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KINETICS AND MECHANISM OF THE NON-ISOTHERMAL DECOMPOSITION

I. Some divalent cross-linked metal-alginate ionotropic gels

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Abstracts

The kinetics of thermal decomposition of Sn(II), Pb(II), Cd(II) and Hg(II) alginate gels have been studied using thermogravimetry (TG) and derivative thermogravimetry (DTG) in static air. The thermal dehydration of each gel complex was found to occur in one step, whereas the decomposition of the dehydrated complexes occurred in two steps. The kinetic parameters were computed by different models and a tentative decomposition mechanism consistent with the kinetic observations is discussed.

Keywords: alginates, gels, kinetics, polysaccharides, thermal decomposition

Introduction

Metal-alginate gels are ionotropic in nature [1, 2] differing from the classical type of thermo-gels in which the long chain molecules are held together with van der Waal's forces, a type of chelation between the interfused divalent metal ions and the carboxylate and hydroxyl groups of the alginate macromolecule chains [3], through an egg-box like structure [4–7], occurring in these ionotropic gel complexes.

Solid gels differ from liquids since they have a rigid network. Therefore, the kinetics of their thermal decomposition depends – to a large extent – on the geometrical structure of the gel, the nature and the orientation of the macromolecular chains toward the chelated metal ion.

Although, many patents [8] and publications have been published on the kinetics of sol–gel transformation, electrical properties and chemical equilibrium and thermal decomposition of alginate macromolecule gels [9–18], little attention has been focused on the kinetics of the thermal decomposition.

In view of the above aspects, the present work has undertaken a series of studies on metal-alginate ionotropic gels [9–15]. The results obtained may throw some lights on the stability of these complexes in terms of strength of chelation and geometrical structure.

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Experimental

Materials

All materials used were of Analar quality (BDH). Metal-alginates in the form of granules were prepared as described earlier [17]. Thermal studies were carried out in a Mettler TA 3000 thermal analyzer in static air. Three heating rates were used: 5, 10 and 15 K min^{-1}.

FTIR spectra were recorded on a Pye Unicam Sp 3 100 spectrophotometer using the KBr disc technique (4000–200 cm^{-1}).

Results and discussion

The replacement of counter ions, Na$^+$, in sodium-alginate by these divalent metal ions is inherently a stoichiometric process [10, 17]. The stoichiometry of such exchange process conforms to the following equation

$$2(\text{Alg–Na})_n+\text{M}^{2+}=(\text{Alg}_2\text{–M})_n+2\text{Na}^+ \tag{1}$$

where *M* denotes Sn, Pb, Cd and Hg metal ions.

The infrared spectra of such prepared ionotropic metal-alginate gel complexes was measured and the vibration assignments of the bands are summarized in Table 1. It is well known that the bands correspond to the stretching vibrations of the OCO group in sodium-alginate lie at 1600 and 1400 cm^{-1}, while that belonging to the stretching vibration of the hydrogen bond of the hydroxyl group lies at 3500 cm^{-1}. As is shown in Table 1, the band of the stretching vibrations of –OCO– group of alginate is shifted from 1600 (ν_{as}) to 1601–1637 cm^{-1}, whereas the band at 1400 cm^{-1}. (ν_s) is shifted from 1400 to 1403–1418 cm^{-1}, respectively. This result indicates the participation of this group in chelation. Again, the shift in the νOH band to lower frequencies in all metal-alginate complexes also indicates the participation of –OH group in the chelation process.

Table 1 Infrared vibrations (cm^{-1}) for sodium and cross-linked metal-alginate ionotropic gels

Compound	ν_sOCO	ν_{as}OCO	νOH	νM–O	Reference
Na-alginate	1400	1600	3500	580	[19]
Sr(II)-alginate	1403	1636	3421	813	this work
Pb(II)-alginate	1407	1631	3488	815	this work
Cd(II)-alginate	1418	1601	3489	820	this work
Hg(II)-alginate	1405	1620	3461	816	this work

TG and DTG curves of these gel complexes are shown in Fig. 1. These complexes exhibit three decomposition steps. The dehydration of each complex takes place in one step; while the decomposition of the dehydrated complexes formed occurs in two steps. The mass loss observed was found to be in good agreement with the theoretically calculated values for the formation products.

Again, DTG curves exhibit a series of thermal changes associated with TG curves (Fig. 1). The mass loss on heating the gel complexes from room temperature was not accompanied by peaks in the DTG peaks analogous to those observed earlier [17, 18]. The thermal analyses of these complexes [20] indicated that the mass loss in the first stage is due to the evolution of coordinated water molecules (three water molecules for Cd(II), alginate and two water molecules for the others). While, the loss in mass observed in the second and third stages can be explained by the decomposition of the dehydrated complexes formed.

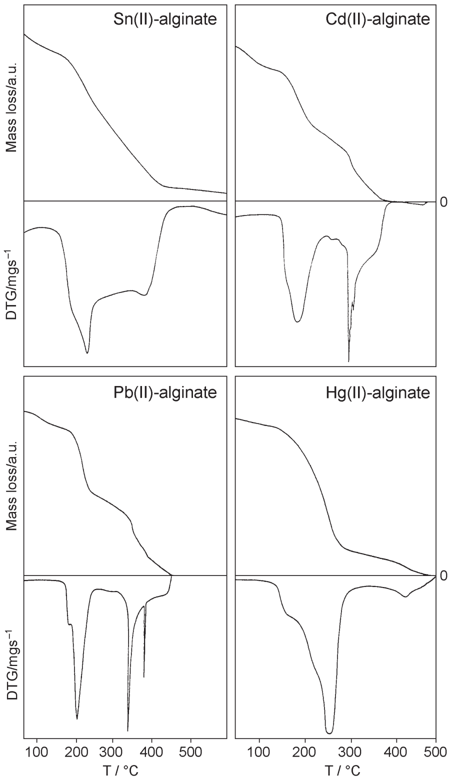

Fig. 1 TG and DTG curves of cross-linked metal-alginate ionotropic gel complexes

The great similarity in the temperature of the peaks of both the second and the third stages for those complexes may reflect the similarity of their thermal decomposition mechanisms.

In view of these interpretations, a mechanism consistent with the experimental observations was suggested by the authors and is to be published in a different paper [20]. It involves the dehydration of the water molecules in the first step.

$$C_{12}H_{14}O_{11}M{\cdot}xH_2O \xrightarrow{\text{first step; up to 170°C}} C_{12}H_{14}O_{11}M+xH_2O \tag{2}$$

followed by formation of an intermediate metal oxalate in case of Pb(II) and Cd(II) or metal carbonate for Sr(II) and Hg(II), respectively, in the second step

$$C_{12}H_{14}O_{11}M+101/2O_2 \xrightarrow{\text{second step; up to 300°C}} MCO_3+11CO_2+7H_2O \tag{3}$$

$$C_{12}H_{14}O_{11}M+10O_2 \xrightarrow{\text{second step; up to 300°C}} MC_2O_4+10CO_2+7H_2O \tag{3'}$$

Then, a decomposition of metal carbonate or oxalate to the metal oxide product occurred in the third step as follows

$$MCO_3 \xrightarrow{\text{third step;>300°C}} MO+CO_2 \tag{4}$$

or

$$MC_2O_4+1/2O_2 \xrightarrow{\text{third step;>300°C}} MO+2CO_2 \tag{4'}$$

The kinetics of non-isothermal decomposition has been discussed by Šesták and Beggren [21] and Stava [22]. The procedure is based on the assumption that the non-isothermal reaction proceed isothermally in an infinitesimal time interval, so that the rate can be expressed by the Arrhenius-type equation.

Table 2 Kinetic parameters for non-isothermal dehydration for cross-linked metal-alginate ionotropic gels

Metal complex	Heating rate/ K min^{-1}	Model	$E^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/ J mol^{-1} K^{-1}	A/s^{-1}
Sn(II)-alginate	5	–	–	–	–
	10	A_3	96.19	–39.57	$6.02{\cdot}10^{10}$
	20	A_3	113.37	–37.58	$8.17{\cdot}10^{10}$
Pb(II)-alginate	5	F_1	120.16	–46.2	$7.18{\cdot}10^{11}$
	10	F_1	136.37	–1.42	$6.49{\cdot}10^{12}$
	20	F_1	116.48	–24.6	$4.08{\cdot}10^{11}$
Cd(II)-alginate	5	A_3	190.38	–14.58	$1.29{\cdot}10^{12}$
	10	A_3	170.21	–21.78	$5.56{\cdot}10^{11}$
	20	A_3	112.42	–38.3	$0.08{\cdot}10^{10}$
Hg(II)-alginate	5	–	–	–	–
	10	F_1	288.28	–25.21	$5.32{\cdot}10^{11}$
	20	F_1	222.51	–31.68	$2.41{\cdot}10^{11}$

However, several methods can be used for the calculation of the kinetic parameters. The following equation was applied

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{\phi E}\left(1-\frac{2RT_c}{E}\right)-\frac{E}{|RT|} \tag{5}$$

where A denotes the frequency factor, ϕ is the heating rate, E is the activation energy, T is the absolute temperature, T_c is the maximum decomposition temperature (T_{max}) and R is the gas constant. Equation (5) is based on the proposed reaction mechanism given by Satava together with the Coats–Redfern equation [25]. For correct kinetic rate equation, the plots of $\ln g(\alpha)/T^2$ *vs.* $1/T$ should be linear as is experimentally observed. The activation energy and frequency factor were determined from the slopes and intercepts of such plots, respectively and calculated using the least-squares method. They are summarized in Table 2.

Again, the entropies of activation, $\Delta S^{\neq}$, were calculated from the relation:

$$A=(k_bT_c/h)\exp(\Delta S^{\neq}/R) \qquad (6)$$

where k_b is the Boltzmann's constant, h is the Planck's constant and T_c is the peak temperature of decomposition, Table 2.

The effect of heating rate 5~20 K min^{-1} on the kinetics of thermal decomposition stages were studied. The peak position on the curves was found to shift to higher temperatures with raising the heating rate.

The negative values of the entropy of activation for all complexes in the initial dehydration step indicate that the activated complexes formed during the dehydration processes are more ordered than the reactants.

The values of activation energies and the maximum temperature for decomposition of the main process may be considered an essential factor for determining the stability of these gel complexes. The observed values reveal that the stability decreased in the following order.

$$\text{Hg–Alg}_2>\text{Cd–Alg}_2\approx\text{Pb–Alg}_2>\text{Sn–Alg}_2$$

in good agreement with the magnitude of M–O bond energies [24] and their coordination geometry [3]. This order was found to be in accordance with that reported elsewhere [20, 25, 27].

Conclusions

The kinetics of non-isothermal decomposition of Sn(II)-, Pb(II)-, Cd(II)- and Hg(II)-alginate ionotropic gel complexes have been studied. TG and DTG curves showed three stages of mass loss along with the presence of a series of thermal decomposition. A dehydration of the coordinated water molecules occurred in the first stage, followed by decomposition of the dehydrated gel complexes formed in the next stages were observed. The activation energies and the maximum temperature of decomposition of the main process showed that the stability decreased in the order Hg>Cd≅Pb>Sn-alginate gel complexes, respectively.

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