



**Kinetics and mechanism of sol-gel transformation between some trivalent- and tetravalent-metal ions and Sodium alginate Anionic polyelectrolyte with formation of coordination Biopolymeric structure polymembranes Hydrogels of Capillary Structures**

**Exener correlation for some gelation processes**

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**Abstract**

The kinetics of sol-gel transformation between  $Al^{3+}$ ,  $La^{3+}$  and  $Th^{4+}$  metal ion electrolytes and sodium alginate sol have been studied complexometrically at various temperatures. In the presence of a large excess of sodium alginate sol concentration over that of metal ion electrolyte, the pseudo first-order plots of exchange showed sigmoidal curves with two distinct stages. The initial part was relatively fast and curved significantly at early times, followed by a slow decrease in the rates of exchange over longer time periods. The rate constants of gelation showed second-order overall kinetics which was first order in the concentration of both reactants. The thermodynamic parameters have been evaluated and tentative gelation mechanisms consistent with the kinetic results of gelation are suggested. The stability of these ionotropic metal-alginate complexes has been discussed in terms of the coordination geometry and strength of chelated bonds.

**Keywords:** Alginates, Polysaccharides, Kinetics, Gelation, Membranes, Polyelectrolytes, Metal ions.

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## 1. Introduction

Alginate, a major structural algal polysaccharide, is a linear block copolymer consisting of  $\beta$ -D-mannuronic and  $\alpha$ -L-guluronic acid units linked in (1 $\rightarrow$ 4) position [1]. It is well known that alginate has a high affinity to chelate with divalent and polyvalent metal ions forming ionotropic metal-alginate complexes of capillary structures [2]. Therefore, ion exchange properties of alginates have attracted considerable attention [3-9] owing to their bearing upon some practical uses in particularly in chromatographic separation of many radioactive nuclides and poisonous heavy metals [10-12]. However, the kinetics of their gelation are still scarce, Hassan and coworkers have investigated the kinetics of sol-gel transformation between divalent metal ions and alginate sol [13-17].

Therefore, the present work is of particular interest to shed some light on the nature of interaction between the interdiffused trivalent and tetravalent metal cations and alginate macromolecule as anionic polyelectrolyte during formation of their corresponding crosslinking ionotropic polymembrane gel complexes in an attempt to elucidate a suitable gelation mechanism. Moreover, the present work is a part of a series of investigations on sol-gel transformation in our laboratory [13-17]. The results obtained may reflect some information on the stability of these ionotropic gel complexes in terms of the coordination geometry

and strength of chelated bonds.

## 2. Experimental

Sodium alginate (Cica Reagent Chem. Co.) was used. The degree of substitution was found to be 4.34 mol/g (0.95 mol/mol). The measured viscosity using an Ubbelohde viscometer for a 4 % alginate solution in water at 20 $^{\circ}$ C was found to be 2.78 dl/g and 9.87 dl/g for the inherent and reduced viscosities, respectively.

Sodium alginate sols of various concentrations were prepared by dissolving the requisite amounts of alginate powder in doubly distilled water. This process was performed by stepwise addition of the powder whilst rapidly stirring the water to avoid the formation of a lumpy precipitate which swells with difficulty.

All other materials were of analytical reagent grade. Doubly distilled conductivity water was used in all preparations. The temperature was controlled within  $\pm 0.1^{\circ}$ C.

### 2.1. Kinetic measurements

One-side closed columns of 2-4 cm diameter and 10 cm in height were smeared with a very thin layer of alginate sol used and dried in an electric oven at 105 $^{\circ}$ C for about 20 minutes, then cooled at the room temperature. The required amount of alginate sol was poured into the columns to about one-third of its height.

The alginate sol and the metal ion electrolyte were equilibrated at the desired temperature in a thermostated water-bath. After the reactants had attained the temperature of the water-bath, fixed known volumes of the metal ion electrolytes were carefully introduced to the internal walls of the columns in such a way to avoid the deterioration of the alginate surface. The time of contact of the metal ion electrolyte with the sol surface was recorded. After known time intervals, known volumes of the electrolyte solution were carefully syringed out and the variation in concentration as a function of time was followed, complexometrically [18]. Before each run a smooth current of air is bubbled in the electrolyte solution to avoid the concentration gradient resulting from the exchange process of the counter ions across the membrane formed.

Some kinetic runs were performed conductimetrically. The results obtained were found to be in good agreement with that obtained complexometrically within experimental errors of  $\pm 5$  % indicating the reproducibility of the results obtained in the present work. The results are an average of at least five experimental runs for each.

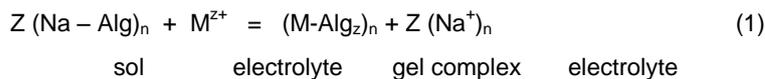
## 3. Results and discussion

### 3.1. Stoichiometry

Solutions of cationic or anionic polyelectrolytes can be transferred into gels through the diffusion of anionic or cationic polyvalent metal ions, respectively. These types of gels called ionotropic gels [5]. Ion exchange is inherently a stoichiometric process [19-23]. Any counter ions which leave their sites in the ion exchanger matrix such as Na $^{+}$  ions of sodium alginate polyelectrolyte must be replaced by an equivalent amount of other counter ions. This is a consequence of electroneutrality requirements. This means that as the Na $^{+}$  counter ions migrate the alginate matrix toward the surrounding electrolyte and, hence, the alginate macromolecule is left with a surplus electric negative charges which must be compensated by taking up an equivalent amount of metal ions from the electrolyte solution. The total charge remains constant, irrespective of the different valencies of the two counter ions. The interdiffused metal ions chelate three or four carboxylate groups and one or more pairs of hydroxyl groups of alginate macromolecule depending on the valency and coordination number of the interdiffused chelated metal ion. This exchange process leads to the transition of the alginate polysaccharide from the sol to the gel state.



The stoichiometry of a such sol-gel transformation was determined as described earlier [13-17]. The experimental observations indicated that the stoichiometry of such gelation processes conforms to



where M denotes the metal ion and Z stands to its valency.

### 3.2. Dependence of gelation rate constants on [Alg] and [M<sup>z+</sup>]

Preliminary experiments indicated that variation of either the metal ion electrolyte or the alginate sol concentration varies the rate constant of gelation. From this point of view and for simplicity in the analytical determination, the kinetics of the present work were performed under pseudo first-order conditions where  $[\text{Alg}]_0 \gg [\text{M}^{z+}]_0$ .

Plots of  $\ln(C_\infty - C_t)$  vs. time were found to curve significantly at early times but became linear and very slow at longer times in an analogous manner to that observed for other gelation processes [14-17]. Typical plots are shown in Fig 1. Therefore, the kinetic results were analyzed using a similar rate-law expression.

$$(C_\infty - C_t) = A_0 \exp^{-k_f t} + B_0 \exp^{-k_s t} \quad (2)$$

where  $k_f$  and  $k_s$  are the observed pseudo-first-order rate constants of gelation (exchange) for the fast initial and the slow final stages, respectively, while  $A_0$  and  $B_0$  represent the initial concentration of the sol in the two gelation processes. The rate constants of exchange shown in Table 1 were obtained by drawing straight lines through the fast time linear portion ( $k_f$ ) of the first-order plots and extrapolation of the line back to zero time ( $A_0$ ). The rate constants of gelation,  $k_s$ , for the slower gelation step were obtained from plots of the form  $\ln[(C_\infty - C_t) - (C_\infty - C_t)]$  vs. time. The quantity  $(C_\infty - C_t)$  represents the experimental point and  $(C_\infty - C_t)$  represents the extrapolated point at time  $t$  [24,25].

It noticed that the observed rate constants of gelation are not in agreement with the suggested rate-law expression at higher concentration of alginate sol ( $[\text{Alg}]_0 > 0.2 \text{ mol dm}^{-3}$ ). This may be attributed to the known dependence of alginate viscosity on the sol concentration that in turn may lead to retard the true exchange process to some extent. Hence, all of experimental runs were performed at  $[\text{Alg}]_0 < 0.2 \text{ mol dm}^{-3}$ . Again, since the gelation rate constants of the second parts were very slow, the kinetics of the present work was mainly concerned with initial gelation parts. The marked slowness observed at the second parts may be explained by the formation of multilayer membrane as the diffusion process is progressed.

The second-order rate constants of gelation ( $R_g$ ) were obtained by dividing the observed first-order rate constants by the initial alginate concentration ( $R_g = k_s / [\text{Alg}]_0$ ). The constancy obtained indicates that the rate constant of gelation is first order in alginate concentration and is second-order overall kinetics of the gelation processes. The rate constants of gelation were calculated by the least-squares method and are summarized in Table 2.

### 3.3. Dependence of gelation rate constants on temperature

The gelation process of the initial stage were studied at various temperatures ranging between 35 and 65°C. The plots of  $\ln(k_g h/kT)$  against  $1/T$  of Eyring's equation [26], gave good straight lines from whose slopes and intercepts, the enthalpy and entropy of activations were determined, respectively. The kinetic parameters were calculated using the method of least-squares and are summarized in Table 3, along with some other gelation processes.

### 3.4. Mechanism of Gelation

As a polyvalent metal ion electrolyte comes in contact with an alginate sol, a primary membrane will be formed on the surface of the alginate sol on immediate contact with the electrolyte solution. The membrane formed will separate the alginate sol from the surrounding metal ion electrolyte solution, whereas the macromolecular chains of alginate sol start to distribute themselves on the lower side of the formed membrane. As a steady state is approached, the sodium counter ions resulting the dissociation of the alginate sol start to diffuse through the primary membrane formed into the outside metal ion electrolyte. Simultaneously, the metal ions began to interdiffuse through that membrane inside the alginate sol. The net process is an exchange reaction which leads to the formation of gel complex with definite structure and orientation. The continuity of such diffusion process leads to the formation of multilayer ionotropic gel membrane [27].

The sol-gel transformation is accompanied by orientation of macromolecular chains and the coordinated solvent molecules toward the interdiffused metal ion [28]. The degree of orientation depends on the nature of the diffused polyvalent metal ion.

These interdiffused metal ions chelate the carboxylate and hydroxyl groups of alginate macromolecular chains through partially ionic and partially coordinate bonds, respectively [19,28]. The number of carboxylate groups participates in chelation depends on the valency of the chelated metal ion, whereas the number of chelated hydroxyl groups depends on the coordination number, respectively. The relative strength of the formed bonds is the determining factor for the degree of orientation and the stability of the complexes formed. Again, the orientation of the macromolecules is responsible for the anisotropic properties of the gel, such as the degrees of shrinkage and swelling [28].

Generally, two spatial models of the geometrical structure in chelation were suggested [29]. The first corresponds to an 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. This



configuration corresponds to planar geometry. The second type of geometry represents 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 obtained is termed non-planar geometry.

Divalent metal ions may chelate the alginate functional groups via inter- or intramolecular association mechanism; while tri- and tetravalent metal ions are restricted to crosslink these functional groups through intermolecular association geometry in their alginate complexes for geometrical reasons based on stability. The fact that trivalent metal ions coordinate with two adjacent carboxylate units and one carboxylate unit of a different chain and, hence, the attraction forces around the metal ion will not be the same in all directions. Therefore, their metal alginate complexes show some tendency to be flattened in their gel alginates, in particularly those prepared from alginate sols of lower concentration. This kind of chelation may reflect the pore mechanical properties observed for handling of these gels. On the other hand, tetravalent metal ions chelate two adjacent carboxylate groups of one chain and another two groups of a different chain. This kind of coordination geometry makes the attraction forces between the metal ions and the carboxylate groups equal in all directions. Here, a sort of bridge between two carboxylate groups and one or two pairs of hydroxyl groups in an egg-carton like structure takes place, depending on the coordination number of the interdiffused metal ion [30-33]. This fact interprets the identical symmetry and good mechanical properties of these gels in handling. The two configurations are shown in Schemes I and II, respectively.

On the other hand, ionotropic gels of di- or tetravalent metal-alginate complexes can be formed in different shapes according to the direction of diffusion of electrolyte [27]. When the metal ions are allowed to diffuse upward, non-capillary gel membranes are formed. While the diffusion of metal ions in the downward direction leads to the formation of gel membranes of capillary structure. These two kinds of diffusion may be termed by ascending and descending techniques, respectively. The sol-gel transformation of ionotropic gels is usually accompanied by the formation of capillaries in the direction of diffusion between the two counter ions. These capillaries are straight, parallel and nearly identical to each other.

Under microscopic investigations, these capillaries appear as fine pores of the same radius in a transverse section for cross-linked thorium(IV)-alginate complex as shown in Fig. 2. The diffusion process takes place stepwise through the formed capillaries forming the ionotropic polymembrane gels. The dehydration of solvent water molecules from the polymembrane gels gives transparent film of homogeneity. The capillaries in this film appear as spiral or cone shaped as shown in Fig. 3. The structural morphology was found to resemble that obtained for cross-linked divalent metal-alginate complexes [27]. Unfortunately, it was difficult to obtain such optical images for trivalent metal-alginate complexes owing to their poor mechanical properties in handling.

The diameter of the pores depends on several factors such as pH of electrolyte, concentration of alginate sol, the ionic radii of the interdiffused metal ion and the orientation of both coordinated water molecules and macromolecular chains of alginate toward the chelated metal ion [27].

The size of the pores in these membranes could be controlled by changing the pH's of the alginate sol through addition of certain electrolytes. These polymembranes can be applied in ultrafiltration and in another analytical purposes such as chromatographic separation of radioactive nuclides and poisonous heavy metal ions. The width in these capillaries may play an important role in the rate of exchange process during the sol-gel transformation. It is possible to separate the multilayer membranes into thin layer membranes [27]. These thin layers can be used in electrophoto conductography as cellular reinforcement screens for X-rays and photographing the electron beams of oscillographs.

In spite of variety of metal ions used in the gelation processes, it seems that the magnitude of the free energy of activation is remained unaltered significantly as shown in Table 3. A plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  of the isokinetic relationship suggested by Leffler and Grunwald [34] was found to be linear as shown in Fig. 4. This result may indicate that the mechanisms of the gelation processes are similar. Again the magnitude of the slope is significant and may be considered as a deserved comment.

Furthermore, the magnitude of the activation energies (Table 3) may reflect the stability for these ionotropic metal alginate complexes. The values obtained may indicate that stability increases in the order  $Al^{3+} < La^{3+} < Th^{4+}$  - alginate complexes. This means that trivalent metal-alginate complexes are less stable than tetravalent ones. This may be attributed to the geometrical configuration of their respective complexes as explained above.

## Conclusions

These polymeric biomaterial hydrogels in particularly metal-alginate membranes are widely used in many potential applications in chromatographic separation [35] for the removal of toxic heavy metal cations and radionuclides from contaminated matters such as seawater and environment [12]. Their sphere and bead shape hydrogels can be used as biocatalysts in immobilization systems such as drug delivery, tissues engineering, medical adhesion [36], ethanol manufacturing [37] and in ultrafiltrations purposes [27]. However, a little attention has been focused with respect to the kinetics of sol-gel transformation processes. Eventhough, the kinetics of gelation for cross-linked copper-alginate hydrogel spheres was investigated for the first time by us earlier [38].



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**Table 1.** The observed first-order rate constants of gelation. [Alg] = 0.05, [M<sup>2+</sup>] = (4-4.5) 10<sup>-3</sup> mol dm<sup>-3</sup> at 45° C.

Metal Ion	Al <sup>3+</sup>		La <sup>3+</sup>		Th <sup>4+</sup>	
	k <sub>f</sub>	k <sub>s</sub>	k <sub>f</sub>	k <sub>s</sub>	k <sub>f</sub>	k <sub>s</sub>
10 <sup>6</sup> Rate, s <sup>-1</sup>	9.49	1.67	13.12	2.18	15.63	1.70

Experimental error ± 3%.

**Table 2.** The rate constants of gelation. [M<sup>2+</sup>] = (4~4.5)×10<sup>-3</sup> mol dm<sup>-3</sup> at 45° C.

10 <sup>2</sup> [Alg], M	Al <sup>3+</sup>		La <sup>3+</sup>		Th <sup>4+</sup>	
	10 <sup>5</sup> R <sub>f</sub> ,s <sup>-1</sup>	10 <sup>4</sup> R <sub>g</sub> ,M <sup>-1</sup> s <sup>-1</sup>	10 <sup>5</sup> R <sub>f</sub> , s <sup>-1</sup>	10 <sup>4</sup> R <sub>g</sub> , M <sup>-1</sup> s <sup>-1</sup>	10 <sup>5</sup> R <sub>f</sub> ,s <sup>-1</sup>	10 <sup>4</sup> R <sub>g</sub> ,M <sup>-1</sup> s <sup>-1</sup>
2.53	0.49	1.92	0.65	2.58	0.78	3.06
5.05	0.95	1.90	1.31	2.59	1.56	3.10
7.58	1.47	1.94	1.87	2.46	2.35	3.10
10.10	1.96	1.94	2.54	2.52	3.12	3.09

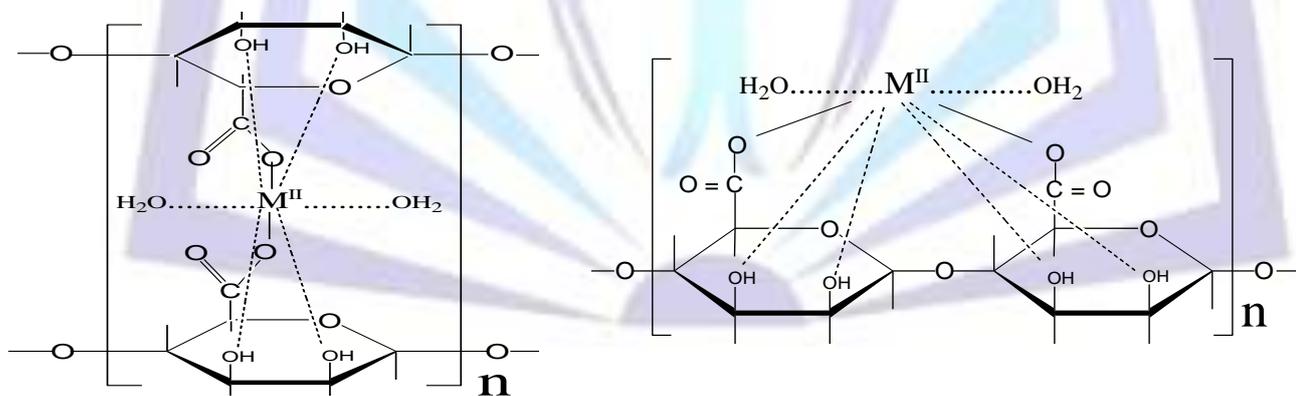
Experimental error ± 3%.

**Table 3.** Kinetic parameters and the second-order rate constants of gelation (at 45° C) for some sol-gel transformation reactions between metal cations and alginate macromolecule (initial autoacceleration stage).

Metal Alginate	$E_a^\ddagger$ k J mol <sup>-1</sup>	$\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\ddagger$ k J mol <sup>-1</sup>	$\Delta G_{298}^\ddagger$ k J mol <sup>-1</sup>	$10^4 R_g$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	Ref.
Al <sup>3+</sup>	26.51	-242.06	23.81	95.94	1.90	This work
La <sup>3+</sup>	17.65	-282.64	9.98	94.21	2.59	This work
Th <sup>4+</sup>	15.46	-272.47	12.69	93.89	3.10	This work
Zn <sup>2+</sup>	27.50	-240.09	24.79	96.34	1.57	17
Cd <sup>2+</sup>	62.99	-116.56	60.34	95.68	5.03	17
Pb <sup>2+</sup>	24.46	-238.29	21.80	92.81	6.53	17
Sn <sup>2+</sup>	16.25	-257.76	13.56	90.37	13.56	17
Hg <sup>2+</sup>	12.62	-285.99	8.72	93.47	2.81	17
Ni <sup>2+</sup>	29.83	-224.49	25.29	92.19	9.31	14
Cu <sup>2+</sup>	15.73	-176.64	37.80	90.44	6.53	15
Co <sup>2+</sup>	38.69	-260.89	14.77	92.50	12.92	16

Experimental error  $\pm 4\%$ .

### Cross Linked Divalent Metal Alginate Complexes



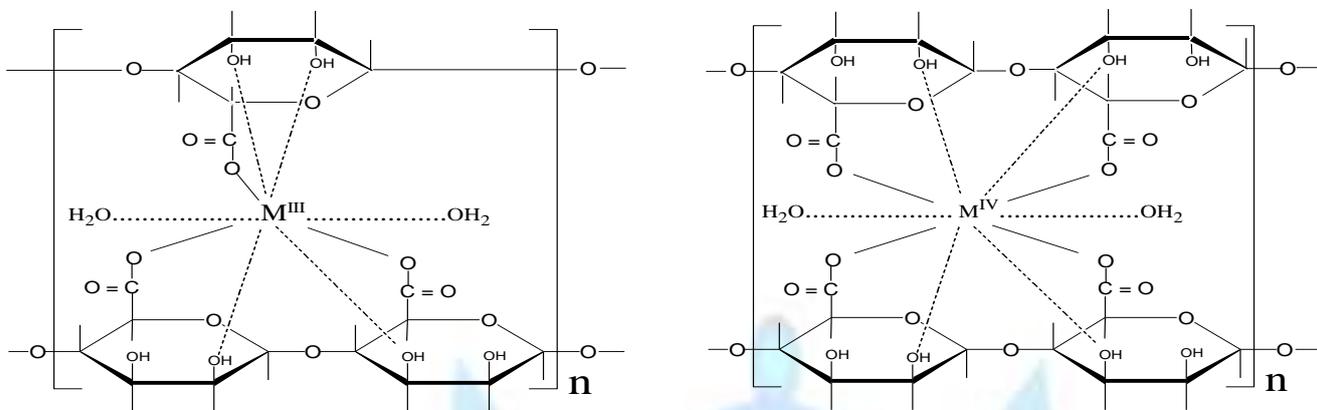
Intermolecular association

Intermolecular association

**Scheme 1**

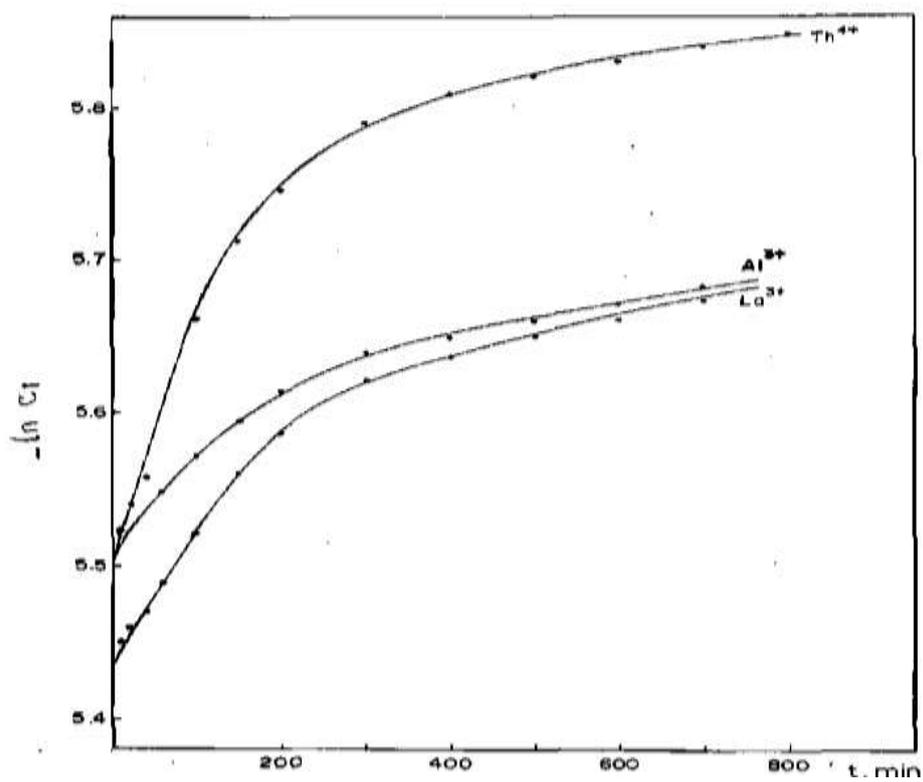


### Cross Linked Trivalent & Tetravalent Metal Alginate Complexes



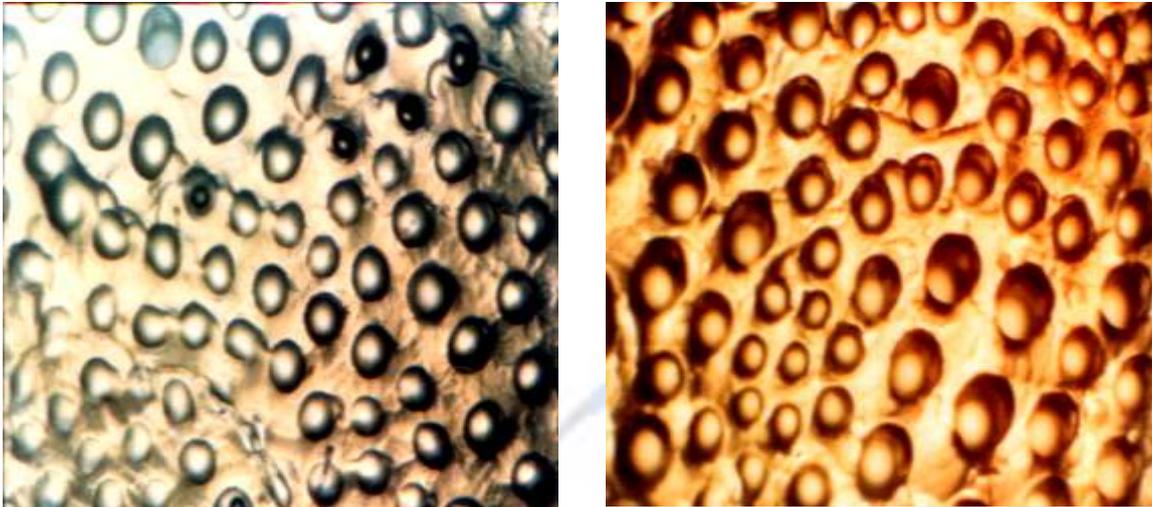
Intermolecular association

*Scheme II*



**Figure 1.** Typical pseudo-first-order plots for some gelation reactions.

$[Alg] = 5 \times 10^{-2}$ ,  $[M^{2+}] = 4 \times 10^{-3}$  mol dm<sup>-3</sup> at 45° C.



**Figure 2.** Optical images of transverse section in cross-linked thorium(IV)-alginate complex.



100  $\mu\text{m}$

**Figure 3.** Microscopical scanning for the pores of cross-linked thorium(IV)-alginate complex.

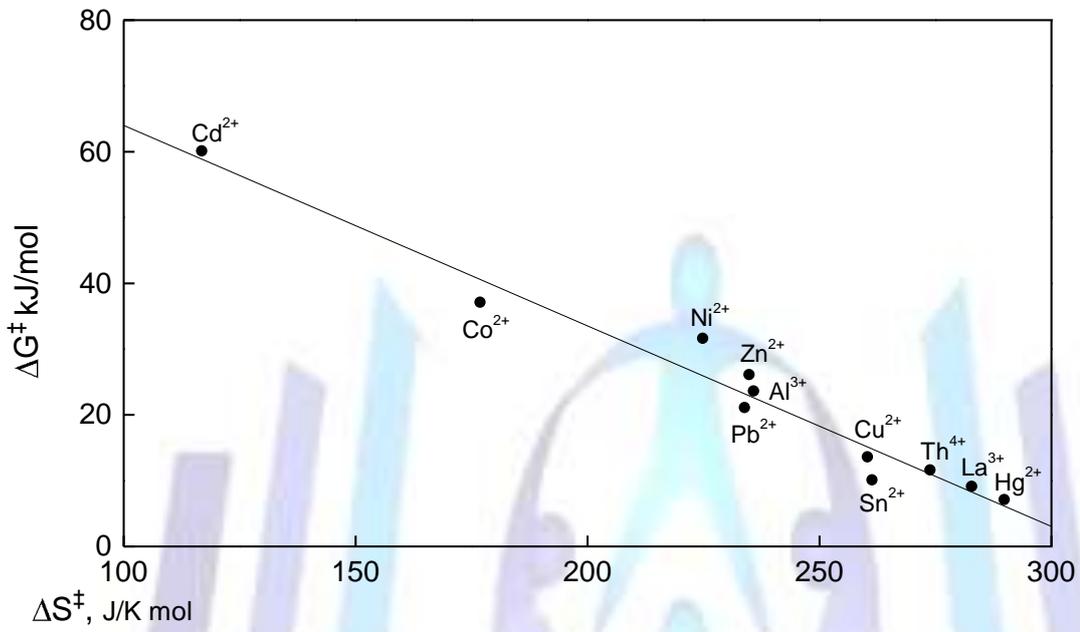


Figure 4. Isokinetic relationship for some gelation reactions.