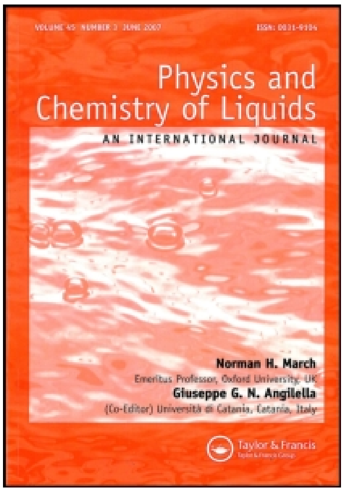

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Physicochemical characterization and ionic studies of sodium alginate from <i>Sargassum terrarium</i> (brown algae)

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Physicochemical characterization and ionic studies of sodium alginate from *Sargassum terrarium* (brown algae)

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Physical and chemical analysis of the polysaccharides isolated from *Sargassum terrarium* (brown algae) of Karachi coast showed characteristics of sodium alginate. The optical rotation and sulphated ash content were found to be -113° and 30.6% respectively. FTIR spectra showed a sharp and strong absorption band at $1600\,\text{cm}^{-1}$ representing carboxylate ion, which confirms high uronic acid content of the product. Viscosity measurements revealed a linear relationship with increases in concentration and decreased with the rise in temperature of aqueous solution of sodium alginate. Thermodynamic parameters were determined by the change in viscosity data as a function of temperature and concentration. The free energy change of activation ($\Delta G\eta$) increased regularly as the concentration of sodium alginate increased, as well as rises in temperature. Higher values of free energy change of activation, showed the higher association of sodium alginate with water at a given temperature. The values of entropy change of activation ($\Delta S\eta$) of viscous flow also increased with the increase in concentration and temperature of sodium alginate solution. The high negative values of entropy change of activation ($\Delta S\eta$) showed that the solution of sodium alginate was more ordered in initial state than the activated one.

Keywords: *Sargassum terrarium*; Sodium alginate; Energy of activation; Latent heat of vaporization; Entropy of activation

1. Introduction

Alginates are the polysaccharides generally extracted from brown algal plants and are the copolymers of L-guluronic and D-mannuronic acids [1,2]. The high viscosity and polyelectrolyte character of alginate solutions and their capacity for gel formation make their widespread industrial use in many pharmaceuticals, textile, food and dairy products [3,4]. Compared with other food gels, sodium alginate (algin) gels have many advantages i.e. form low calorie food, quickly and easily melt in mouth, non-toxic nature and low in cost.

Sodium alginate also forms thick and stable gel when it comes in contact with calcium ions in solution by cross-linking between the carboxylate ions of alginate guluronate

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units and the calcium ions [5]. The viscosity method is employed for the determination and confirmation of compounds and their behaviour in different solvents. Viscosity is affected by a number of parameters such as molecular mass, shape and size of molecules, concentration, temperature and intermolecular attractions i.e. ion–ion and ion–solvent interactions [6]. Ample data are available in literature on rheological studies of alginates [7,8]. However, little attention has been paid on physicochemical characterization of the alginates obtained from brown algae of Karachi coast.

The present investigation deals with chemical characterization, spectral and thermodynamic study of the sodium alginate isolated from brown algae of Karachi coast. Various thermodynamic parameters such as energy of activation (E_η), free energy change of activation (ΔG_η), latent heat of vaporization (L_η) and entropy change of activation (ΔS_η), for the viscous flow of aqueous sodium alginate solutions were studied as a function of temperature and concentration. The activation energy of flow gave information about the behaviour of sodium alginate in water and FTIR spectral analysis helped to study the structure of sodium alginate.

2. Materials and methods

2.1. *Isolation of sodium alginate*

Sargassum terrarium (S. terrarium) of class pheophyceae (brown algae) was collected from paradise point of Karachi coastal area in March 2004. The plant material was cleaned from epiphytes, washed with tap and distilled water, dried and ground to a fine powder in a domestic model mixer. Algal powder (50 g) was de-pigmented and extracted by the method described previously [9]. The gel (sodium alginate) obtained after alcohol treatment (1 : 2 v/v) was dried at low temperature at 45–50°C.

2.2. *Chemical methods*

Moisture content was determined as described earlier [10]. The analysis of sulphated ash was carried out by the conventional method of ashing in the presence of concentrated sulphuric acid. pH of 0.1% algin solution was recorded by a digital pH meter. Total sugar content was determined by the phenol sulphuric acid [11]. Assay for sulphate group was done by modified method [12]. Total acidic sugar was determined by uronic acid carbazole method [13]. Reactions with calcium chloride, sodium hydroxide and mineral acids were performed [14]. Optical rotation of aqueous solution of algin of known concentration (1%) was determined with Digital Polarimeter (Jas. Co. Dip. 360) using 50 mm tubes and sodium D line at 589 cm wavelength. FTIR analysis was performed on Nicolet Avatar 370 DTGS Fourier Transform Infrared Spectrometer.

2.3. *Viscosity measurement*

All glass wares used were of Pyrex A grade quality. A 0.5% stock solution was prepared in 100 mL volumetric flask by dissolving the 0.5 g of isolated sodium alginate in deionized water having conductivity less than 1 $\mu S\,cm^{-1}$ with constant stirring till clear solution formed, then volume was made to the mark. This stock solution was used to prepare further dilutions ranging from 0.05 to 0.25%. Relative viscosities were measured with Ubbehlode Viscometer type techniconominal constant 0.1 cSt capillary ASTM D 445. The viscometer was placed inside a glass tube connected with thermostatic water bath (type VWP Scientific, model 1120, Ser 9143791) having a constant circulation of water throughout the course of the experiment. The temperature of the water bath was kept constant with the help of temperature control device type Haake Delab Instrument (Electro Laboratoriet, Copenhagen) with ±0.1°C. A known volume of solvent (water) and solution was placed in the viscometer for at least 15 min to attain the required temperature and the time of flow was recorded.

Densities of solvents and solutions were measured with the help of a relative density bottle (10 mL) at different temperatures. The reproducibility of results was checked by repeating the measurements three times. The uncertainty in the experimental data was found to be $\pm 0.001\,\mathrm{g\,mL^{-1}}$ and $\pm 0.002\,\mathrm{cP}$ respectively.

3. Results and Discussion

Yield of Algin (sodium alginate) isolated from brown algae, *S. terrarium* was about 30% (w/w) of the dry plant. The yield was much higher than that reported earlier i.e. 23.7% [15]. Physicochemical properties of isolated algin and a commercial sample purchased from the local market were compared, significant differences were observed in the optical rotations and in the sulphated ash contents (table 1). Isolated product showed a rotation of −113° and was present in the range as described earlier [16]. However, optical rotation cannot be taken as a criterion of quality or a reliable index of purity. Chemical analysis revealed that isolated sample exhibited 20% sugar and low sulphate content (0.12%). Uronic acid content was 8%, which is in good agreement with that reported by Johnson *et al.* [17]. Sometimes variables used during extraction procedures like type of solvents, concentration of solvents and also the seasonal variations influence and affect the yield, apparent viscosity, colour and chemical composition of the product [18]. Infra red (IR) spectroscopy is a simple and

Table 1. Physicochemical properties of commercial and isolated samples of sodium alginate (algin).

Tests	Isolated algin	Commercial algin
Colour	Light brown	Light brown
Moisture (% w/w)	12.4	15.1
Sulphated ash (% w/w)	30.6	41.9
pH (0.1% solution)	6.6	6.6
Aqueous gel strength (2% w/v)	Yellow transparent gelling solution at 4°C	Pale yellow turbid solution at 4°C
Optical rotation $[\alpha]_D^{25}$	−113°	−68°
Total sugar content (% w/w)	20	16
Uronic acid content (% w/w)	8	9.2
Sulphate content (% w/w)	0.12	0.73
Reactions with		
Calcium chloride (2.5%)	Gelatinous precipitate formed	Same
Sodium hydroxide (3N)	Clear yellow solution on heating	Same
Mineral acids	Gelatinous precipitate formed	Same

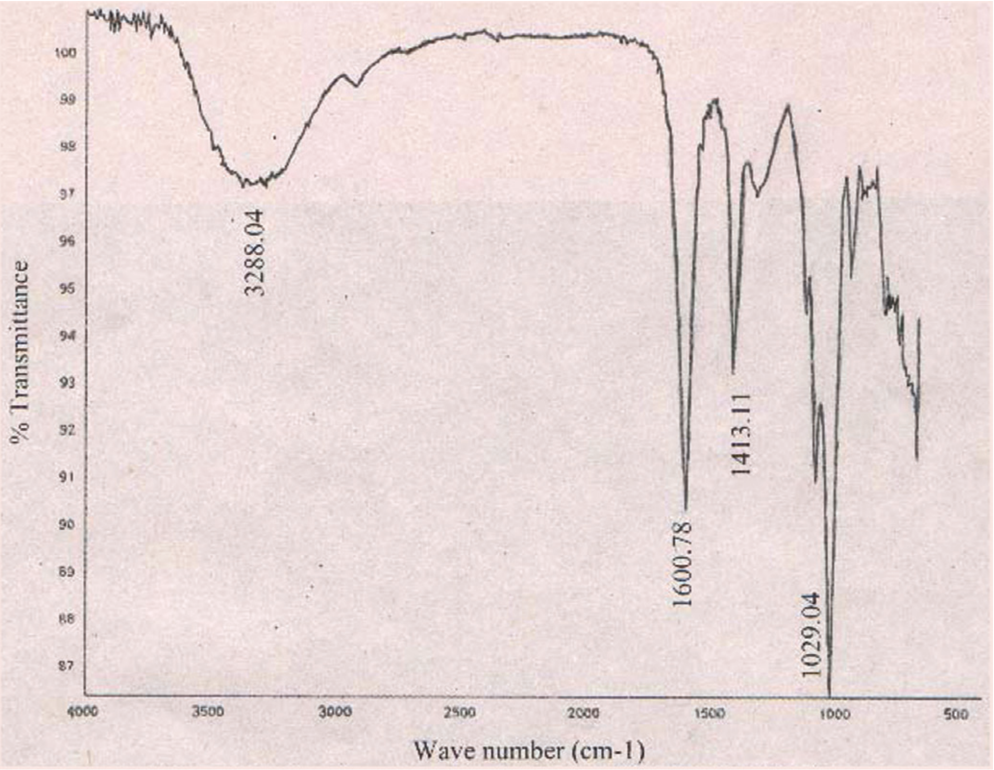

Figure 1. Infrared spectra of isolated algin (sodium alginate).

faster technique used for the characterization of alginates [19,20]. IR spectra of the product showed a sharp and strong absorption band at 1600 cm^{-1} and represented the carboxylate antisymmetric stretching which is in accordance with the high uronic acid content of the sample, (figure 1, table 1). The spectra is identical and resemble the finger print region of the typical spectrum of sodium alginate [21].

In this article we describe the viscosity measurements of aqueous solution of sodium alginate from 30 to 50°C at the rate of 5°C increments at various dilutions ranging from 0.05 to 0.25 g dL^{-1}. Solution properties of chemical substances in the region of extreme dilution are of great importance, both theoretically and experimentally. Viscosities of various aqueous solutions of isolated algin at five temperatures are recorded in table 2. The results showed a regular increment in viscosity with the increase of concentration of solutes at each temperature i.e. 303, 308, 313, 318 and 323 K respectively. The viscosity of the solutions seems to decrease with the rise of temperature as reported earlier [8,22]. The increase in viscosity on addition of sodium alginate to water is understood, to be due to increase in the degree of solvation. Representative plot of η_{sp}/C (reduced viscosity) *versus* concentration of aqueous sodium alginate solution at 323K is shown in figure 2. The values of reduced viscosity (η_{sp}/C) of each sample of aqueous sodium alginate solution were studied systematically.

Viscosity measurement is one of the most appropriate techniques used to study various types of interaction occurring in solutions. The viscosity data are computed

Table 2. Viscosity η (cP) of sodium alginate aqueous solution at various concentrations and temperatures.

	Temperatures (K)				
Concentration ($g\,dL^{-1}$)	303	308	313	318	323
0.05	1.9964	1.6990	1.4450	1.2750	1.2080
0.10	2.9655	2.7780	2.4240	2.0990	1.9930
0.15	4.4668	3.9070	3.4470	2.9440	2.8960
0.20	5.2109	4.9100	4.2640	3.5470	3.5220
0.25	6.3400	5.6800	5.0870	4.4840	4.4020

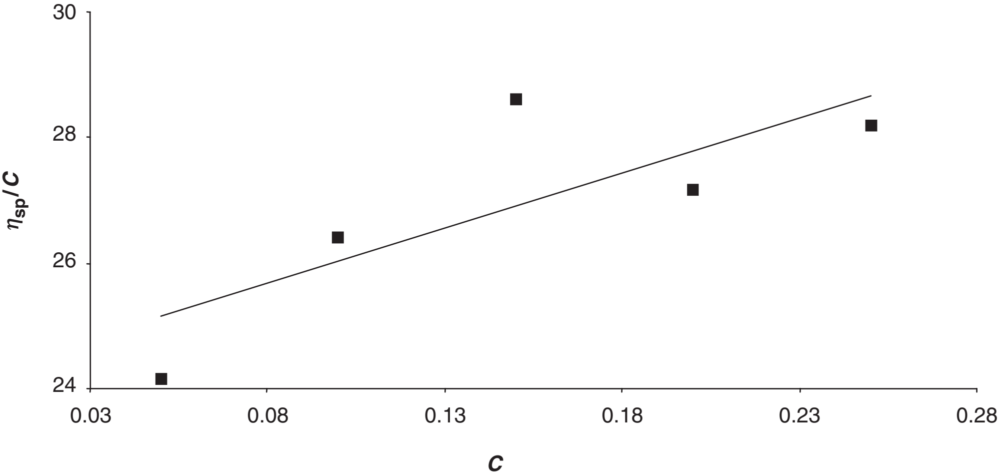

Figure 2. Plot of η_{sp}/C *vs*. concentration for aqueous sodium alginate solution at 323 K.

by using Jones–Dole equation [23]. A representative plot of $\eta_{sp}/C^{1/2}$ *versus* $C^{1/2}$ at 308 K is shown in figure 3.

$$\frac{\eta_{sp}}{C^{1/2}} = A + BC^{1/2} \tag{1}$$

where η_{sp} is the specific viscosity, A and B are coefficients which represents ion–ion and ion–solvent interactions respectively, C is the concentration of algin solution in $g\,dL^{-1}$. The values of A and B coefficients were determined from the intercept and slope of the linear plots of $\eta_{sp}/C^{1/2}$ *versus* $C^{1/2}$. The regression method was applied for this purpose and the resulting A and B coefficients are summarized in table 3. The negative values of coefficient A do not have any significance. In this case, A values have been found to decrease with the rise of temperature, which is due to dielectric constant of the medium and decrease in the ion–ion interactions. The values of coefficient B calculated are found to increase with the increase of sodium alginate content at all the temperatures. A solute with a positive B coefficient is expected to have a structure-making effect. Our data show the regular variation of B-values with the rise of temperature, this may be due to the different degrees of hydrolysis in the given solvents. In this case as our solutes are of high molecular weights, high B-values show that the ion–solvent interactions are strong i.e. structure maker.

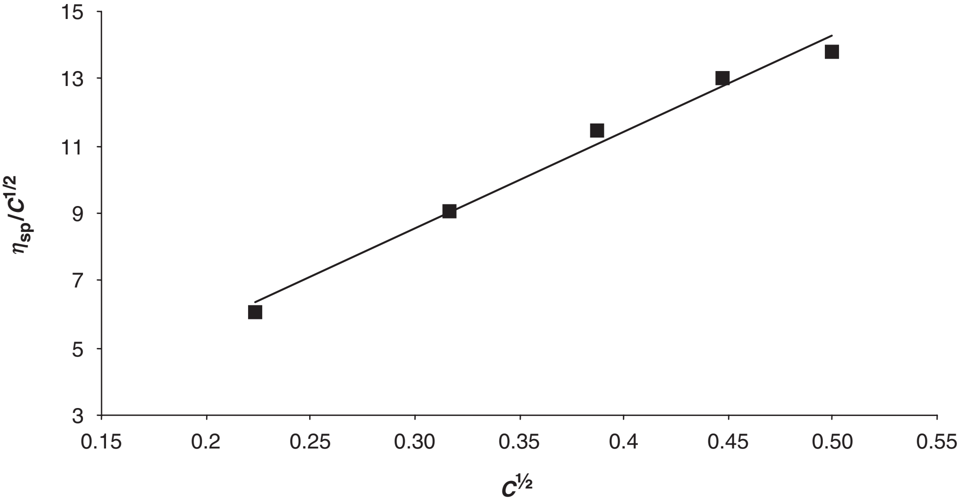

Figure 3. Plot of $\eta_{sp}/C^{1/2}$ *vs*. square root of concentration of aqueous sodium alginate solution at 308 K.

Table 3. Values of ionic interactions of aqueous sodium alginate solution in terms of Jones–Dole coefficients *A* and *B* at various temperatures.

	A and *B* coefficients of Jones–Dole equation	
Temperatures (*K*)	*A* ($mol^{-1/2}\,dm^{3/2}$)	*B* ($mol^{-1}\,dm^{3}$)
303	$+0.7124 \pm 0.003$	26.624 ± 0.004
308	-0.0732 ± 0.002	28.697 ± 0.003
313	-0.9452 ± 0.001	29.713 ± 0.001
318	-0.9881 ± 0.002	29.886 ± 0.003
323	-1.4432 ± 0.003	31.108 ± 0.002

3.1. *Energy of activation*

The relationship between viscosity and energy of activation is given by the following equation.

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right) \tag{2}$$

where η is the viscosity of the algin solution. E_η is the energy of activation, R is the universal gas constant and T is the absolute temperature. The activation energy (E_η) was evaluated from the Arrhenius relation [24] and the representative plot of $\log \eta$ *versus* $1/T$ as a function of sodium alginate concentrations is shown in figure 4. The latent heat of vaporization (L_η) was evaluated from following relation,

$$E_\eta = 0.4 L_\eta. \tag{3}$$

The values of energy of activation and latent heat of vaporization are tabulated in table 4. Decrease in energy of activation and latent heat of vaporization, as temperature rises is due to weakening of the inter molecular forces between the molecules of sodium alginate by uncoiling aggregated molecules there by reducing entanglement between them. The energy of activation is related to the work required to

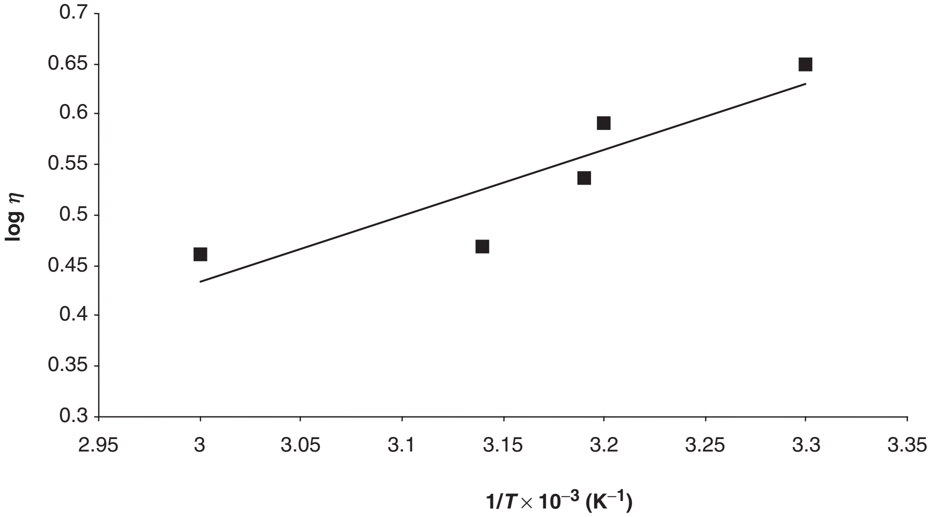

Figure 4. Plot of $\log \eta$ *vs.* $1/T$ for sodium alginate in water at $0.15\,\mathrm{g\,dl^{-1}}$.

Table 4. Energy of activation (E_η) and latent heat of vaporization (L_η) of aqueous sodium alginate solution.

Composition of algin ($\mathrm{g\,dL^{-1}}$)	Energy of activation (E_η) ($\mathrm{J\,mol^{-1}}$)	Latent heat of vaporization (L_η) ($\mathrm{J\,mol^{-1}}$)
0.05	14.1970	35.4920
0.10	12.5010	31.2520
0.15	12.0300	30.0750
0.20	11.7810	29.4520
0.25	11.2700	28.1750

form a hole in the liquid. The holes are necessary for a liquid to flow. Hence, it is concluded that the values of activation energy are found high in pure water.

3.2. *Free energy and entropy of activation*

The free energy change of activation for viscous flow (ΔG^*_η) is given by the following expression.

$$\Delta G^*_\eta = 2.303RT\log\eta/10^{-3} \tag{4}$$

where R is the universal gas constant, T is the absolute temperature and η is the viscosity. The values of ΔG^*_η, control the rate of flow in fluid process. The flow process is governed by the activity of the molecule to move into the prepared hole and the readiness with which the holes are prepared in the liquid. The values of free energy change of activation are calculated and tabulated in table 5.

The entropy change of activation is given by

$$\Delta S_\eta = \frac{\Delta H_\eta - \Delta G_\eta}{T}. \tag{5}$$

Table 5. Free energy change of activation (ΔG_η) of aqueous sodium alginate solution at various concentrations and temperatures.

	Free energy change of activation (ΔG_η) at different concentrations of algin ($\mathrm{kJ\,mol^{-1}}$)				
Temperatures (K)	0.05 ($\mathrm{g\,dL^{-1}}$)	0.10 ($\mathrm{g\,dL^{-1}}$)	0.15 ($\mathrm{g\,dL^{-1}}$)	0.20 ($\mathrm{g\,dL^{-1}}$)	0.25 ($\mathrm{g\,dL^{-1}}$)
303	19.1460	20.1430	21.2860	21.5630	22.0570
308	19.2310	20.1960	21.2990	21.6010	22.1030
313	19.4610	20.2530	21.3560	21.6980	22.2590
318	19.6990	20.3110	21.3870	21.8170	22.4210
323	19.8090	20.4050	21.4080	21.9340	22.5330

Table 6. Entropy change of activation (ΔS_η) of aqueous sodium alginate solution at various concentrations and temperatures.

	Entropy of activation (ΔS_η) at different concentration of algin ($\mathrm{kJ\,mol^{-1}}$)				
Temperatures (K)	0.05 ($\mathrm{g\,dL^{-1}}$)	0.10 ($\mathrm{g\,dL^{-1}}$)	0.15 ($\mathrm{g\,dL^{-1}}$)	0.20 ($\mathrm{g\,dL^{-1}}$)	0.25 ($\mathrm{g\,dL^{-1}}$)
303	−63.1410	−66.2370	−68.2200	−70.1260	−72.5250
308	−63.3920	−66.5300	−68.3130	−70.2940	−72.7260
313	−63.6300	−66.6660	−68.7910	−70.9850	−72.9130
318	−63.9010	−66.8310	−68.9160	−70.8690	−72.0990
323	−64.1840	−67.1340	−69.1410	−70.0700	−72.2110

Energy of activation (E_η) does not differ appreciably from enthalpy change of activation (ΔH_η)

$$\Delta S_\eta = \frac{E_\eta - \Delta G\eta}{T}. \tag{6}$$

The values of entropy change of activation are summarized in table 6. The data show that in some cases the values of E_η and ΔS_η are found lesser than that of the pure solvent indicating that the solvent structure is broken by the presence of solutes. In some cases, these values are found to be higher, which are attributed to the excess of energy necessary to break the hydrogen bonds in solution. When these values are found equal to that of the solvent, the hydrogen bond breaking of the solvent is not significantly affected by the solutes.

The Mark–Houwink equation is used for estimation of average molecular weight of alginic acid of sodium salt in water at 323 K.

$$[\eta] = 1.60 \times 10^{-2}\, M^{0.748}. \tag{7}$$

The average molecular weight is found approximately >100,000, whereas commercially available alginate has molecular weight between 32,000 and 200,000 and the degree of polymerization of alginate is 180–930 [25].

Chemical analysis and other physical data such as optical rotation, FTIR spectral studies etc. revealed that isolated algin is a representative of sodium alginate. Viscometric study confirms that associative interaction between the isolated product and water exists at specific temperature. Rheological studies described algin as a gelling, thickening and viscosity increasing agent for the given solvent i.e. water.

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