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Alginate polyelectrolyte ionotropic gels

Part XV *Physicochemical properties of uranyl alginate complex especially the chemical equilibrium and electrical conductivity related to the coordination geometry*

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The heterogeneous equilibrium for exchange of UO_2^{2+} counter-ions in uranyl alginate exchange resin by H^+ ions has been investigated using titrimetric and spectrophotometric techniques. The thermodynamic equilibrium constant was found to be 15.51 ± 0.33 at 25 °C. The electrical conductivity of uranyl alginate in the form of circular discs has been examined as a function of temperature. The Arrhenius plot of log δ versus $1/T$ showed a complicated behaviour where three regions of conduction were separated by two distinct transition zones. This behaviour was interpreted by the transfer of electrons from alginate to the cross-linked uranyl ion with formation of free radicals and uranium ions of lower oxidation states in a sequence, followed by dimerization of these radicals in the final stages. The X-ray diffraction pattern indicated that the uranyl alginate complex is amorphous in nature. Infrared absorption spectra indicated the presence of UO_2^{2+} chelated to the alginate macromolecular chains, and displayed $\gamma_a CO_2^-$ and $\gamma_s CO_2^-$ in the ranges of 1591 and 1410 cm^{-1} respectively. Two geometrical structures for chelation of UO_2^{2+} with the functional groups of alginate macromolecules have been suggested.

1. Introduction

Electrical conduction in polymers has great importance due to their wide application in thin-film devices. Alginate gels containing chelated metal ions have attracted much attention and have gained wide practical use because of their excellent chemical and mechanical stabilities [1–5].

The electrical conductivity under the influence of very high frequencies for the acid, divalent and trivalent ionotropic metal alginate gels have been previously reported [6, 7], whereas analogous studies of the change in conductance as a function of temperature for Ag(I), Cr(III) and Fe(III) alginate resinates have recently been presented [8, 9].

Therefore, the present study is of great importance to gain some information on the electrical conductivity of alginates containing multiequivalent metal ions as well as to compare the results with that obtained earlier.

2. Experimental procedure

2.1. Materials

The sodium alginate used was Cica-Reagent (Kanto Chem. Co.). All other materials were of analytical grade. Doubly distilled conductivity water was used in all preparations.

2.2. Preparation of uranyl alginate resin

Uranyl alginate complex in the form of a solid resin was prepared by the replacement of Na^+ counter ions of alginate macromolecules by UO_2^{2+} cations. This process was performed by stepwise addition of alginate salt to the electrolyte of uranyl nitrate while rapidly stirring the solution to avoid the formation of a gelatinous precipitate of uranyl alginates in the gel form which swells with difficulty. After completion of this exchange, the resin grains formed were washed with deionized water until the resultant water became

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free of UO_2^{2+} ions and then dried under vacuum. The prepared uranyl alginate complex was stored in dark bottles to avoid the effect of light. Samples in the form of circular discs of diameter 13 mm and thickness 1–2 mm were obtained using an infrared disc press at a constant pressure of 1500 p.s.i. (10^3 p.s.i. = 6.89 N mm^{-2}).

2.3. Equilibrium measurements

Aqueous solutions containing mixtures of uranyl alginate grains and H^+ ions ($HClO_4$) of known concentrations were thermally equilibrated in a constant temperature water-bath maintained at the desired temperature within ±0.1 °C with continuous stirring using a magnetic stirrer. After equilibrium had been attained (24 h), clear solutions containing both reactants were syringed out and the concentrations of H^+ and UO_2^{2+} were determined titrimetrically and spectrophotometrically [10], respectively.

The ionic strength of the mixtures was maintained constant at 0.1 mol dm^{-3} by adding $NaClO_4$ as an inert electrolyte.

2.4. X-ray diffraction

The X-ray diffraction pattern was obtained using a Philip 1710 diffractometer, with copper as a target, and nickel as a filter ($\lambda = 0.154178$ nm) at 40 kV and 30 mA (298 K).

2.5. Infrared spectrum

The infrared spectrum was scanned on BIO-RAD FTS-40 spectrophotometer using KBr powder technique.

2.6. Conductance measurements

The d.c. conductance was measured over the temperature range 290–380 K using a Keithely 610C Electrometer. The uranyl alginate disc was sandwiched under light pressure between two standard electrodes (graphite, copper or silver paste) mounted on to a specially designed temperature-controlled electric furnace provided with a standard copper–constantan thermocouple. The sample was kept short-circuited for about 5 h to make it ready for the experiment. The electrical resistance of the sample was measured, and from this the electrical conductivity, σ, was calculated as follows

$$\sigma = \frac{1}{R}\frac{L}{a} \qquad (1)$$

where R is the Ohmic resistance (Ω), a is the area of the sample surface (cm^2) and L is the thickness of the specimen (cm).

2.7. Scanning electron micrographs

The scanning electron microscopy of the beads was carried out using an electron microscope model JEM-6A, Jeol (Japan).

3. Results and discussion

Sodium alginate shows a high affinity for chelation with multicharged metal ions [1–9]. The replacement of Na^+ counter-ions in alginates with these metal ions leads to the formation of capillary ionotropic metal alginate gel complexes. The gelation process between UO_2^{2+} ions and sodium alginate can be expressed stoichiometrically as follows

$$\underset{(aq)}{UO_2^{2+}} + \underset{(aq)}{2Na\text{–}Alg} = \underset{(gel)}{UO_2 - Alg_2} + \underset{(aq)}{2Na^+} \qquad (2)$$

when alginates in the sol form are allowed to fall from a dropper into uranyl electrolyte solution, pellets of high elasticity and spherical shape are formed. The mechanism of the gelation process was described in detail previously [11]. These pellets are ionotropic in nature in which the interdiffused metal ions are chelated to the functional groups of the alginate macromolecular chains by partially ionic and partially coordinate bonds. A porous structure was observed in a transverse section in these pellets, while trapping capillaries were shown in a longitudinal section [12]. On the other hand, when sodium alginate salt is added step-by-step to uranyl electrolyte solution with rapid stirring, uranyl alginate resin grains are formed as follows,

$$\underset{(aq)}{UO_2^{2+}} + \underset{(s)}{2Na\text{–}Alg} = \underset{(s)}{UO_2\text{–}Alg_2} + \underset{(aq)}{2Na^2} \qquad (3)$$

In uranyl alginate complexes, the interdiffused uranyl ion chelates the functional groups of alginate macromolecular chains by two distinct association mechanisms. In the first mechanism, the uranyl ion cross-links the functional groups of two different chains (Fig. 1) and the plane containing the chelated metal ion is perpendicular to the plane of alginate chains. This structure corresponds to an intermolecular association or non-planar geometry [13]. The second type of chelation is termed an intramolecular association or planar geometry (Fig. 2) in which the uranyl ion chelates the functional groups of the same chain and the plane containing the metal ion is parallel to the plane of alginate chains [14]. The nature of chelation depends on the coordination number of the interdiffused metal ion.

Ion exchange equilibrium has been attained when the UO_2^{2+} counter ions in the alginate resin are replaced by other different counter cations such as H^+ ions [1]. The equilibrium of ion exchange between UO_2^{2+} and H^+ ions can be expressed by

$$\underset{(s)}{UO_2\text{–}Alg_2} + \underset{(aq)}{2H^+} \overset{K_c}{\rightleftharpoons} \underset{(s)}{2H\text{–}Alg} + \underset{(aq)}{UO_2^{2+}} \qquad (4)$$

Applying the mass action law for such a heterogeneous system and assuming that the activities of the solid phase are always unity [15] and the ratio of the activity coefficients in the solid phase is constant [16], the following relationship is obtained

$$K_a = K_c \frac{\gamma UO_2^{2+}}{\gamma^2 H^+} \qquad (5)$$

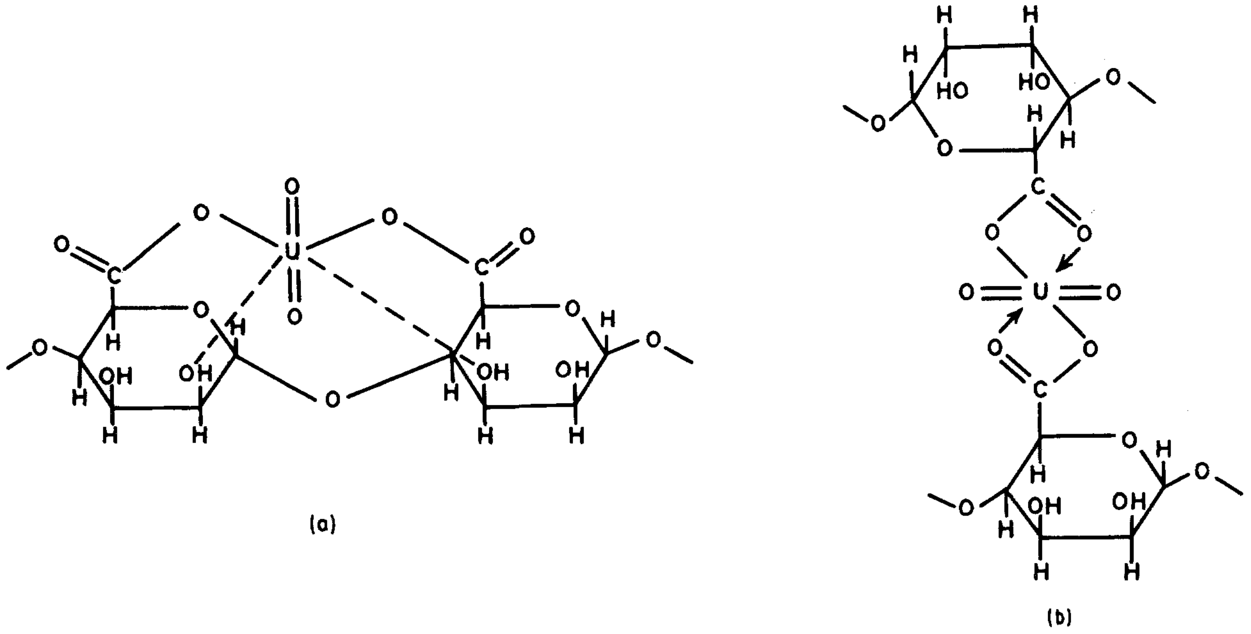

Figure 1 Chelation in uranyl alginate complex: (a) intramolecular, (b) intermolecular.

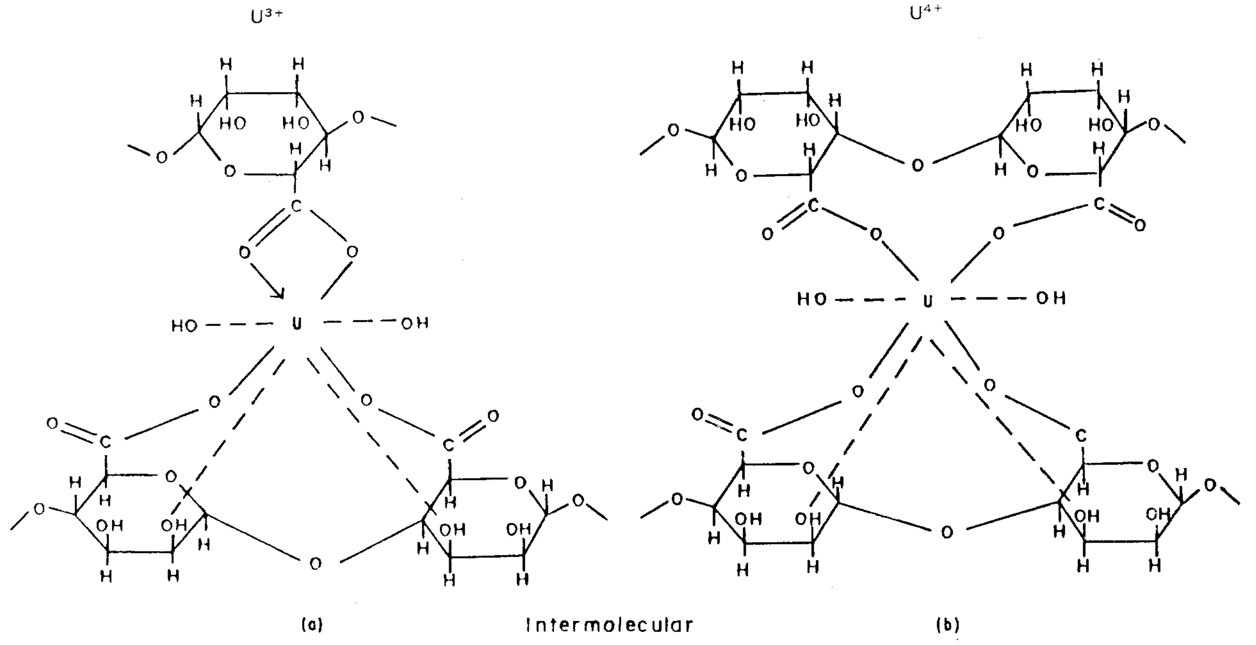

Figure 2 Chelation in (a) trivalent and (b) tetravalent metal alginate complexes.

where γ is the activity coefficient of the respective ions, K_a is the thermodynamic equilibrium constant and may vary with the composition of the solid phase and K_c is the equilibrium constant and can be defined as

$$K_c = \frac{[UO_2^{2+}]}{[H^+]^2} \qquad (6)$$

The value of K_a was found to be 15.52 ± 0.33 at 25 °C.

Again, the standard free energy of exchange can be calculated from the well-known equation [16–18].

$$-\Delta G^\circ = RT \ln K \qquad (7)$$

The value of ΔG° was found to be -6.79 ± 0.27 kJ mol^{-1} at 25 °C.

The X-ray diffraction patterns indicate that uranyl alginate polymer is amorphous in nature and, hence, the stacking of alginate chain blocks is mediated by the uranyl ions. Relevant infrared bands which provide considerable structural evidence for the mode of attachment of alginate functional groups to the UO_2^{2+} ion are shown in Fig. 3. The appearance of a band at 930 cm^{-1} indicates the presence of chelated uranium ions in the form of uranyl species [17]. The bands of $\gamma_a CO_2^-$ and $\gamma_s CO_2^-$ are shifted from 1600 and 1400 cm^{-1} to 1591 and 1410 cm^{-1}, respectively indicating the complexation of UO_2^{2+} and functional groups of alginate chains. The broad band observed near 3410 cm^{-1} is due to γ_{OH} of water (or OH-free functional groups) of the alginate ligand. The free ligand has a strong band in the 1735 cm^{-1} which can be assigned to the carbonyl stretching vibration of the carbonyl group [18]. The displacement of this band to 1747 cm^{-1} in the spectrum of uranyl alginate (Fig. 3) may indicate the coordination of the carboxylate

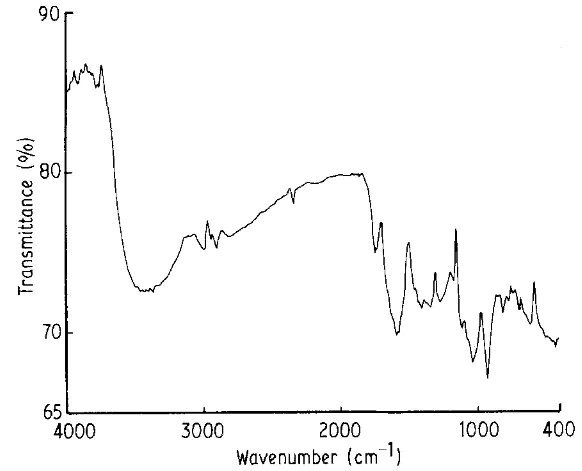

Figure 3 Infrared spectrum of uranyl alginate complex.

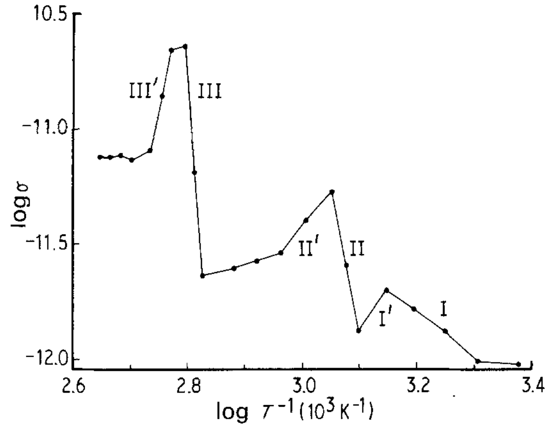

Figure 4 Plot of log σ versus $1/T$ for uranyl alginate complex.

group with the appearance of both the asymmetric, γ_a, and symmetric, γ_s, vibrations of the $\mathrm{COO^-}$ group. Again, the location of γ_aOCO is diagnostic of a bridging carboxylate group.

The values of electrical conductivity were measured using different electrodes such as graphite, copper and silver paste. The results obtained were found to be in good agreement with each other confirming the reproducibility of the conductance measurements. The plot of log σ versus $1/T$ displayed a complicated behaviour as shown in Fig. 4. This behaviour may be explained by the multi-equivalent states of chelated uranium ions. Uranium ions are known to possess various oxidation states varying from U(VI), U(V), U(IV) to U(III) [19]. The observed increase in the electrical conductivity with increasing temperature at Stages I, II and III, indicates the presence of various oxidation states of cross-linked uranium ions. These oxidation states are formed by the transfer of electrons from the alginate macromolecules to the cross-linked uranyl ion with the formation of free radicals. This process takes place in a sequence of one-electron changes as follows

$$(\mathrm{RCOO^-})_{\dot{n}_1}\mathrm{U^{VI}} \longrightarrow (\mathrm{RCO}_2^{\cdot})_{\dot{n}_1}\mathrm{U^{V}} \qquad (8)$$

$$(\mathrm{RCOO^-})_{\dot{n}_2}\mathrm{U^{V}} \longrightarrow (\mathrm{RCO}_2^{\cdot})_{\dot{n}_2}\mathrm{U^{IV}} \qquad (9)$$

$$(\mathrm{RCOO^-})_{\dot{n}_3}\mathrm{U^{IV}} \longrightarrow (\mathrm{RCO}_2^{\cdot})_{\dot{n}_3}\mathrm{U^{III}} \qquad (10)$$

where $\mathrm{RCO_2}$ represents the alginate macromolecule monomers and $\mathrm{RCO}_2^{\cdot}$ is the formed radical.

Again, the decrease in σ values observed in Stages I′, II′ and III′ may be explained by the dimerization of the free radicals formed, thus

$$(\mathrm{RCO}_2^{\cdot})_{\dot{n}_1}\mathrm{U^{V}} + (\mathrm{RCO}_2^{\cdot})_{\dot{n}_1}\mathrm{U^{V}} \longrightarrow 2(\mathrm{RCO_2})_{\dot{n}_1}\mathrm{U^{V}} \qquad (11)$$

$$(\mathrm{RCO}_2^{\cdot})_{\dot{n}_2}\mathrm{U^{IV}} + (\mathrm{RCO}_2^{\cdot})_{\dot{n}_2}\mathrm{U^{IV}} \longrightarrow 2(\mathrm{RCO_2})_{\dot{n}_2}\mathrm{U^{IV}} \qquad (12)$$

$$(\mathrm{RCO}_2^{\cdot})_{\dot{n}_3}\mathrm{U^{III}} + (\mathrm{RCO}_2^{\cdot})_{\dot{n}_3}\mathrm{U^{III}} \longrightarrow 2(\mathrm{RCO_2})_{\dot{n}_3}\mathrm{U^{III}} \qquad (13)$$

The discontinuity in the decreasing electrical conductivity with the appearance of two distinct steps at the second stage (II′) may be attributed to the recombination of $(\mathrm{RCO}_2^{\cdot})_{n_1}$ and $(\mathrm{RCO}_2^{\cdot})_{n_2}$ free radicals or to the change in the structure of uranium ion from the oxygenated type $\mathrm{U^VO_2^+}$ to the deoxygenated one, U(IV).

It has been previously reported [20] that the metal alginates of planar geometry show electrical properties similar to those of insulators, whereas metal alginates of non-planar structure possess electrical conductivity values in the range of semiconductors. Hence, the values of electrical conductivity observed in the initial stage (I) suggest that the uranyl ion chelates the functional groups of alginates via an intramolecular association mechanism. This suggestion coincides with the coordination geometry of the uranyl ion, which tends to be of octahedral structure in its complexes [17]. This fact is confirmed by the presence of the uranium ion as $\mathrm{U^{VI}O_2^{2+}}$ in the first stage (Fig. 3). On the other hand, the magnitudes of electrical conductivities in the second and third stages (II and III) may indicate the presence of intermolecular association mechanisms for the chelated uranium ions. In turn, this requires the presence of tetra- and trivalent uranium ions, which may be formed by the reduction of U(VI) through Equations 9 and 10, chelated to the alginate macromolecules. This fact can be explained by the charge carriers which tend to gain maximum speed in the case of perpendicular geometry, owing to the presence of multi-channels around the planes. These channels facilitate the migration of charge carriers and, hence, the electrical conductivity increases.

Furthermore, the change in colour of the uranium alginate complex before and after temperature treatment may confirm the formation of various oxidation states of the uranium ions chelated to the alginate macromolecules [19]. Typical photos are shown in Fig. 5. The sharp break observed for the decrease in conductance in the first stage can be explained by the instability of the uranium(V) formed at this stage which tends to decompose rapidly to give a more stable uranium(IV) ion [21]. The difference in heights of the observed peaks, i.e. the magnitude of the electrical conductivity confirms the presence of various oxidation states of chelated uranium ions. The slopes of such peaks may be considered as a determining factor for the electrical conductivity of the uranium alginate complexes formed. The experimental observations indicated that the slopes increase in the order

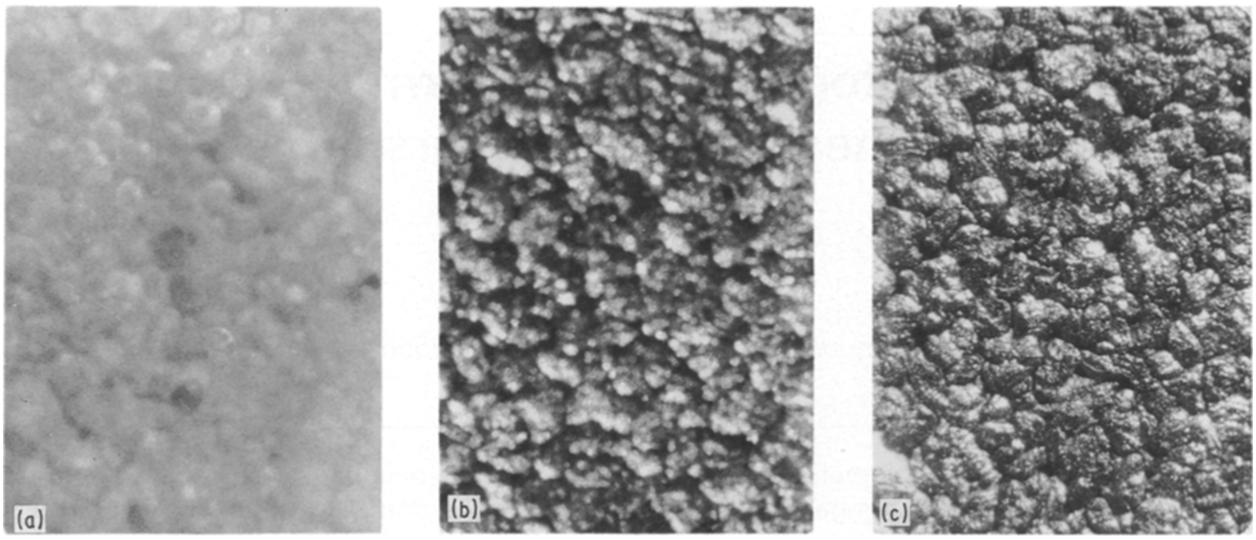

Figure 5 Optical images in uranyl alginate complexes (a) before, (b) during, and (c) after treatment.

(III) > (II) > (I) alginates. This means that the conductance of U(VI) < U(V) < U(IV) in their alginates, respectively. This fact is supported by the reduction potentials of U(VI)/U(V) (0.06 V), U(V)/U(IV) (0.58 V) and U(IV)/U(III) (−0.61 V) couples [22]. This fact is in good agreement with the electrical conductivities of the metal alginate complexes [8, 9, 20, 23].

The region at which no change occurs in σ values at the very high temperatures (IV) may be interpreted in terms of achievements of a steady-state equilibrium for the decarboxylation processes. An alternative explanation may be considered: the degradation of alginate molecules following the decarboxylation processes and/or the removal of water molecules present in the amorphous region of the complex in the final stage. Thermogravimetric analysis (TGA) of the uranyl alginate complex indicated that the water content does not exceed 5%–8% and the thermal decomposition of the complex occurs at temperatures >425 K. This can be considered as an indirect evidence for the suggested mechanism to be published in *J. Thermochem. acta.*

The energies of activation were calculated from the Arrhenius plot and found to be 0.37 ± 0.12, 2.57 ± 0.28 and 6.03 ± 0.35 eV for Stages I, II and III, respectively. These values may reflect the stability of uranium alginate complexes which decreases with decreasing valency of the chelated uranium ion, i.e. it decreases in the order U(III) > U(IV) > U(V) > U(VI) alginates.

It is well known that the conductance in polymeric compounds occurred via two conduction types: ionic and electronic mechanisms, respectively. This depends on the nature of the charge carriers within the frame network of the macromolecular chains. The formation of free radicals and various oxidation states of chelated uranium ions may suggest the demonstration of the electronic conduction mechanism. The activation energy values support this suggestion [24].

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