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Physicochemical studies on cross-linked thorium(IV)–alginate complex especially the electrical conductivity and chemical equilibrium related to the coordination geometry

Ishaq A. Zaafarany ^{a,*}, Khalid S. Khairou ^a, Refat M. Hassan ^b, Yasuhisa Ikeda ^c

^a Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 13401, Saudi Arabia

^b Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

^c Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo 152-8550, Japan

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Abstract The electrical conductivity of cross-linked thorium(IV)–alginate complex in the form of circular disc has been investigated as a function of temperature. The Arrhenius plot of $\log \sigma$ vs. $1/T$ showed a simple parabolic shape at the early stages, followed by a sharply increase in σ values with raising the temperature at the final stages. This behaviour was interpreted by the formation of free-radicals at the initial stages, followed by the degradation of the complex at elevated temperatures to give rise to thorium oxide product. The heterogeneous chemical equilibrium for exchange of Th^{4+} counter ions in the complex by H^+ ions has been investigated by titrimetric and complexometric techniques. The thermodynamic equilibrium constant was found to be $26 \pm 0.25 \text{ dm}^3 \text{ mol}^{-1}$ at 25 °C. The X-ray diffraction pattern indicated that thorium(IV)–alginate complex is amorphous in nature. Infrared absorption spectra indicated that Th^{4+} is chelated to alginate macromolecular chains and displayed $t_s \text{ OCO}^-$ and $t_{as} \text{ OCO}^-$ in the ranges of 1419 and 1635 cm^{-1} , respectively. A geometrical structure for chelation of thorium(IV) to the functional groups of alginate macromolecule is suggested and discussed in terms of complex stability.

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* Corresponding author.

E-mail address: ishaq_zaafarany@yahoo.com (I.A. Zaafarany).



1. Introduction

Alginic acid is a polyuronide comprising D-mannuronic and L-guluronic acids linked through $\beta(1 \rightarrow 4)$ positions in a linear block copolymer structure (Specker et al., 1954; Thiele et al., 1955, 1957; Haug and Smidsrod, 1965; Muzzarelli, 1972). It is well known that alginate has a high affinity for chelation with polyvalent metal ions to form the corresponding cross-linked complexes in either gel or granule forms depending on

the method of preparation (Awad et al., 1979; Awad and El-Cheikh, 1981; Hassan et al., 1992, 1988). A kind of chelation occurs between the interdiffused metal ions and the carboxylate and hydroxyl groups of the alginate macromolecular chains (Rees et al., 1972; Hirst and Rees, 1965; Rees and Scott, 1971; Schweiger, 1962, 1964; Hassan et al., 1991; Hassan, 1993).

Although, the electrical conductivity of synthetic polymer complexes (Khan and Khan, 2007a,b) has attracted many investigators from both theoretical and practical points of view, a little attention has been focused to that of natural polymers such as metal–alginate complexes. Indeed, Hassan and coworkers studied the electrical conductivity of these natural polymer derivative complexes under the influence of high frequencies for the acid, divalent and trivalent metal–alginate complexes in either gel (Hassan, 1989; Hassan et al., 1989) or granule (Abdel-Wahab et al., 1997; Ahmed et al., 1997) forms. On the other hand, analogous studies of the change of conductance as a function of temperature for monovalent (Hassan, 1991), divalent (Khairou and Hassan, 2002), trivalent (Zaafarany et al., in press) and hexavalent (Hassan et al., 1993) metal–alginate complexes in the form of granules have been reported earlier.

In view of the above aspects, the present study seems to be of interest to gain some information on the electrical properties and chemical equilibrium of alginate complexes containing cross-linked tetravalent metal ions. In addition, the results obtained may shed some light on the stability of these complexes in terms of their coordination geometry.

2. Experimental

2.1. Materials

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

2.2. Preparation of thorium(IV)–alginate granules

Thorium(IV)–alginate complex in the form of granules was prepared by the replacement of Na^+ counter ions of alginate macromolecule by Th^{4+} cations. This process was performed by stepwise addition of the alginate powder to an electrolyte of thorium(IV) ions while rapidly stirring the solution to avoid the formation of lumps, which swell with difficulty. After completion of the exchange process, the grains formed were washed with deionized water until the resultant water became free of Th^{4+} ions and then dried under vacuum as described elsewhere (Hassan, 1991; Khairou and Hassan, 2002).

Samples in the form of circular discs of diameter 13 mm and thickness 2–3 mm were obtained using an infrared disc press at a constant pressure of 1500 psi (10^3 psi = 6.89 N m^{-2}).

2.3. X-ray diffraction

The X-ray diffraction patterns was obtained using a Philip 1710 diffractometer, with copper as target and nickel as a filter ($\lambda = 1.54178 \text{ \AA}$) at 40 kV and 30 mA. The scanning speed was 3.6 min^{-1} in the range of $2\theta = 2\text{--}60$ (298 K) as described elsewhere (Hassan, 1991; Khairou and Hassan, 2002).

2.4. Infrared spectrum

The IR spectra were scanned on a Pye Unicam Sp3100 spectrophotometer using the KBr disc technique ($4000\text{--}400 \text{ cm}^{-1}$). The method include mixing few mgs of a fine powder of the sample with KBr powder in agate mortar. The mixture was then pressed by means of a hydraulic press. The transmittance was automatically registered against wavenumber (cm^{-1}). Relevant IR bands which provide considerably structural evidence for the mode of attachment of alginate functional groups to thorium(IV) were obtained.

2.5. Conductance measurements

The dc conductance was measured over the temperature range 290–560 K using a Keithely 610 C electrometer as described previously (Hassan, 1991; Khairou and Hassan, 2002; Zaafarany et al., in press; Hassan et al., 1993). The thorium(IV)–alginate complex was sandwiched between two standard electrodes (graphite, copper or silver paste) mounted into a specially designed temperature-controlled electric furnace provided with a special copper–constantan thermocouple. The sample was kept 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:

$$\sigma = (1/R)(L/a), \quad (1)$$

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

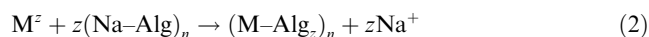
2.6. Equilibrium measurements

Aqueous solutions containing mixtures of thorium(IV)–alginate complex grains and hydrogen ions (HClO_4) of known concentrations were thermally equilibrated in a constant temperature water-bath maintained at the desired temperature within $\pm 0.05^\circ\text{C}$ 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 Th^{4+} were determined titrimetrically and complexometrically (Hassan, 1991; Vogel, 1978), respectively.

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

3. Results and discussion

The replacement of Na^+ counter ions of alginate macromolecule by a polyvalent metal ions is an inherent stoichiometric exchange process (Muzzarelli, 1972; Hellferich, 1962) which leads to the formation of the corresponding cross-linked metal–alginate complexes as follows:



where M denotes the polyvalent metal ion and z stands to its valency. The interdiffused metal ions chelate the carboxylate and hydroxyl functional groups of alginate macromolecular chains by partially ionic and partially coordinate bonds (Awad et al., 1979; Awad and El-Cheikh, 1981; Khan and Khan, 2007a,b), respectively.

In general, there are two types of chelation in these cross-linked metal–alginate complexes (Hassan, 1993). The first type

in which the interdiffused metal ion cross-links the functional groups of two different chains and the plane containing the chelated metal ion is perpendicular to the plane of alginate chains. This type of chelation corresponds to the intermolecular association or non-planar geometry. The second type of chelation represents the intermolecular association or planar geometry in which the metal ion cross-links the functional groups of the same chain and the plane containing the metal ion is parallel to the plane of alginate chains. The type and nature of chelation depends on the valency and coordination number of the interdiffused metal ion, respectively.

It is well known that most of the divalent metal cations are of octahedral six coordination geometry in their complexes (Martell, 1972). Therefore, these metal ions have the choice to chelate the functional groups of alginate via either inter- or intramolecular association in order to attain the octahedral geometry.

However, in tri- and tetravalent metal cations, the octahedral geometry can be attained only via an intermolecular association. This fact is owing to the difficulty of stretching the chemical bonds to involve three or four neighbor monomers of the same chain in case of intramolecular association. The chelates of metal ions in case of intramolecular association mechanism, resemble an egg-carton like structure (Rees et al., 1972; Hirst and Rees, 1965; Rees and Scott, 1971; Schweiger, 1962, 1964).

The X-ray diffraction patterns indicate that thorium(IV)–alginate complex is amorphous in nature and, hence, the stacking alginate chains blocks are mediated by thorium(IV) ions. Relevant infrared bands which provide considerable structural evidence for the mode of attachment of alginate functional groups to Th^{4+} ion are shown in Fig. 1. The appearance of a band at 890 cm^{-1} indicates the presence of chelated thorium(IV) ions (Cozzi et al., 1965; Bellamy, 1975). The bands of $\nu_s\text{CO}_2^-$ and $\nu_{as}\text{CO}_2^-$ are shifted from 1400 and 1600 cm^{-1} in alginate to 1419 and 1635 cm^{-1} in the complex, respectively, indicating the complexation of Th^{4+} ion and the functional groups of alginate chains. The broad band observed at 3461 cm^{-1} is due to ν_{OH} of water or (OH-free functional groups) (Cozzi et al., 1965). The displacement of this band to 1749 cm^{-1} of the spectrum of thorium(IV)–alginate complex

(Fig. 1) may indicate the coordination of the carboxylate group with the appearance of both symmetric (t_s) and asymmetric (t_{as}) vibrations of COO^- groups. Again, the location of $t_s\text{OCO}$ is diagnostic of a bridging carboxylate groups.

The values of electrical conductivity which were measured using different electrodes were found to be in good agreement with each other confirming the reproducibility of the conductance measurements. The plot of $\log \sigma$ vs. $1/T$ displayed a simple parabolic shape at the early stages, followed by a slight increase in σ values on raising temperatures. Then, a sharply increase in the electrical conductivity is observed at elevated temperatures of measurements as shown in Fig. 2.

It has been previously reported (Hassan, 1993) that the metal–alginate complexes of planar geometry show electrical properties similar to those of insulators, whereas those of non-planar structure possess electrical conductivity values in the range of semiconductors. This fact can be explained by the charge carriers which tend to gain maximum speed in case of a perpendicular geometry owing to the presence of multi-channels around the planes. These channels facilitate the migration of charge carriers and, hence, an increase in the electrical conductivity occurs.

3.1. Conductance mechanism

In general, the electrical conductivity of polymeric materials is usually attributed to the presence of low molecular mass impurities of free-ions not connected chemically with the macromolecules (Seanor, 1968; Miyoshi and Saito, 1968; Baird, 1970). Therefore, a suitable conductance mechanism for the electrical properties of Th^{4+} –alginate complex may be suggested. The small increase of σ values observed at the initial stages (i) may be attributed to the slight density of charge carriers (intrinsic conductance). The subsequent appreciable increase of σ values may be due to either the dehydration process of the coordinated water molecules in the complex sphere or the formation of free-radicals.

Since the alginate complexes of divalent metal ions contain similar coordinated water molecules in their atmospheric

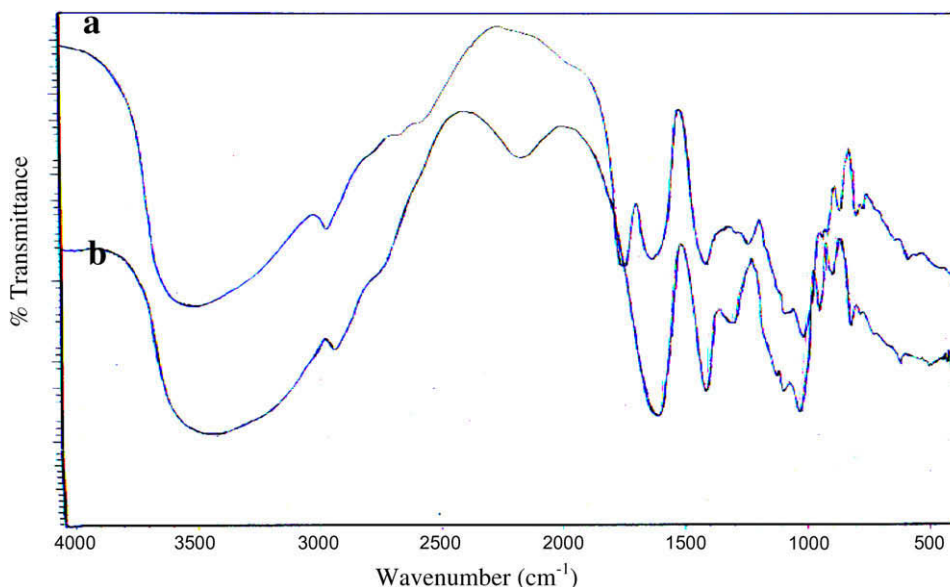


Figure 1 Infrared spectrum of (a) alginate (b) cross linked thorium(IV)–alginate complex.

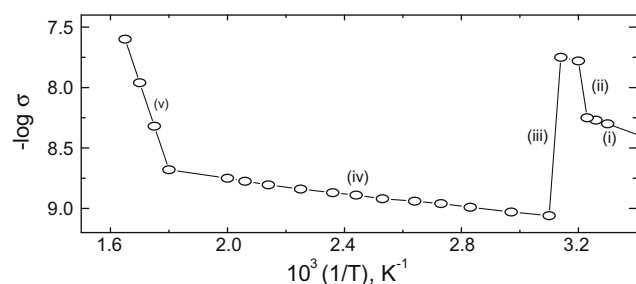
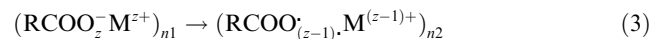


Figure 2 The electrical conductivity as a function of temperature for cross-linked thorium(IV)-alginate complex.

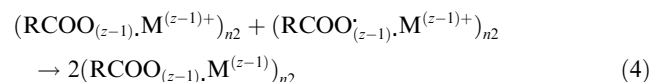
region (Said and Hassan, 1993; El-Gahami et al., 2003) and there is no any parabolic behaviour (Khairou and Hassan, 2002), then the suggestion based on increasing the electrical conductivity by the dehydration process would be excluded. Hence, the formation of free-radicals is the more favorable explanation for the increase of σ values of the parabolic shape.

Similar parabolic behaviour was observed with respect to cross-linked trivalent (Zaafarany et al., in press) and hexavalent (Hassan et al., 1993) metal-alginate complexes. The increase of σ values was interpreted by the formation of free-radical complexes as a result of electron transfer from alginate macromolecule to the chelated metal ions to form metal ions of lower oxidation states. However, there is no evidence for existence of any lower oxidation states for thorium cation in solution (Cotton and Wilkinson, 1972), the existence of Th^{3+} and Th^{2+} is possible in the solid state (Cotton and Wilkinson, 1972; Moller, 1967).

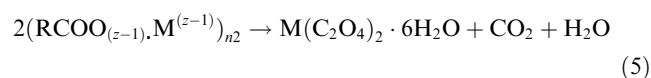
Consequently, the increase of σ values in the parabolic shape at the early stages (ii) can be interpreted by the formation of free-radical complex with lower oxidation state of thorium ion as follows:



where RCOO^{\cdot} represents the alginate macromolecule, RCOO^- is the formed radical, M is the thorium metal ion and z stands for its valency. Again, the dimerization of the free-radicals should be accompanied by a decrease in the electrical conductivity as it is experimentally observed in region (iii):



The thermal decomposition of thorium(IV)-alginate complex (Hassan and Zaafarany, submitted for publication) indicated that the dehydration of the coordinated water molecules occurs at the initial stage (< 375 K). This dehydration is followed by a degradation process to form the corresponding metal oxalate (< 450 K). This intermediate is subsequently decomposed to give the metal oxide product at the final stage. Accordingly, the region at which a slightly increase in σ values (iv) can be explained by the formation of oxalate intermediate resulting from the decomposition of the complex formed (Eq. 4)



Again, the sharp increase in σ values (v) observed at high temperatures (> 450 K) can be attributed to the decomposition of

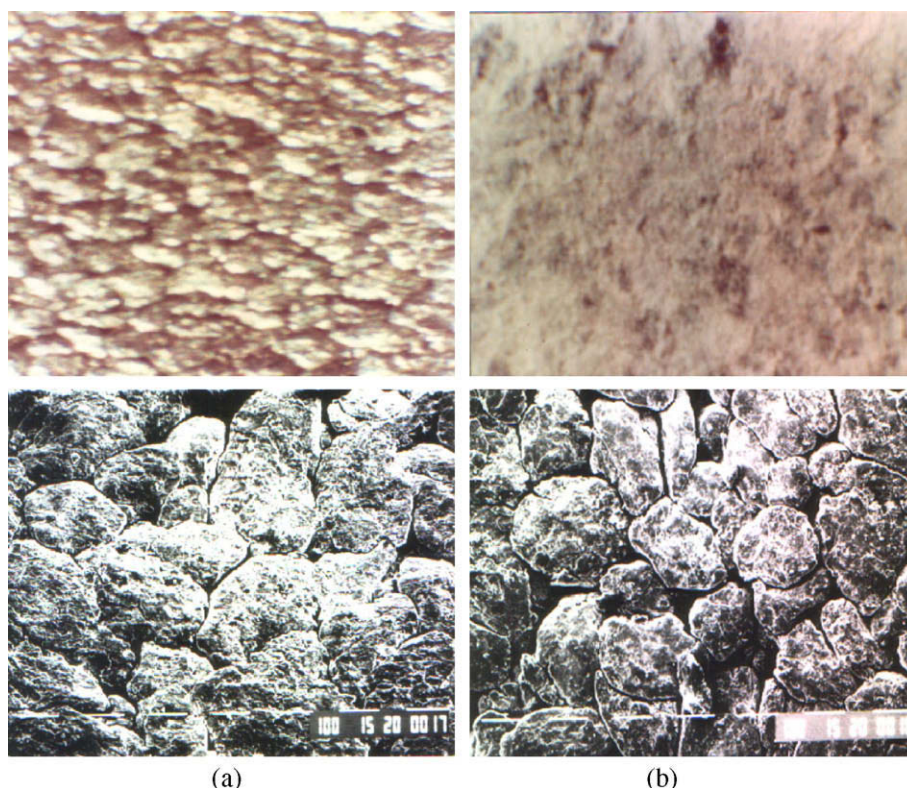
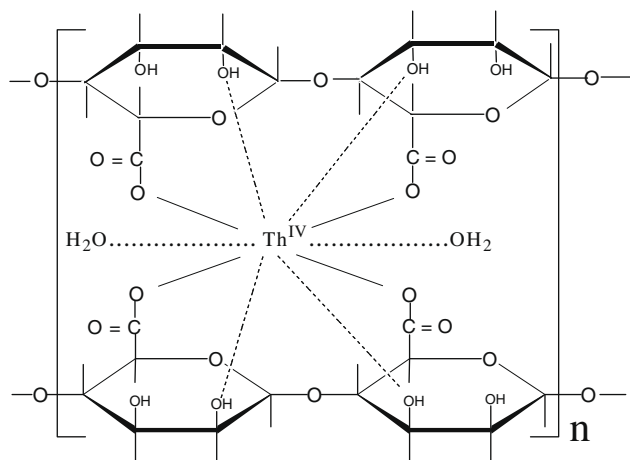


Figure 3 Optical images in cross-linked thorium(IV)-alginate complex: (a) before and (b) after treatment.

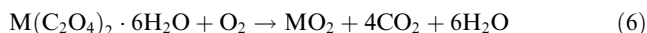


Scheme 1

Table 1 The electrical conductivity of some cross-linked metal–alginate complexes at 290 K.

Metal–alginate complexes	σ ($\Omega^{-1} \text{ cm}^{-1}$)	Reference
U ^{VI} –alginate	1.69×10^{-12}	Hassan et al. (1993)
Th ^{IV} –alginate	2.01×10^{-9}	This work
Cr ^{III} –alginate	1.0×10^{-10}	Zaafarany et al. (in press)
Fe ^{III} –alginate	2.0×10^{-9}	Zaafarany et al. (in press)
Ca ^{III} –alginate	1.3×10^{-13}	Khairou and Hassan (2002)
Cu ^{II} –alginate	1.82×10^{-12}	Khairou and Hassan (2002)
Cd ^{II} –alginate	2.40×10^{-12}	Khairou and Hassan (2002)
Pb ^{II} –alginate	1.84×10^{-12}	Khairou and Hassan (2002)
Ag ^I –alginate	1.78×10^{-8}	Hassan (1991)

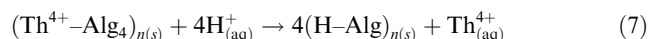
the oxalate intermediate to give rise to thorium oxide product at the elevated temperatures as follows:



Furthermore, the change in colour for cross-linked thorium(IV)–alginate complex before and after temperature treatment may confirm the formation of various oxidation states of thorium ion and, hence, supports the suggested mechanism. Typical photos are shown in Fig. 3.

Ion exchange equilibrium has been attained when the Th^{4+} counter ions in the alginate complex grains are replaced by other different counter cations of the same sign. Hydrogen ions were selected for replacement owing to the easiness and simplicity of exchange (Hassan, 1993). The equilibrium of

ion exchange between Th^{4+} and H^+ ions can be expressed by the following stoichiometric equation:



Applying the mass action-law for such a heterogeneous system and assuming that the activities of the solid phase are always unity (Glasstone and Lewis, 1960) and the ratio of the activity coefficient in the solid phase is constant (Baugh et al., 1972; Eisenman, 1962), the following relationship is obtained:

$$K_a = K_c (\gamma_{\text{Th}^{4+}} / \gamma_{\text{H}^+}), \quad (8)$$

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

$$K_c = [\text{Th}^{4+}] / [\text{H}^+]^4. \quad (9)$$

The values of K_a were found to be 25.75 and 15.40 $\text{dm}^9 \text{mol}^{-3}$ at 25 °C and 40 °C, respectively. The values of the thermodynamic parameters were calculated from the temperature dependence of the equilibrium constant and found to be $\Delta H^\circ = -4.76 \text{ kJ mol}^{-1}$, $\Delta S^\circ = +10.92 \text{ J K}^{-1} \text{mol}^{-1}$ and $\Delta G^\circ = -8.05 \text{ kJ mol}^{-1}$, respectively.

In view of these interpretation and the experimental observation, thorium(IV) should be chelated to the functional groups of alginate macromolecular chains via intermolecular association mechanism of non-planar geometry (Scheme 1). This configuration may be considered as an indirect evidence to explain the high electrical conductivity of the complex, which lies in the magnitude of semi conductors, compared to that of other complexes of planar structures and low electrical conductivities (Khairou and Hassan, 2002) which lie in the region of insulators as shown in (Table 1).

The conductance of polymeric compounds is usually occurred by two conductance mechanisms, ionic and electronic, depending on the nature of the charge carriers existing within the network of the macromolecular chains (Khairou and Hassan, 2002). The formation of free-radicals demonstrates the electronic conduction mechanism. Therefore, the gradual increase in the conductance at the initial stage of Th^{IV} –alginate can be explained by the increase of charge carriers within the solid, whereas the sharp increase in σ values at the final stage may be interpreted by the formation of thorium oxide, respectively.

The activation energy may reflect the mechanism of conductance. The activation energy is evaluated from the slope of $\log \sigma - 1/T$ plot using the Arrhenius equation as following:

Table 2 The activation energies in eV for some cross-linked metal–alginate complexes.

Metal–alginate complexes	E_a (initial stage)	E_a (final stage)	Reference
U ^{VI} –alginate	0.37	–	Hassan et al. (1993)
Th ^{IV} –alginate	0.86	1.20	This work
Cr ^{III} –alginate	0.16	2.74	Zaafarany et al. (in press)
Fe ^{III} –alginate	0.22	1.41	Zaafarany et al. (in press)
Ca ^{III} –alginate	–	2.12	Khairou and Hassan (2002)
Cu ^{II} –alginate	–	5.21	Khairou and Hassan (2002)
Cd ^{II} –alginate	–	1.75	Khairou and Hassan (2002)
Pb ^{II} –alginate	–	0.18	Khairou and Hassan (2002)
Ag ^I –alginate	0.21	3.15	Hassan (1991)

$$\sigma = \sigma^0 \exp(-E_a/RT) \quad (10)$$

where σ is the electrical conductivity, σ^0 is a constant and E_a is the activation energy of the charge carriers. This value was evaluated by using the least-squares method and is summarized along with the values of other cross-linked metal–alginate complexes in Table 2. The lower activation energy ≤ 1.0 eV corresponds to the electronic structure, whereas the higher values refer to the ionic conduction mechanism.

The magnitude of the equilibrium constant for exchange obtained, may indicate the high stability of the thorium(IV)–alginate complex. The negative value of ΔH° indicates that the exchange process is an exothermic process. Whereas, the negative value of ΔG° reflects the spontaneity of a such exchange process (Hassan, 1992).

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