

# Effect of calcium chloride on rheological behavior of sodium alginate

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## Abstract

Sodium Alginates are widely used in several industries as gelling agent, coagulant, thickener and encapsulation matrices. Since they can be used in aqueous solutions, it becomes more interesting to study their behavior as non-Newtonian fluids and how adding divalent cations such as calcium can influence it. In this work, intrinsic viscosity, apparent viscosity and rheological behavior of sodium alginate in different salt concentrations have been investigated. Obtained data have shown that the salt concentration plays a key role in the crosslinking process of this polymer. Copyright © 2017 VBRI Press.

**Keywords:** Sodium Alginate, Ca<sup>2+</sup> binding, Rheological properties, Intrinsic viscosity.

## Introduction

Alginates are polysaccharides occurring in large amount in nature [1] extracted primarily from brown algae (*Laminaria claustroni*, *Laminaria digitata*, *Ascophillum nodosum*...) or synthesized by bacteria (like *Azotobacter vinelandii*...). They have many applications in several industries but one of the most important characteristics of those polymers is to be used as a matrix for the encapsulation and/or delivery of various molecules and particles [2].

They are unbranched copolymers (1=> 4) linked beta-D mannuronic acid (M) and alpha-L guluronic acid (G) residues. If the uronic acid groups are in the acid form (-COOH), the polysaccharide called alginic acid is water insoluble. The sodium salts of Alginic Acid (-COONa) or Na-Alg are water-soluble [3].

In the recent years, the interest in using those biopolymers has increased, consequently, the works and studies on their physical and chemical properties progressed [4].

Among the studies that sodium alginate can undergo: Rheological behavior and determination of intrinsic viscosity. They are investigated in order to suit the aimed application such as textile printing, pharmaceutical, food and paper industries... etc.

In this paper, the intrinsic viscosity and rheological behavior have been evaluated by varying parameters as solvent, polymer and salt concentrations in order to determine the optimal concentrations of the polymer gelation.

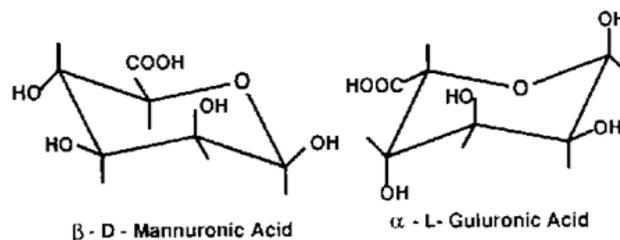


Fig. 1. Classical Formulas of the two monomeric units of alginic acid.

## Experimental

Alginate Sodium LS has been purchased from Panreac with the following properties: 15% of loss on drying at 105°C, 30% of residue on ignition and 0,004% of heavy metals. Calcium chloride CaCl<sub>2</sub>, 6H<sub>2</sub>O from fisher scientific international company and Sodium chloride NaCl from Fluka Chemika.

### Characterization

#### Infrared spectroscopy

In order to identify the structures and the chemical bonds of Sodium Alginate, a FTIR -8400S SHIMADZU spectrophotometer has been used to establish the IR spectra of the polymer with scanning from 500 to 4000cm<sup>-1</sup>.

In order to make the pellets, the sample has been crushed with potassium bromide before measurement.

## TGA

For the TGA measurement, a SHIMADZU TA-60WS thermal analyzer has been used with an initial sample mass of 12.6mg in an alumina sample holder at heating rate of 20°C/min under a dynamic air.

### Intrinsic viscosity

Intrinsic Viscosity was examined using an Ubbelohde capillary type viscometer from FUNGILAB with a constant equal to 0,40907. The reading of the samples flow has been done using a stopwatch.

### Samples preparation

Sodium Alginate concentration ranged from 0.2g/l to 1g/l and have been dissolved in two different solvents, distilled water and 0.1M NaCl solution at 25°C in the pH solution 5,5. The samples were stirred overnight at 650 rpm, filtered and then measured. The measurement has been done in triplicate and the average has been recorded and used for the calculations.

For each sodium alginate concentration, the following viscosities were determined following the given equations:

$$\text{Relative viscosity: } t/t_s$$

$$\text{Specific viscosity: } t-t_s/t_s$$

$$\text{Reduced viscosity: } \text{specific viscosity}/C$$

With  $t$ = flow time of the sample (s),  $t_s$ = flow time of the solvent (s) and  $C$  the polymer concentration (g/ml).

The reduced viscosity was plotted against sodium alginate concentrations. The value of intrinsic viscosity can be calculated by extrapolating the graph of reduced viscosity vs. polymer concentration when the concentration tends to zero.

The average Molecular Weight has been determined using the following equation:  $\eta = KM_w^a$ .

Where  $\eta$  is the intrinsic viscosity in ml/g,  $M_w$ = the average molecular weight in Da,  $K$  and  $a$  are constants of Mark-Houwink.

### Viscosity and rheological measurements

Viscosity and rheological measurements have been carried out using a Brookfield RS-CPS+ Rheometer plate-plate model, assisted by Rheo 3000 software, at 10g/l of sodium alginate and different calcium chloride concentrations for 1200s, a shear stress between 19 and 140 Pa in isothermally shear mode at 20°C. The samples were carefully poured into the surface of the lower plate; the upper plate was lowered until it reached a 0,045 mm gap distance.

## Results and discussion

### Characterization

#### Infrared spectroscopy

The obtained IR spectrum for the Na-Alg was done in the range of 500-4000  $\text{cm}^{-1}$ . The Fig. 2 shows the result. The spectra of this polymer presented a strong peak at 1050  $\text{cm}^{-1}$  due to the bending vibrations of OH. The two

strong peaks that appear at 1420 and 1619  $\text{cm}^{-1}$  are the results of symmetrical and asymmetrical  $-\text{COO}-$  stretching vibrations of the free carboxyl observed by Huang [5]. At 2900  $\text{cm}^{-1}$ , there is a peak corresponding to the C-H stretching and a peak at 3450 due to the hydroxyl group stretching [6]

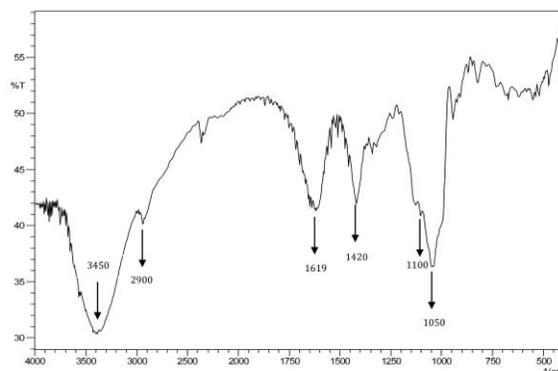


Fig. 2. Infrared spectrum of Sodium Alginate.

### TGA

The TGA curve pathway presented in Fig. 3 reveals that under heating, the polymer shows a dehydration (water loss) process between 26°C and 229°C with a weight loss of 18.25%. Then the degradation to  $\text{Na}_2\text{CO}_3$  and the fast decomposition of carbonized material from 408°C occurs. The total mass loss was equal to 77.58%. According to Newkirk [7]; the  $\text{Na}_2\text{CO}_3$  degradation depends on the sample holder and the atmosphere used. In this work such decomposition appeared above 400°C approximately in agreement with Belalia [8].

A vigorous liberation of  $\text{CO}_2$  was observed while a dark insoluble residue remained in the sample holder at the end of the decomposition. Oppositely, Soares [9] found that the decomposition appeared above 800 °C in agreement with the findings of those author using Pt crucible and  $\text{N}_2$  atmosphere. The difference in results is probably due to a different origin of the polymer, the nature of the sample holder, the heating rate and the atmosphere of the manipulation.

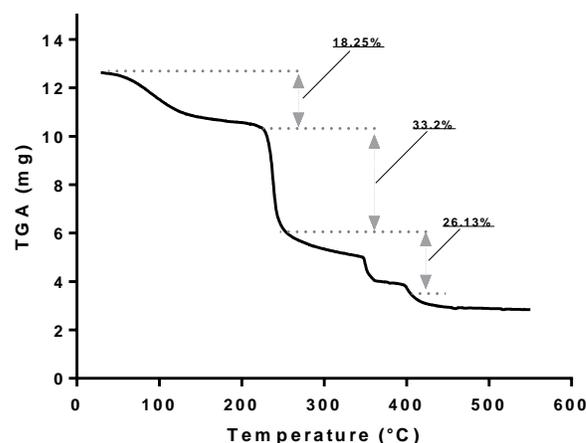


Fig. 3: TGA spectrum of Sodium Alginate.

**Intrinsic viscosity**

Intrinsic viscosity is a characteristic property of a single macromolecule in a given solvent and is a measure of the hydrodynamic volume occupied by the polymer itself, it depends primarily on molecular weight, solvent quality and chain rigidity[10]

The Intrinsic Viscosity is related to the average molecular weight via the well known Mark-Houwink equation:  $\eta = KM^a_w$

By using Donan and rose’s results [11], intrinsic viscosity has been estimated by extrapolating the plot of the reduced viscosity VS concentrations of sodium alginate when the concentration tends to zero (Fig. 4 and 5).

The Table 1 shows the values of intrinsic viscosity, the average molecular weight and the Mark Houwink constants that were obtained from the literature [12].

**NaCl**

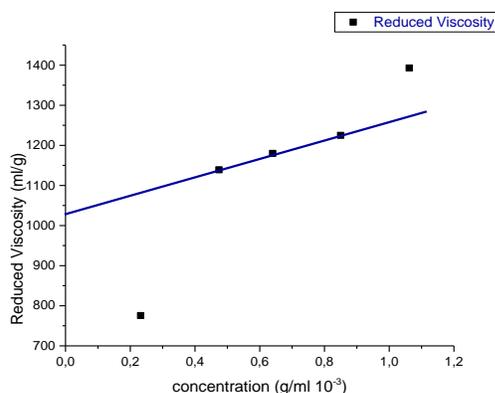


Fig. 4. Determination of intrinsic viscosity of sodium alginate in 0.1M NaCl

**Distilled water**

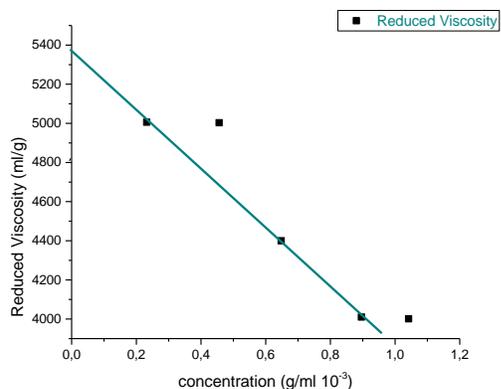


Fig. 5. Determination of intrinsic viscosity of sodium alginate in distilled water.

Table 1. Values of intrinsic viscosity, average molecular weight and Mark Houwink constants of aqueous alginate solutions.

Solvent	Intrinsic Viscosity (ml/g)	Mark-Houwink Coefficients		Molecular Weight (Da)
		K (ml/g)	a	
Distillated Water	5389	-	-	338925,7496
NaCl	1030	0.0501	0.9 10	54898,4255

**Viscosity and rheological measurements**

**Viscosity measurements**

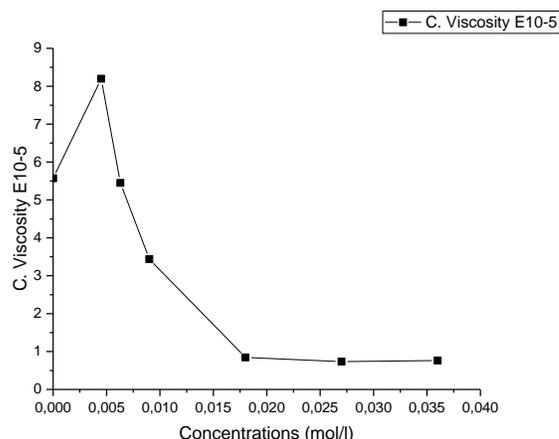


Fig. 6. Viscosity curve of sodium alginate at different calcium chloride concentrations.

The viscosity behavior of sodium alginate in various salt concentrations shows that the adding of the divalent cation has increased the viscosity comparing to the salt-free solution. The curve pathway shows that the viscosity passes through a maximum and decreases in higher salt concentrations were a flocculation and total separation between the gel and the aqueous phase appears. According to Bourgoin [12], in high calcium concentrations; interanionic bonds are established and a labile tridimensional structure is formed and become more stable in greater salt concentrations. Haug, *et al.* [13] have found the same results for different salt that was explained by a loose gel structure occupying the total volume of the mixture. Further addition of calcium leads to a decrease in the gel volume and measurements become irreproducible as the mixture becomes heterogeneous. Smidsrød, *et al.* [14] have also worked on the effect of calcium chloride on the alginate solutions viscosity and have shown that the sodium, which in our case is already present in the polymer, is found to have two oppositely direct effects:

1-Displacing the ion exchange equilibrium in the direction of lower values of calcium



2-Salting-out effect due to the high ionic strength. Salting out occurs in aqueous solutions of high ionic strength that reduce the molecule's solubility causing certain precipitating

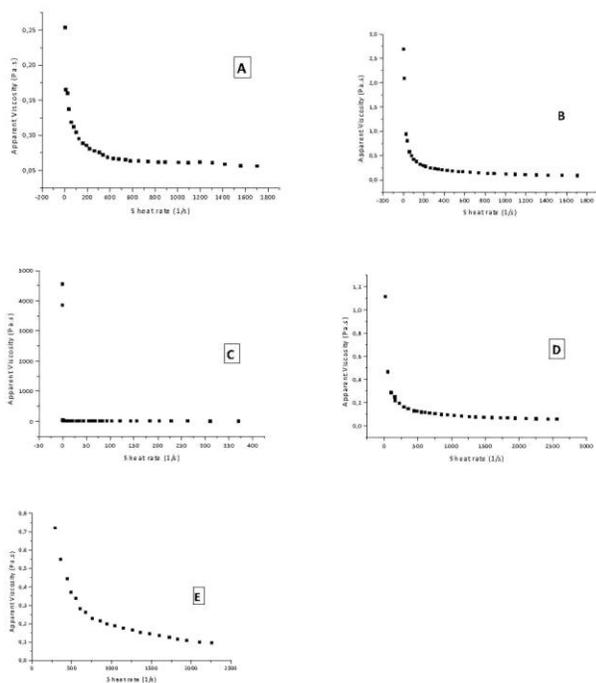
**Rheological measurements**

Fig. 7 shows the apparent viscosity of sodium alginate aqueous dispersions at different calcium chloride concentrations at 20°C. It can be noted that the apparent viscosity depends not only on calcium concentrations but also on shear rate. When the latest increases, apparent viscosity decreases with time.

The shear stress data were analyzed by fitting the power-law model and its parameters are summarized in Table 2. As shown in Table 2, the sodium alginate solutions exhibited the property of pseudoplastic fluid with a flow behavior of  $n$  less than 1.

For sodium alginate an increase in the salt concentration caused an increase in the pseudo plasticity, which showed a decrease in the flow behavior index [15]

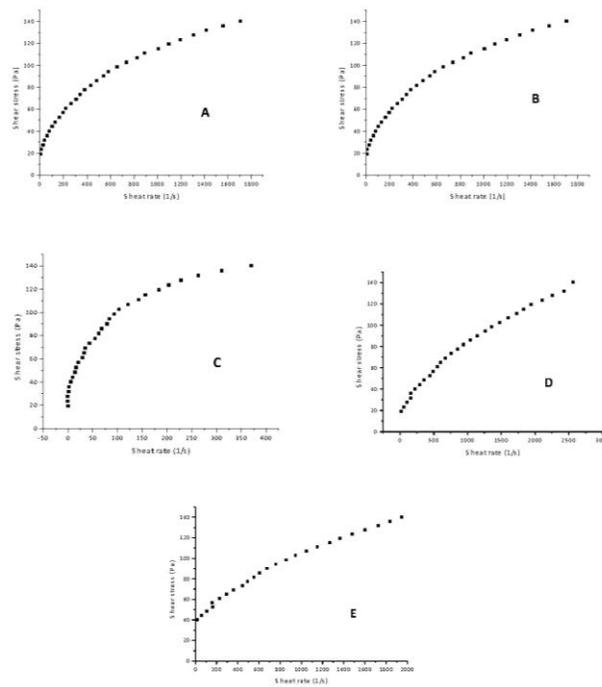
The experimental results have been described by the mean of the Ostwald- de Waele model  $\tau = k \cdot \dot{\gamma}^n$  where  $\tau$  is the shear rate (Pa) and  $\dot{\gamma}$  is the shear stress (1/s),  $k$  and  $n$  are respectively the coefficients of consistency index and flow behavior index, which is equal to 1 for Newtonian fluids [10]. Both of these coefficients were estimated by using the square methods. In terms of regression coefficients  $R^2$  determination, the sodium alginate flow curves had a high correlation (for each salt concentration  $R^2$  was greater than 0.99) to the power-law model and were finely linear which indicated that the power-law model was suitable. These results are in accordance with those described by Cevoli, *et al.* [16] using Ostwald-de Waele model.



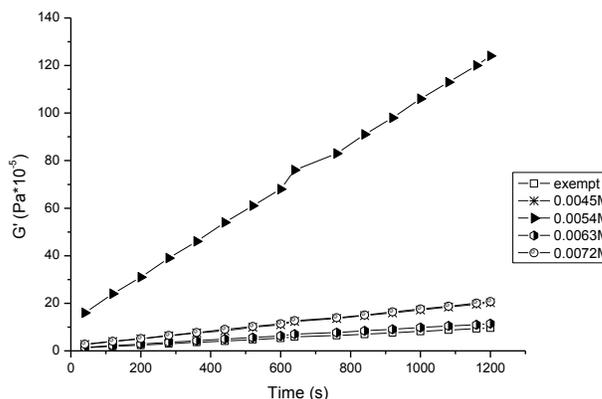
**Fig. 7.** Apparent Viscosity as function of shear rate at different calcium chloride concentration : A : exempt salt ; B : 0.0045M ; C : 0.0054M ; D : 0.0063M ; E : 0.0072M

**Table 2:** Influence of Calcium chloride concentrations on rheological parameters.

Salt Concentration	k	n	$R^2$
Exempt	1.5043	0.5577	0.9997
0.05	6.7831	0.4059	0.9995
0.07	7.9076	0.3161	0.9965
0.08	10.8282	0.3329	0.9996



**Fig. 8.** Influence of calcium chloride concentrations on shear rate as function of shear stress. A : exempt salt ; B : 0.0045M ; C : 0.0054M ; D : 0.0063M ; E : 0.0072M.



**Fig. 9.** Variation of moduli  $G'$  as a function of the time at different salt concentrations.

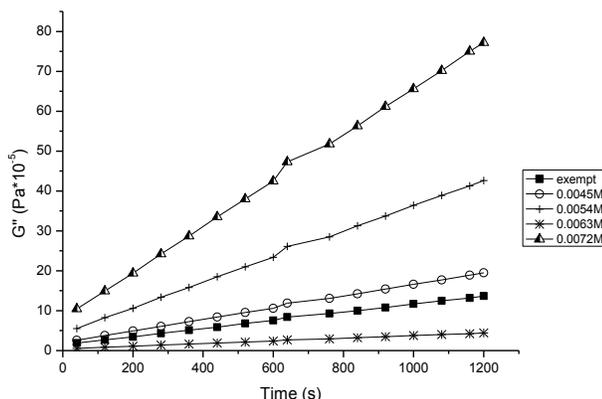
When comparing the evolution of  $G'$  and  $G''$  for systems at different calcium chloride concentrations, different responses were observed. For the variation of the elastic moduli  $G'$  during time, the highest value of the latter was recorded at 0.0054M (Fig. 9) of calcium chloride where the polymer exhibits an elastic behavior since  $G'$  is higher than  $G''$ . Therefore, the highest value of viscous moduli  $G''$  was registered at 0.0072M (Fig. 10) what seems to be a viscous behavior related to a fluid structure. These results can be explained by the facts:

That at optimal concentrations (0.0054M),  $G' > G''$  so the material has some capacity to store energy and behave like an elastic solid but not an ideal one.

That at high calcium concentrations, a flocculation occurs [12] from 0.018M and  $G''$  becomes larger than  $G'$  what can be explained by the fact that the majority of the

energy was dissipated by viscous flow and showed fluid like viscoelastic behavior.

At higher calcium concentrations the flocculation makes the measurements irreproducible.



**Fig. 10.** Variation of  $G''$  moduli as a function of time at different calcium chloride concentrations.

## Conclusion

This study concluded that aqueous solutions of sodium alginate show a shear thinning non-Newtonian behavior in a given range of calcium concentrations.

The sodium alginate seems to be a good fit as a thickener agent at optimal concentrations.

The calcium chloride salt plays a key role in the binding of the polymer and arranging it in egg-box structure. At higher concentrations the polymer tends to flocculate what makes the measurements no longer producible.

The polymer response for the rheological behavior depends initially on the salt concentration and gives different behavior for each concentration. It has been observed that  $G'$  is larger than  $G''$  for 0.0054M which is the optimal concentration to obtain an adequate gel for further applications. While at 0.0072M,  $G''$  is larger than  $G'$  meaning that the applied force collapsed the microstructure what makes the material flows.

With the obtained data, it seems that the solutions exhibit a viscoelastic behavior.

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