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Thermal and electrical studies on some metal alginate compounds

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Abstract

The thermal decomposition of Ag–alg, Se–alg_4 and UO_2–alg_2 compounds has been studied using thermogravimetry (TG), differential thermal analysis (DTA) and electrical conductivity measurements. The original samples are characterized by FTIR spectra. The results obtained reveal that the decomposition of these compounds proceeds via the formation of metal oxalates as intermediate fragments. The electrical conductance of these compounds at low temperature indicates that their geometric structures are non-planar and possess electrical conductivity values which lie in the range of semiconductors. Moreover, the remarkable increase in the conductance values during the decomposition of the intermediate metal oxalates is attributed to the hopping mechanism between the different valencies which exist during their thermolysis. Finally, detailed mechanisms of the various decomposition stages of the metal alginate compounds are suggested.

INTRODUCTION

Alginates are known to possess a high tendency to gelatinize on addition of polyvalent metal ion electrolytes [1–4]. The properties of alginates with different metal ions have been examined [5–10]. From a literature survey, it was found that little work has been published on the thermal behaviour of metal alginate complexes [7]. However the conductance of alginate compounds is very important due to their wide application in photographic films. Some reports have been published on the electrical conductance of metal alginates at low temperature [11–13], but no work has been carried out on the electrical conductance of alginate complex at high temperature. Therefore, the present work was undertaken to study the thermal and electrical properties of silver, selenium and uranyl alginate complexes from room temperature up to 600°C. The techniques employed in this work are TG, DTA, IR and electrical conductivity measurements.

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EXPERIMENTAL

Materials

Analytical reagent grade chemicals were used throughout. Metal alginates in the form of grains were prepared by replacement of Na^+ counter ions in the alginate macromolecules by Ag^+, Se^{4+} and $(UO_2)^{2+}$. This was achieved by stepwise addition of alginate salt to the metal ion electrolyte solution (about 1.0 M) while rapidly stirring the electrolyte solution to avoid the formation of lumpy gelatineous precipitate of metal alginate gel. After completion of the exchange process, the metal alginate grains formed were washed with dionized water, followed by doubly distilled water until the washings became free of the metal ions. The gel samples were dried at 100°C under vacuum over anhydrous $CaCl_2$ or P_2O_5. Sodium alginate sols were prepared as described earlier [14].

Techniques

Thermogravimetry (TG) and differential thermal analysis (DTA) of the alginate compounds were carried out using a Shimadzu computerized thermal analysis system DT-40 (Kyoto, Japan). The system includes programmes which process data from the thermal analyzer with the Chromatopac C-R3A. The rate of heating of the samples was kept at $10\,k\,min^{-1}$ using an air atmosphere at $40\,cm^3\,min^{-1}$. α-Alumina powder for DTA standard was applied as a reference.

FTIR spectra of gel complexes were recorded in transmission mode using a Nicolet Dx-20 B Fourier transform IR spectrometer while the calcined complexes were recorded in KBr discs using a Pye-Unicam SP3-300 infrared spectrometer (Cambridge, UK).

The electrical conductivity measurements accompanying the thermal decomposition of alginates were carried out using the method which has been described previously [15].

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the overall gelation reaction of alginate sol with excess metal ions was determined compleximetrically. The mixture of alginate sol and the ion electrolyte was maintained at room temperature for about 48 h. The stoichiometry of such a sol–gel transformation process can be represented by the equation

$$\underset{\text{sol}}{n\text{Na–alg}} + \underset{\text{electrolyte}}{\text{M}^{n+}} \rightarrow \underset{\text{gel}}{\text{M–alg}_n} + \underset{\text{electrolyte}}{n\text{Na}^+}$$

where M^{n+} is Ag^+, Se^{4+} or UO_2^{2+}.

Infrared spectroscopy

The FTIR spectra of the original samples of Ag, Se and UO^{2+} alginates are given in Fig. 1. They show a broad band near 3410 cm^{-1} due to the stretching vibration of hydrogen bonded hydroxyl groups of the alginate ligand [16]. The bands of γ_aOCO and γ_sOCO groups are shifted from 1600 and 1400 cm^{-1} to 1591 and 1410 cm^{-1}, respectively, for both silver and uranyl alginates and to 1408 and 1626 cm^{-1}, respectively, for selenium alginate. The free ligand has a strong band located at 1735 cm^{-1} which can be assigned to the carbonyl stretching vibration of carbonyl group [17]. The displacement of this band to 1745, 1743 and 1747 cm^{-1} in the spectrum of silver, selenium and uranyl alginates, respectively, may indicate the coordination of the carboxylate group and the appearance of both the

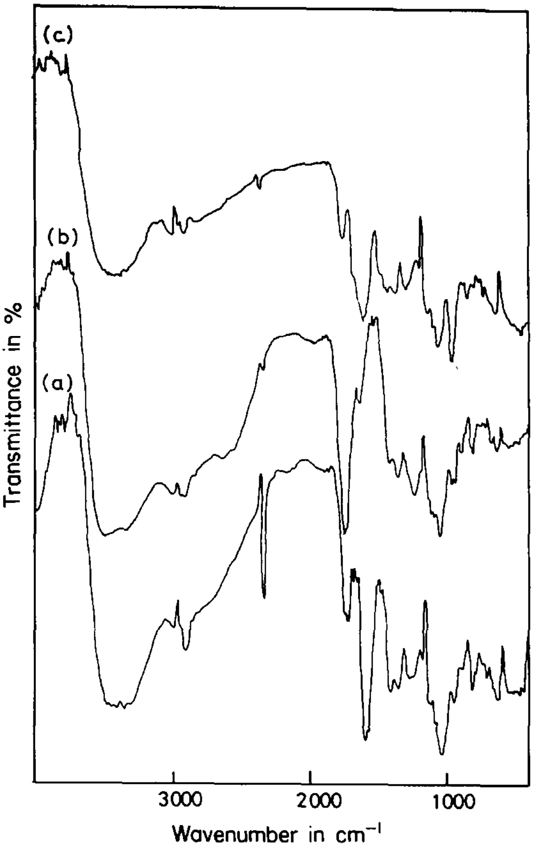


Fig. 1. FTIR spectra for silver alginate (curve a), selenium alginate (curve b) and uranyl alginate (curve c).

asymmetric (γ_a) and symmetric (γ_s) vibrations of the COO^- group. Again, the location of $\gamma_a OCO$ is diagnostic of a bridging carboxylate group.

Thermal decomposition of metal alginate gel compounds

Silver alginate complex

Figure 2 shows the TG and DTA curves of the silver alginate complex while the mass loss and the decomposition temperature range of the decomposition stages are cited in Table 1.

The DTA curve shows that the decomposition of Ag–alg proceeds in two steps. The first exothermic peak has a maximum at 176°C corresponding to the dehydration of Ag–alg. The second, strong and sharp exothermic, peak has a maximum at 350°C and appears to be associated with the breakdown of the intermediate formed during the heating of the Ag–alg to form silver

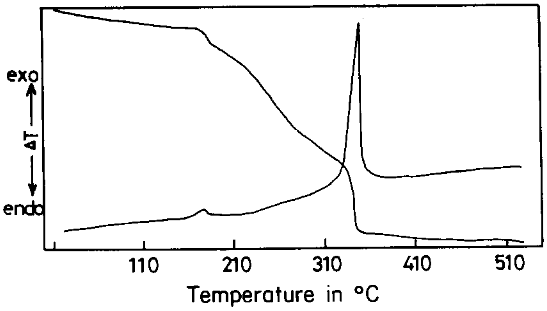


Fig. 2. TG–DTA curves of silver alginate.

TABLE 1

The temperature range and mass loss accompanying the three decomposition stages of alginate complexes

Complex	Temperature range/°C	Mass loss/%	
		Found	Calculated
Ag–alginate	16–210	12.7	12.7
	210–310	27.3	27.2
	310–360	22.4	21.9
Se–alginate	30–190	7.0	6.8
	190–400	58.0	56.9
	420–513	26.0	22.5
UO_2–alginate	45–165	9.4	9.3
	180–316	25.8	22.2
	470–596	19.9	21.2

metal as the end product. The TG curve is characterized by three mass-loss regions. The first mass loss (12.7%) displayed on heating the complex up to 210°C corresponds to the evolution of two water molecules. The second decomposition step, starting above 210°C and extending to about 310°C, involves a mass loss of about 27.3%. This value may correspond to the degradation of Ag–alg by rupture of the bonds to form an intermediate compound. However, the second mass loss is not accompanied by any peak observed on the DTA curve. This behaviour suggests that the formation of the intermediate occurs smoothly, i.e. without gain or loss of heat. On increasing the temperature, the TG curve shows that the third decomposition stage is associated with a 22.4% mass loss. This value corresponds to the decomposition of the intermediate to the final product, silver metal. It is clear that from the above results, the decomposition of Ag–alg proceeds in three stages. These stages can be interpreted as follows:

$$C_6H_7O_6Ag \xrightarrow{20\text{–}210^\circ C} C_6H_3O_4Ag + 2H_2O \tag{1}$$

$$2C_6H_3O_4Ag + (19/2)O_2 \xrightarrow{210\text{–}310^\circ C} Ag_2C_2O_4 \cdot 2H_2O + H_2O + 10CO_2 \tag{2}$$

$$Ag_2C_2O_4 \cdot 2H_2O \xrightarrow{310\text{–}360^\circ C} 2Ag + 2CO_2 + 2H_2O \tag{3}$$

Selenium alginate complex

Thermal decomposition of Se–alg_4 is shown in Fig. 3. The DTA curve shows that the decomposition of Se–alg_4 proceeds in two stages. The first endothermic peak, centred at 186°C, may be attributed to the evolution of both physically adsorbed water and water of crystallization. The second sharp exothermic peak with a maximum at 458°C may correspond to the decomposition of the intermediate fragment formed during the heating of Se–alg_4.

The TG curve shows mass losses in three steps; the first, associated with

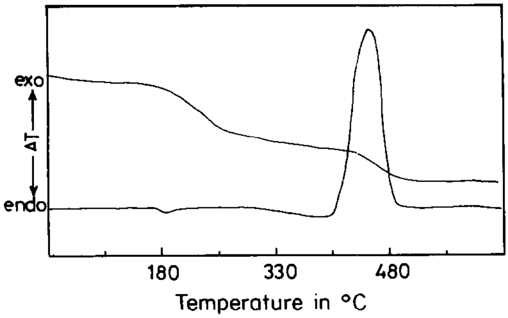


Fig. 3. TG–DTA curves of selenium alginate.

a 7.0% loss, occurs at temperatures up to 190°C and seems to be associated with the loss of three molecules of water. The second mass loss (58%), displayed over the temperature range 190–400°C, corresponds to the degradation of dehydrated Se–alg$_4$ and formation of an intermediate compound. The third mass loss (24%), which occurs in the temperature range 420–512°C, corresponds to the decomposition of the intermediate formed in the second stage to metal oxide as a final product. However, according to the above results, the thermal decomposition of Se–alg$_4$ can be suggested to occur as follows:

$$C_{24}H_{28}O_{22}Se \cdot 3H_2O \xrightarrow{30\text{–}190^\circ C} C_{24}H_{28}O_{22}Se + 3H_2O \quad (4)$$

$$C_{24}H_{28}O_{22}Se + 20O_2 \xrightarrow{190\text{–}400^\circ C} Se(C_2O_4)_2 \cdot 2H_2O + 12H_2O + 20CO_2 \quad (5)$$

$$Se(C_2O_4)_2 \cdot 2H_2 + O_2 \xrightarrow{420\text{–}512^\circ C} SeO_2 + 2CO_2 + 2H_2O \quad (6)$$

Uranyl alginate complex

The TG and DTA curves of uranyl alginate are shown in Fig. 4, from which it may be seen that the DTA curve undergoes two decomposition steps whereas the TG curve exhibits three stages of mass loss. The loss in mass (9.4%) on heating the complex up to 165°C is not associated with any peak on the DTA curve and corresponds to the evolution of four water molecules. On increasing the temperature, the DTA curve exhibits two peaks centred at 198 and 511°C. The first small endothermic peak which is accompanied by 25.8% mass loss may correspond to the degradation of UO$_2$–alg$_2$ to an intermediate compound. It is worth noting that this intermediate is stable on heating to 490°C. The second sharp and strong exothermic peak has a maximum at 511°C and loses 19.9% in mass; this may be attributed to the decomposition of the stable intermediate formed in the second stage to the metal oxide.

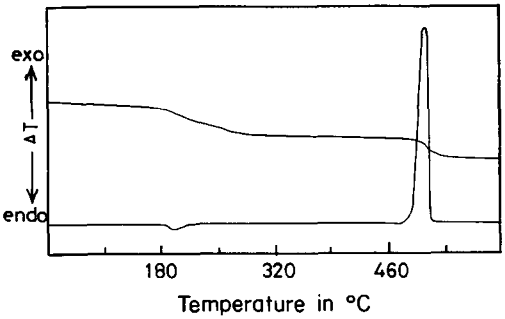


Fig. 4. TG–DTA curves of uranyl alginate.

According to the thermal decomposition behaviour of UO_2–alg_2, the processes of the degradation may proceed as follows:

$$C_{12}H_{14}O_{11}UO_2 \xrightarrow{40\text{–}165°C} C_{12}H_6O_7UO_2 + 4H_2O \qquad (7)$$

$$C_{12}H_6O_7UO_2 + 9O_2 \xrightarrow{185\text{–}316°C} U(C_2O_4)_2 + 3H_2O + 8CO_2 \qquad (8)$$

$$U(C_2O_4)_2 + 1.5O_2 \xrightarrow{470\text{–}596°C} UO_3 + 4CO_2 \qquad (9)$$

From the TG and DTA results of all metal–alginate complexes, we can conclude that similar behaviour occurs in the thermal decomposition of mono-, tetra- and hexavalent metal alginate complexes. In addition, the main sharp and strong peak observed in the DTA curves corresponds to the formation of similar intermediate compounds. Moreover, from Table 1, it is noticed that the observed mass loss is in good agreement with the theoretical value, i.e. with the suggested equations accompanying the thermal degradations. However, recently [7] we reported that the thermolysis of divalent metal alginate compounds was accompanied by the formation of metal oxalates as intermediate fragments. The loss in mass accompanying the main decomposition stage of silver, selenium and uranyl alginates was found to be in good agreement with the calculated masses for the decomposition of the corresponding metal oxalates. Figure 5 shows a comparison of the absorption bands of the IR spectra of Se–alg_4 and UO_2–alg_2 calcined at 300°C and Ag–alg calcined at 220°C for 2 h with that

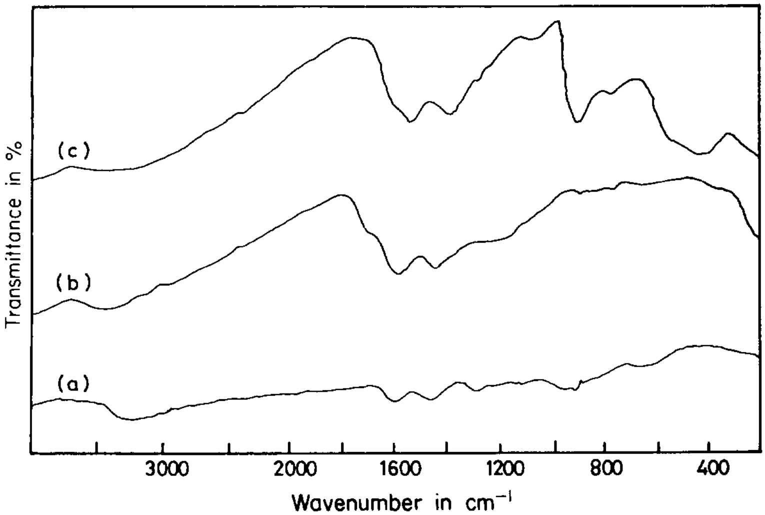


Fig. 5. IR spectra for silver alginate calcined at 220°C for 2 h (curve a), and selenium alginate (curve b) and uranyl alginate (curve c) calcined at 300°C for 2 h.

of their original samples. Figure 1 indicates the presence of bands at 1650 and 1400 cm^{-1} which are assignable to the presence of C=O stretching vibrations [17] and confirm the formation of oxalate groups. Thus, we can suggest that the metal alginates under investigation decompose via metal oxalate intermediates. In addition, from Table 1 the temperature range corresponding to the main decomposition stage reveals that the stabilities of these complexes are in the order UO_2–alg_2 > Se–alg_4 > Ag–alg. The stability of these compounds is in the sequence of the ionic volumes of the metal ions [18].

Electrical conductivity accompanying the thermal decomposition of metal alginate compounds

The electrical conductivities of silver, selenium and uranyl alginates have been measured during their thermal decomposition. The variations of log σ with $1/T$ in the range $20° < t > 500°C$ and under an atmosphere of air are shown in Fig. 6, (curves a, b and c are for silver, selenium and uranyl alginates respectively). Firstly, similar behaviour is observed in the change of conductance with temperature with all the samples. From these curves, some trends and conclusions can be drawn as follows:

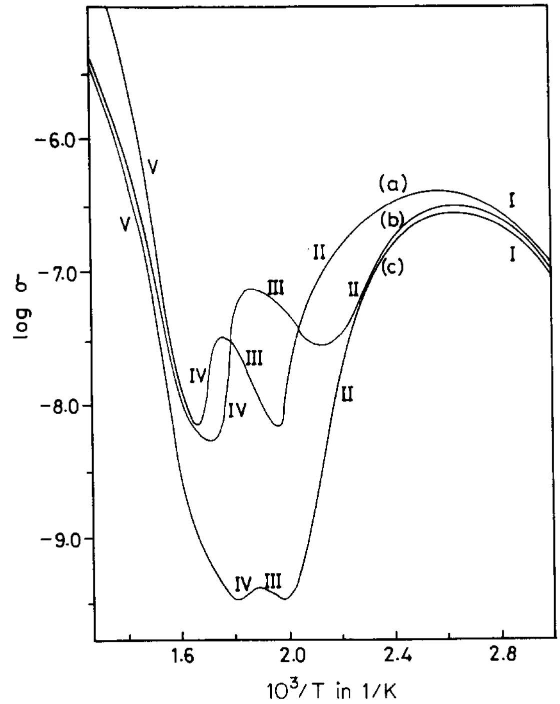
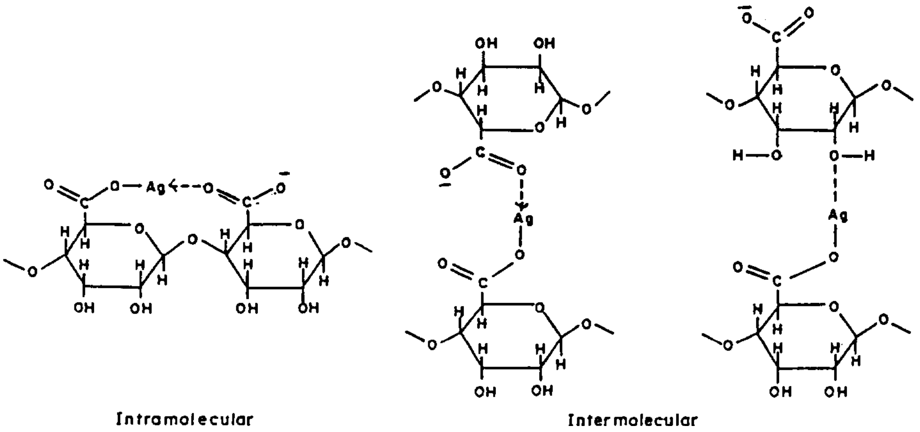


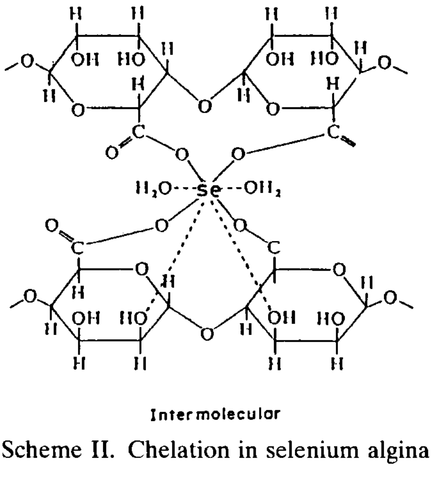
Fig. 6. Variation of log σ with $1/T$ for silver alginate (curve a), selenium alginate (curve b) uranyl alginate (curve c) during their decomposition in air atmosphere.



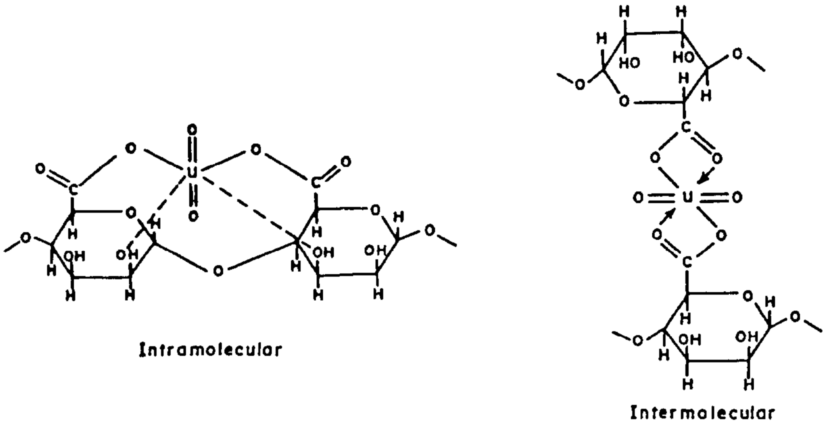
Scheme I. Chelation in silver alginate complex.

(i) In region I, there is a continuous increase in the sample conductance with the increase of temperature which reaches a maximum at about 120°C for all the complexes. The increase in σ values at low temperature may correspond to semiconducting properties of these compounds. It has previously been reported [19] that the metal alginates of planar geometry show electrical properties similar to those of insulators, whereas that of non-planar structure possess electrical conductivity value in the region of semiconductors. Hence, the values of electrical conductivity obtained at stage I suggest that these ions chelate intermolecularly with the functional groups of the alginates. Thus the suggested structures of silver, selenium and uranyl alginates are as shown in Schemes I, II and III, respectively [20].

(ii) The decrease in the conductance values of all samples in region II which reaches a minimum at temperatures between 197 and 235°C may be attributed to the evolution of water molecules. This process may be



Scheme II. Chelation in selenium alginate complex.


Intramolecular

Intermolecular

Scheme III. Chelation in uranyl alginate complex.

accompanied by a decrease in charge carriers due to a rearrangement of bonds inside the molecules.

(iii) On increasing the heating temperature, an increase in the conductance values (region III) has been observed which reaches a maximum in the temperature region 255–295°C. This behaviour indicates that the degradation of the metal alginates is accompanied by an increase in charge carriers. The decrease in the conductance values of these compounds above the maximum (region IV) corresponds to the formation of metal oxalates.

(iv) The steady increase in the conductance values on increasing the temperature as shown in region V is attributed to the decomposition of the intermediate compounds (metal oxalates) to metal or metal oxides. It is well known that the conductance in polymeric compounds occurs via two conduction mechanisms, ionic and electric, depending on the nature of the charge carriers existing within the network of the macromolecular chains. The formation of free radicals and various oxidation states of chelated metal ions demonstrates the electronic conduction mechanism. Thus the sharp increase in the conductance value after the second minimum can be explained by the increase in charge carriers within the solid. The existence of different oxidation states during thermolysis may be facilated by the hopping conduction mechanism which eventually increases the electrical conductivity. These oxidation states are formed by the transfer of electrons from the alginate macromolecules to the cross linked metal ion with the formation of free radical.

The activation energies of the silver, selenium and uranyl alginates in the presence of air are obtained from the slope of the σ–T cooling curves using the relation [21]

$$\sigma = \sigma_0 \exp(-E_a/RT)$$

where σ is the conductance, σ_0 is a constant, E_a is the activation energy of

TABLE 2

The activation energies in eV of metal alginates in air atmosphere

Complex	E_{a_1}	E_{a_2}	E_{Total}
Se–alg$_4$	0.83	0.33	1.16
UO$_2$–alg$_2$	0.62	0.46	1.08

charge carriers. The variation of log σ with $1/T$ is shown in Fig. 6 and the calculated E_σ values are cited in Table 2.

Figure 7 shows that the variation of conductance with $1/T$ exhibits two linear dependences. Of interest is the jump of the conductance of selenium and uranyl alginates on cooling at 315 and 333°C, respectively. These results again support the conclusions drawn from the decomposition of the intermediates which are accompanied by a sharp increase in conductance. Thus this jump may be associated with the change in the valencies of Se and U and a corresponding increase of the hopping mechanism. However it is worth mentioning that the calculation of activation energy for Ag–alg from

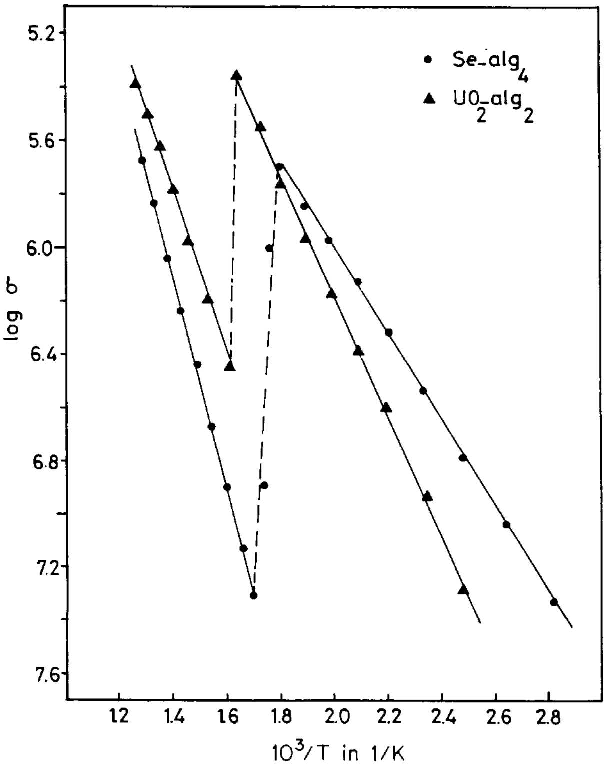


Fig. 7. σ–T cooling curves for selenium alginate (●) and uranyl alginate (▲) under air atmosphere.

the cooling curve in the presence of air atmosphere is impossible because its conductivity is very high and the variation of σ with cooling temperature is very low. This behaviour is attributed to the reduction of Ag–alg to silver metal [12] as the end product.

CONCLUSIONS

These investigations have shown that Ag–alg, Se–alg_4 and UO_2–alg_2 are stable compounds. Their thermolysis proceeds via the formation of metal oxalates as intermediate fragments. The conductance values of these compounds at low temperature indicate that their geometric structures are non-planar and possess electrical conductivity values in the range of semiconductors. Moreover, the noticeable increase in their conductance during decomposition of the intermediate metal oxalates is attributed to the hopping mechanism between the different valencies which exist during thermolysis.

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