

Kinetics and Mechanism of Non-Isothermal Decomposition of Ca(II)-, Sr(II)- and Ba (II)- Cross-Linked Divalent Metal-Alginate Complexes

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Abstract

The kinetics of thermal decomposition of Ca(II)-, Sr(II)- and Ba(II)- cross-linked metal–alginate biopolymeric complexes as biocatalysts have been studied using thermogravimetric (TG) and differential thermogravimetric (DTG) techniques in static air. The TG curves showed three stages of weight loss, whereas the DTG 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, followed by decomposition of the formed dehydrated complexes through the other following stages. The second stage was corresponding to the formation of oxalates as intermediate fragments, whereas the third stage indicated the formation of metal oxides as final product of such decomposition. The kinetic parameters were computed by different models and tentative decomposition mechanism is discussed.

Keywords: thermal decomposition, alginates, polysaccharides, kinetics, biopolymers, complexes

1. Introduction

It is well-known that alginate as anionic polyelectrolyte has a high affinity for chelation with polyvalent metal ions in particularly with cations of alkaline-earth metal forming the corresponding cross-linked metal alginate complexes (Haugh & Smidsrod, 1965; Smidsrod, 1965; Haugh, Larsen, & Smidsrd, 1974; Schewiger, 1964; Thiele & Anderson, 1955; Thiele & Hallich, 1957) through an egg-carton like-structures (Morris, Rees, & Thomas, 1978; Rees, 1972). Although, these polymeric metal alginate biomaterials are of great importance and has wide application in industrial technology such as in biomedical sensors, drug delivery, tissues engineering, skin grafting, medical adhesive, immobilization systems and textiles (Saha et al., 2011; Espevik & Sejak-Braek, 1996), for wound dressing application (Meng, Tian, & Yang, 2010; Kim et al., 1999), pervaporation dehydration processes (Huang & Moon, 1999), biocatalysts in immobilization systems for ethanol manufacturing (Torres et al., 1998), wastewater purification (Torres, Sanchez-de-la-Vega, Bettran, & Jimenez, 1998), and for removal of toxic heavy metal cations (Nita et al., 2007; Wu, Mimura, & Niibori, 2009). A little attention has been focused on their thermal decomposition.

This chelation takes place between the metal ions and the carboxylate and hydroxyl functional groups of alginate macromolecule through the formation of partially ionic and partially coordinate bonds, respectively. In case of the complexes of divalent metal ions with alginate, two carboxylate groups shared in chelation, whereas the number of hydroxyl groups depends on the coordination number of the chelated metal ion (Hassan, 1993; Schweiger, 1964).

In view of the above aspects and our interesting on studies of thermal decomposition of macromolecules (Said & Hassan, 1993; Said, Abd El-Wahab, & Hassan, 1994; Khairou, 2002; El-Gahami, Khairou, & Hassan, 2003; Zaaferany, 2010; Fahad & Hassan, 2012), the present work has been undertaken to throw further highlights on the chemistry of these complexes in terms of their chemical stabilities based on the model structure, strength of chelation and geometrical.

2. Experimental

2.1 Materials

Analytical reagent grade chemicals were used throughout. Metal alginate complexes in the form of granules were prepared by the replacement of counter ion, Na^+ , of alginate macromolecule (Cica Reagent Chem. Co.) with Ca^{2+} , Sr^{2+} and Ba^{2+} metal ions. This process was performed by stepwise addition of alginate powder to the metal ion electrolyte solutions (ca. 0.5- 1.0 M) while rapidly stirring the electrolyte solution to avoid the formation of lumpy gelatinous precipitates of metal alginate gels, which swell with difficulty. After completion of the exchange process, the metal alginate granules formed were washed with deionized water several times, then with doubly distilled water until the resultant washings became free from the non-chelated metal ions. The samples were dried at 105°C under vacuum over anhydrous CaCl_2 or P_2O_5 .

2.2 Techniques

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

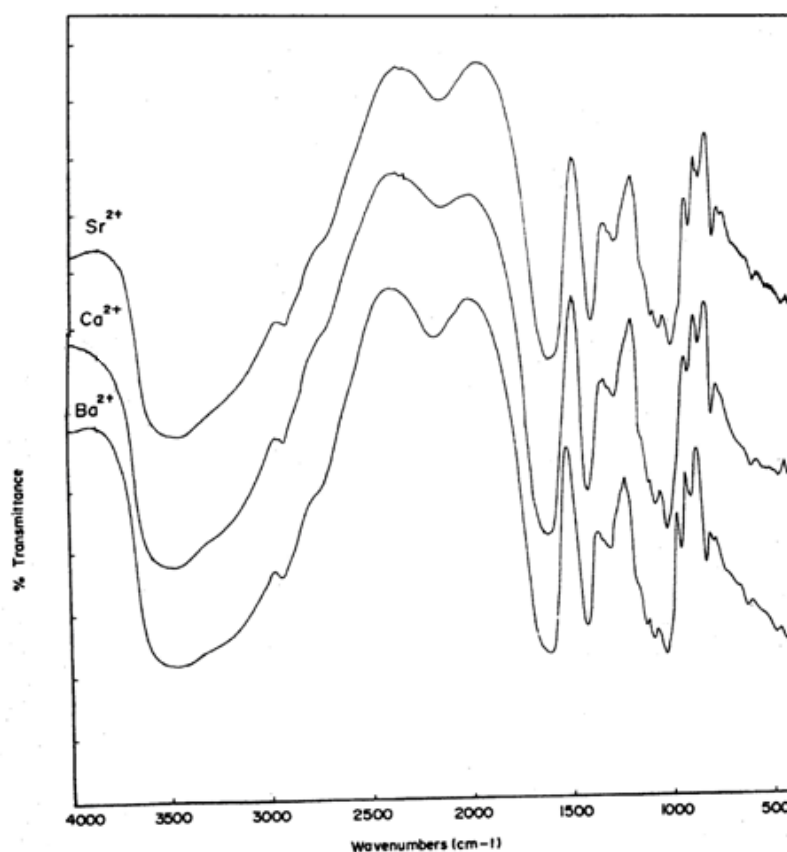


Figure 1. FTIR of cross-linked alkaline earth metal alginate complexes

Thermogravimetry (TG) and differential thermogravimetry (DTG) of alginate complexes were carried out using a Mettler TA 3000 thermal analyzer. Three heating rates were used as 5, 10, and 20 K/min. The results are shown in Figure 2.

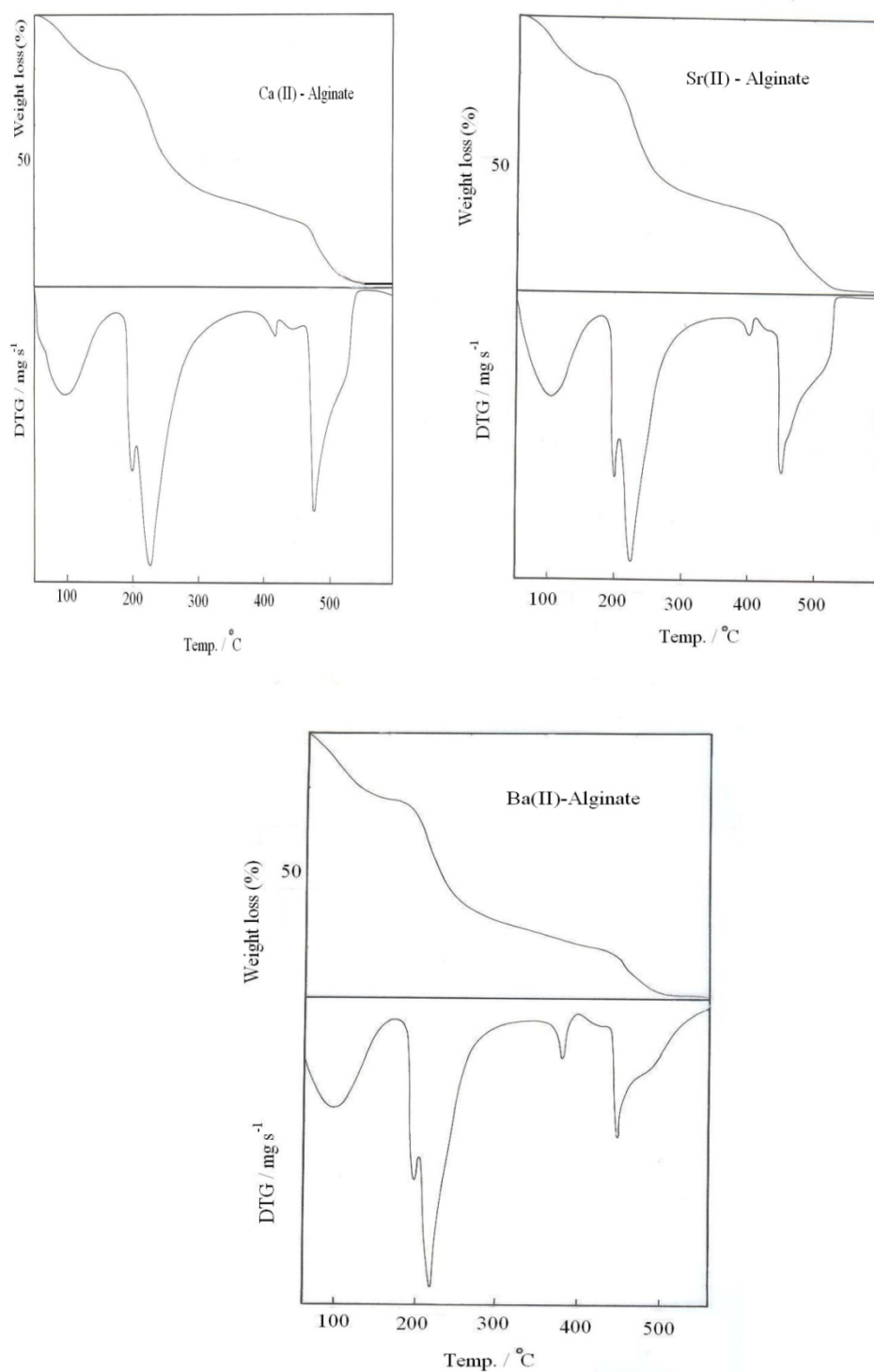
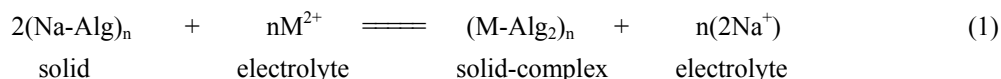


Figure 2. TG and DTG thermograms of cross-linked alkaline earth metal alginate complexes

X-ray diffraction patterns were obtained by a Philips 1710 diffractometer, the patterns run with copper as a target and nickel as a filter ($\lambda = 1.54187 \text{ \AA}$) at 40kV and 30 mA. The scanning speed was 3.6 K/min in the range $2\theta = 2-60$.

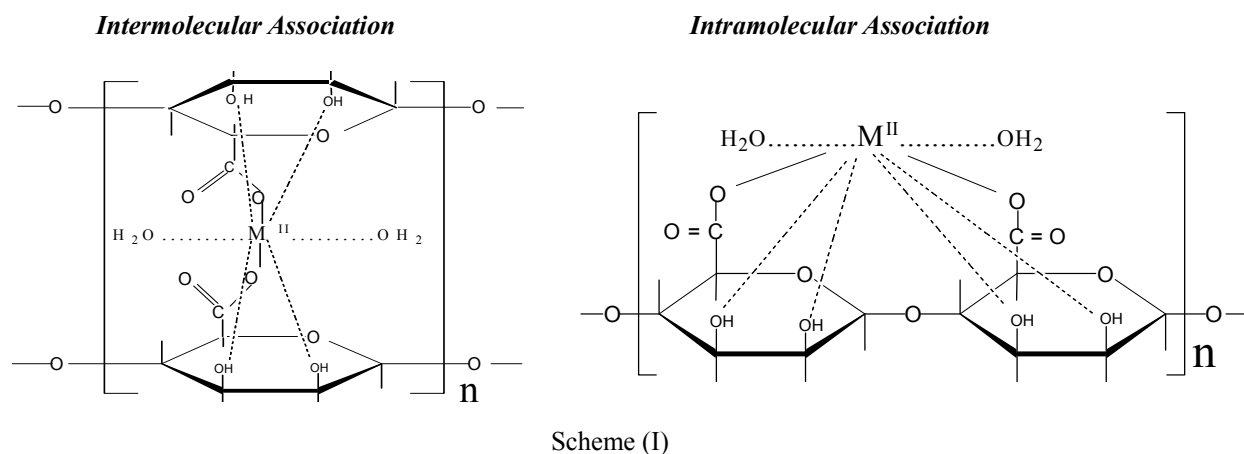
3. Results and Discussion

The exchange process between divalent metal ions of electrolyte solutions and the sodium counter ions of alginate polysaccharide macromolecule conforms to the following stoichiometric equation.



where M represents to Ca, Sr and Ba metals. This exchange process occurs stoichiometrically irrespective of different valences and mobilities of the two exchanging counter ions in order to maintain the electroneutrality requirements (Hellferich, 1962; El-Shatoury, Hassan, & Said, 1992).

The chelation between divalent metal ions and both the hydroxyl and carboxylate functional groups of alginate macromolecule is not just simple. The interdiffused metal ions chelate two carboxylate groups and two or more pairs of the hydroxyl groups of the alginate macromolecule depending on the coordination number of chelated metal ion. Two types of chelation may be suggested (Hassan, 1993; Hassan, El-Shatoury, Mousa, & Hassan, 1988). The first one such chelation refers to the intramolecular association in which the functional groups involved in chelation belong to the same chain. Hence, the plane involving the chelated metal ion is parallel with the plane of alginate macromolecular chains and this configuration may be called a planar geometry. The second type of chelation corresponds to the intermolecular association in which the plane containing the metal ions is perpendicular to the plane of alginate chains. Here, the involved functional groups are related to different chains and the configuration is termed a non-planar structure. The two geometrical configurations are illustrated by Scheme (I).

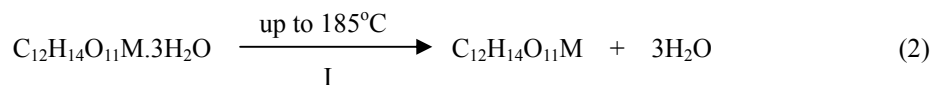


The X-ray diffraction patterns showed that the cited metal alginate complexes are amorphous in nature. The infrared spectra of these complexes indicate that the asymmetric and symmetric vibrations of the carboxylate group, ($\nu_{as} \text{OCO}$) and ($\nu_s \text{OCO}$), are shifted to more or less wavelengths than that of the free ligands (Said, & Hassan, 1993; Khairou, 2002). This indicates the complexation between the metal ions and the carboxylate groups of alginate macrostructure. Again the shift in the ν_{OH} band of 3500 cm^{-1} to lower frequencies which it becomes more broader than that of sodium alginate may support that the OH groups take part in chelation in these metal alginate complexes. FTIR spectra are shown in Figure 1. The vibration assignments are summarized in Table 1.

Table 1. Infrared frequencies (cm^{-1}) for Sodium alginate and cross-linked metal alginate complexes

Compound	$\nu_s \text{OCO}$	ν_{as}	ν_{OH}	$\nu_{\text{M-O}}$	Ref.
Na-alginate	1600	1400	3500	850	Said & Hassan (1993)
Ca(II)- alginate	1595	1421	3288	816	This work
Sr(II)- alginate	1597	1417	3440	813	This work
Ba(II)- alginate	1593	1413	3280	814	This work

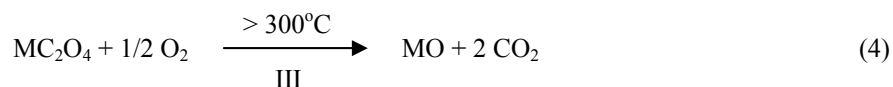
The TG and DTA thermograms (Said & Hassan, 1993) for these metal alginate complexes showed that these complexes exhibited three decomposition stages. A dehydration of the coordinated water molecules occurred in the first step, followed by the decomposition of the dehydrated complexes in the other two steps. A mechanism consistent with the experimental results has been suggested. It involves the dehydration of the coordinated water molecules in the first step,



followed by the formation of metal oxalate intermediates in the second step.



Then, a fast decomposition of these metal oxalates occurred in the third forming the metal oxides as final products as follows,



Since these metal-alginate complexes have a rigid network of linear block structures, the kinetics of their thermal decomposition depends on the model structure of the formed complexes, nature of metal ion, the strength of chelation and the orientation of the macromolecular chains of alginate toward the chelated metal ion.

Evaluation of the reaction mechanism by non-isothermal methods has been discussed by Sestak and Berggen (1970) and Satava (1971), the method is based on the assumption of an existing an infinitesimal time intervals for non-isothermal reactions, so that the rate can be expressed by the Arrhenius type equation

$$\frac{d\alpha}{dt} = Z e^{-E/RT} F(\alpha) \quad (5)$$

where Z is the pre-exponential factor, t is the time, α is the decomposition fraction, and $F(\alpha)$ depends on the process mechanism. Sharp and Co-workers (Sharp, Brindley, & Achar, 1966) suggested a reduced time theoretical method in order to distinguish between the different methods where the time scales in the kinetic equation is:

$$g(\alpha) = kt \quad (6)$$

where, $g(\alpha)$ is the integrated form of $F(\alpha)$ which altered so that

$$g(\alpha) = A(t/t_{0.5}) \quad (7)$$

Here, $t_{0.5}$ is the time for 50% decomposition and A is a constant depending on the form of $g(\alpha)$.

The time $t_{0.5}$, which corresponds to $\alpha = 0.5$, was determined from the experimental data and used to convert the data to curves of the form α against $(t/t_{0.5})$. The non-isothermal data were analyzed by the linear regression analysis according to the various kinetic model functions $g(\alpha)$ (Sestak & Berggen, 1970). The best fitting models for the dehydration processes for the investigated samples are summarized in Table 2.

Table 2. The peak temperature (T_p) and the weight loss accompanying the stage of decomposition for cross-linked metal alginate complexes (heating rate =20 K/min)

Complex	Stage	TG(°C)			Weight loss %	T_p (°C)	Formula
		T_i	T_f	T_m			
Ca(II)-alginate	1 st	51	179	107	11.5	230	$C_{12}H_{14}O_{11}Ca.3H_2O$
	2 nd	179	371	230	48.5		
	3 rd	371	592	418	18.6		
Sr(II)- alginate	1 st	51	174	113	12.9	226	$C_{12}H_{14}O_{11}Sr.3H_2O$
	2 nd	174	303	226	35.6		
	3 rd	303	589	453	21.9		
Ba(II)- alginate	1 st	53	185	117	15.6	222	$C_{12}H_{14}O_{11}Ba.3H_2O$
	2 nd	185	335	22239	27.6		
	3 rd	335	589	2	23.9		

Three different heating rates were used by employing 10 mg of the samples in order to obtain reliable kinetic parameters. The following equation was applied to calculate the kinetic parameters.

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{ZR}{\phi E^{\ddagger 2}} - \ln \frac{2ZR^2 T_p}{\phi E^{\ddagger 2}} - \frac{E^{\ddagger}}{2.303T} \quad (8)$$

where Z denotes the frequency factor, ϕ is the heating rate, E^{\ddagger} is the activation energy, T is the absolute temperature, T_p is the peak temperature of decomposition and R is the gas constant. Equation (8) is based on the proposed reaction mechanism given by Satava together with Coats's-Redfern equation (Coats & Redfern, 1964). This equation required that plots of $\ln g(\alpha)/T^2$ against $1/T$ should be linear as is experimentally observed. The activation energy and frequency factor were determined from the slopes and intercepts of such plots, respectively. These values were calculated by using the method of least-squares and are summarized in Table 3.

Table 3. Kinetic parameters for non-isothermal decomposition of cross-linked metal alginate complexes

Complex	Heating rate K/min	Kinetic model			$E^{\ddagger}, kJmol^{-1}$			$\Delta S^{\ddagger}, J K^{-1} mol^{-1}$			Z, s^{-1}		
		Stages											
		1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd
Ca(II)-alginate	5	F1	A3	F1	122.5	218.5	300.5	-12.0	48.3	93.6	1.7×10^{12}	13.0×10^{13}	
	10	F1	F1	F1	135.4	190.4	317.6	-10.1	27.7	85.6	2.3×10^{12}	13.7×10^{13}	-
	20	A3	A3	A3	77.6	240.2	380.4	-57.2	69.5	80.4	8.1×10^9	13.9×10^{12}	
Sr(II)-alginate	5	-	-	-	-	-	-	-	-	-	-	-	-
	10	R3	A3	F1	95.6	145.4	311.2	-52.7	-20.1	69.2	1.4×10^9	9.2×10^{11}	-
	20	R3	R3	F1	80.4	175.4	256.4	-80.0	-20.2	49.6	5.3×10^8	5.6×10^{13}	
Br(II)-alginate	5	R3	F1	R3	111.9	140.2	300.1	-20.8	-11.1	83.4	6.1×10^{11}	2.9×10^{12}	
	10	R3	F1	F1	120.2	135.4	260.2	-18.7	-17.8	60.2	8.1×10^{11}	1.2×10^{12}	-
	20	R3	R3	R3	89.4	165.9	315.4	-49.5	-7.3	94.5	2.1×10^{10}	4.3×10^{13}	

Again, the entropies of activation can be evaluated from the following relationship (Coats & Redfern, 1964).

$$Z = (k_B T_p / h) \exp(-\Delta S^{\ddagger} / R) \quad (9)$$

where k_B is the Boltzmann's constant and h is the Planck's constant. The negative value of the activation entropies for all complexes in the dehydration stage indicate that the activated complexes formed during the dehydration

processes are more ordered than that of the reactants. The activation energy values obtained along with the peak temperature of decomposition may be considered as a determining factor of complex stability. These values reveal that the stability follow the order $\text{Ca} > \text{Sr} \geq \text{Ba}$ -alginates in good agreement with the magnitude of M-O bond energies (Sanderson, 1976). Again, this order of stability was found to be in good consistent with that reported elsewhere (Haugh & Smidsrod, 1965; Smidsrod, 1965; Schewiger, 1964; Smisrod & Skajak-Brack, 1990; Hassan, El-Shatoury, Mousa, & Hassan, 1988; Hassan, Makhlowf, Summan, & Awad, 1989).

Furthermore, it was found that $\log Z$ values were related linearly with the E values indicating the demonstration of the kinetic compensation effect.

4. Conclusion

Non-isothermal decomposition of the cited biopolymeric metal alginates showed that these complexes were stable until around 300 °C and their thermolysis were proceeding via formation of metal oxalate intermediate fragments. The stability in these studied metal alginate biopolymers follows the order $\text{Ca (II)} > \text{Sr (II)} > \text{Ba (II)}$ in their alginates. Again, the first stage of decomposition indicated that the hydration processes are more ordered than that of the reactants where the kinetic model R_3 was the more predominant for Sr(II) - and Ba (II) - alginates, whereas F_1 kinetic model was preferable for Ca(II) - alginate complex.

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