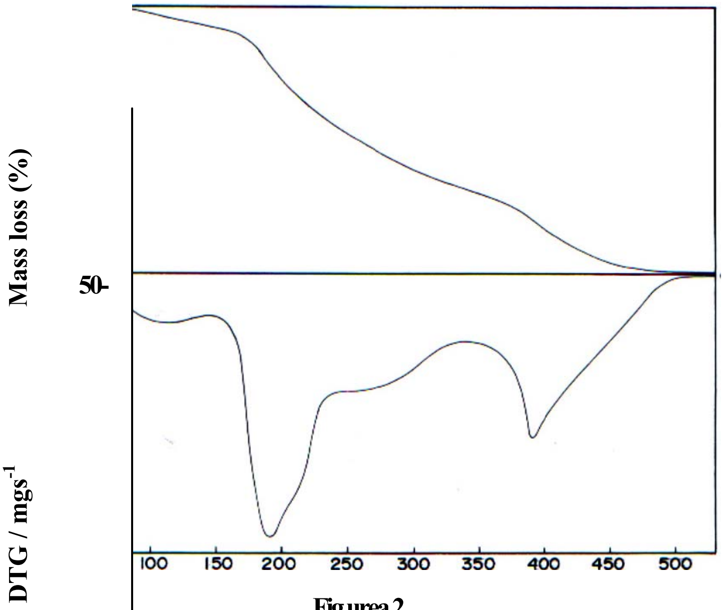
Figure 1. Infrared spectrum of (a) sodium alginate, (b) cross-linked aluminum(III)-alginate complex, (c) cross-linked iron(III)-alginate complex and (d) cross-linked chromium(III)-alginate complex.

Al^{III} – alginate

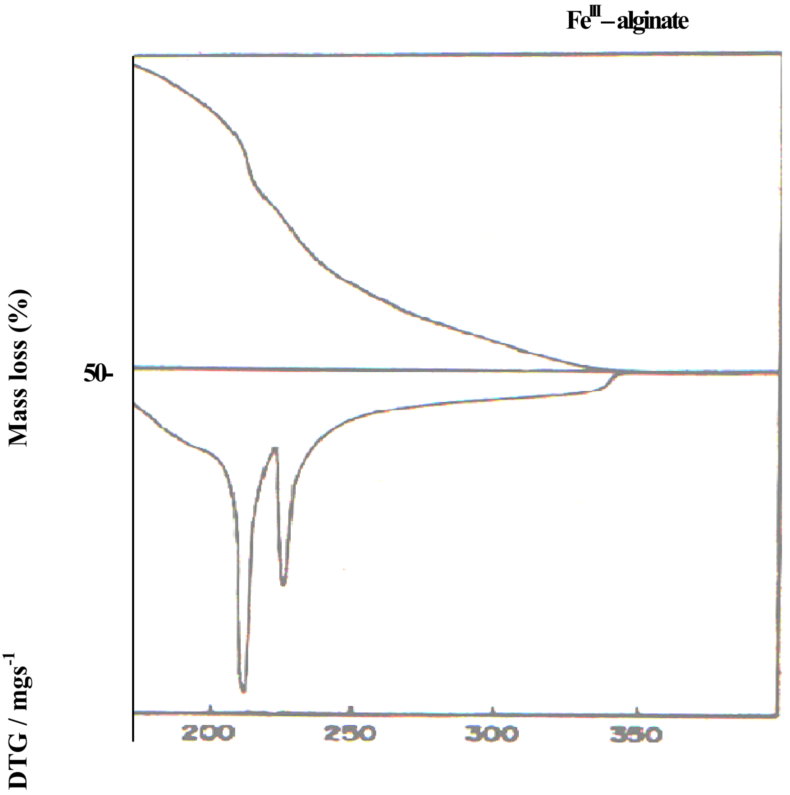


Figurea 2.

Cr^{III} – alginate



Figurea 2.



Figurea 2.

T/°C

Figure 2. TG and DTG curves of cross-linked metal-alginate complexes

CONCLUSION

The thermal decomposition of Al^{III} -, Cr^{III} - and Fe^{III} - alginate complexes have been studied using thermogravimetry (TG) and differential thermogravimetry (DTG) methods. The experimental observations showed the presence of three stages of weight loss (TG) associated with a series of thermal decomposition (DTG) curves. The first stage was explained by the evolution of four coordinated water molecules for all cited complexes. Then, the dehydrated complexes are decomposed in the second stage to give transient intermediate fragments, followed by fast decomposition of these fragments to give the corresponding metal hydroxie, oxalate and carbonate as intermediates for Al-, Cr- and Fe-alginate complexes, respectively, in the second stage. These intermediates are decomposed in the third stage to give rise to the corresponding metal oxides as final products.

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