ELSEVIER

PII: S0144-8617(97)00248-8

Carbohydrate Polymers 35 (1998) 215–221
© 1998 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0144-8617/98/$19.00+0.00

Salt effects on the cross-linking mechanism of cupric-induced sol–gel transition in alginate solutions

Honghe Zheng[a],*, Hucheng Zhang[a], Qingzhi Zhang[a], Mokio Konno[b], Shuting Yang[a] and Jianji Wang[a]

[a]*Department of Chemistry, Henan Normal University, Xinxiang Henan 453002, People's Republic of China*
[b]*Department of Molecular Chemistry and Engineering, Faculty of engineering, Tohoku University, Sendai 980, Japan*

(Received 3 July 1997; revised 5 December 1997; accepted 5 December 1997)

The viscosity behaviour of alginate–Cu^{2+}–NaCl systems has been experimentally examined at various concentrations of cupric and sodium salts. Dependence of the intrinsic viscosity of alginate as a function of NaCl concentration is discussed to supplement the previous study which shows a similar behaviour to that found for other polyelectrolytes in aqueous solution in the presence of an added salt. The effects of sodium ions on the cupric association in cupric-induced alginate solutions were investigated by means of viscosity measurements. The mechanisms of complex formation in the presence of the simple added salt were studied. It was found that, at a given NaCl concentration, the viscosity of the mixture will pass through a maximum with increasing cupric concentration. The amounts of cupric cations corresponding to the maximum depends on the concentration of NaCl in the solution. Comparison of salt effects on the viscosity behaviour of alginate solutions during sol–gel transition reveals that an optimum NaCl concentration of 10^{-2} mol l^{-1} exists where the viscosity of the mixture gives a maximum value at a certain cupric amount. This result indicates that salt effects play an important role in the sol–gel transition of the polyelectrolyte solutions. The observed phenomenon was interpreted in terms of conformational change of polyelectrolyte chain due to the addition of salt resulting in a different cross-linking mode in the system. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Alginate is a major structural polysaccharide extracted from brown seaweed consisting of (1–4)-linked α-L-guluronate (G) and β-D-mannuronate (M) residues arranged in non-regular blockwise pattern of varying proportion of GG, MG and MM blocks (Haug et al., 1966, Larsen et al., 1970, Haug et al., 1974). It is of considerable technological importance both for its solution properties and as a widely used gelling agent. Alginate has been well known to form ionotropic hydrogels in the presence of divalent cations (exclusive of Mg^{2+}) which act as cross-linkers between the functional groups of alginate monomers (Smidsrod and Haug, 1972a, Smidsrod, 1974, Grasdalen et al., 1979, Grasdalen et al., 1981, Wang et al., 1992, Wang et al., 1993, Wang et al., 1994). Interactions between alginate and divalent cations in aqueous media have been studied by many researchers to elucidate the mechanisms of its gelification. Comprehensive studies have now shown that alginate chain interacts with divalent cations to form two types of complex, monodial and didiol. Both these cross-linkings are chemically equivalent. Most experimental investigations seem to have been performed on the chemistry of the cross-linking process in semi-concentrated solutions, mainly with the help of light scattering and osmotic pressure (Kohn and Larsen, 1972), viscosity and rheological (Smidsrod and Haug, 1965a, Smidsrod and Haug, 1965b, Mackie et al., 1980")

---

*To whom correspondence should be addressed.

studies, and various kinds of modern spectroscopic techniques (Rinaudo and Ravanat, 1980, Yokio et al., 1986a, Yokio et al., 1986b, Zheng, 1997), with the view to obtaining an insight into the detailed reaction mechanisms of metal–alginate complexes. However, the situation is less satisfactory with regard to the behaviour of alginate solution in the presence of a second added salt during gel formation, which will invariably play an important role in the application of alginate in agriculture, food processing, medicine and industry, mainly as a food emulsifier, stabilizer, thickener, and more recently as an important medium for enzyme immobilization. In fact, only a few studies have been made on the salt effects of alginate gelations (Smidsrod and Haug, 1972b). The carboxyl and hydroxyl groups present on alginate monomers, as we know, are very familiar functional groups of natural macromolecules. Investigations on the interaction of metal–alginate in the presence of a second added salt could give some clues to analyses of the interactions of heavy metal ions with various natural macromolecules.

In the present study, the viscosity behaviour of cupric-induced alginate solutions has been investigated both in the absence and in the presence of sodium chloride. Experimental results were interpreted in terms of conformational change of the polyelectrolyte chain due to the added salt effects on the cross-linking mechanism between monomers via cupric ion during the phase transition of alginate solution.

EXPERIMENTAL

Material

Sodium alginate used in this study is obtained from *Lessonia nigresens*, with an average molecular weight of 2.1×10^5, which was determined by means of gel permeation chromatography calibrated by pullulan standard samples. A mannuronate to guluronate ratio of 1.0 was determined by the method as described by Haug et al. (1967). The alginate samples were first dialyzed twice in distilled water using cellulose tubular membranes, and then further dialyzed in deionized water for 3 h. The dialyzed product was centrifuged at 20 000 r.p.m. for 20 min to remove any water-insoluble substances, and finally freeze-dried to obtain a purified sample. The cupric cations employed were cupric chloride, which was of reagent grade without further purification.

Sample preparation

Samples for sol–gel transition measurements were prepared at room temperature by mixing 10 ml of 0.5 g/100 ml alginate aqueous solution with a certain concentration and 1 ml of cupric chloride solution. All samples were homogenous after gentle magnetic stirring for 10 h; the were then left alone for 24 h before the determination being made, in order to obtain reproducible results in viscosity measurements. The addition of the salt solution somewhat decreased the alginate concentration in the system. We prepared a standard solution, which had the same alginate concentration as samples prepared by addition of 1 ml salt solution, by addition of 1 ml deionized water.

Intrinsic viscosity measurements

Intrinsic viscosity, $[\eta]$, for samples of this study was evaluated by using Huggins' (Huggins, 1942) and Kraemer's (Kraemer, 1938) equations which are given as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 \quad \text{(Huggins equation)} \qquad (1)$$

$$[\ln(\eta/\eta_s)]/c = [\eta] + k''[\eta]^2 \quad \text{(Kraemer equation)} \qquad (2)$$

where η and η_s are viscosities of alginate solutions and solvents, while η_{sp}/c and $[\ln(\eta/\eta_s)]/c$ are reduced viscosity and inherent viscosity, respectively. η_{sp} is the specific viscosity defined as $(\eta - \eta_s)/\eta_s$, k' and k'' are constants, and c is the alginate concentration (g/100 ml). Since the viscosity of a polyelectrolyte sample is ionic strength dependent, constant salt concentrations were kept in the determination of $[\eta]$ during the dilution process. For samples with cupric cation in sol–gel transition, as when cupric chloride is added to a solution of sodium alginate there exists a cation exchange leading to liberation of sodium ions, the added salt concentration must be $c_s = c_{NaCl} + 2c_{CuCl_2}$ in all the samples. Efflux times were measured at 30 ± 0.02°C. The data were extrapolated to zero concentration to give the intrinsic viscosity as reported previously. The constant of Huggins' equation, k', was calculated from the slope of the η_{sp}/c *versus* c line using Huggins' equation.

Relative viscosity measurements

Viscosities of our samples during sol–gel transition were measured at 30 ± 0.02°C by using an Ostwald-type capillary viscometer. The efflux time for the lowest viscosity sample was more than 150 s. We calculated relative viscosity, η_{rel}, as the ratio between the viscosities of the solutions with and without cupric ions, used as a measure for describing the extent of gel formation. The viscometers were calibrated with water at 30°C.

RESULTS AND DISCUSSION

The viscosity behaviour of alginate solution in the presence of NaCl salt

Intrinsic viscosities of sodium alginate at different NaCl concentrations are given in Table 1. The series of viscosity measurements were carried out with the aim to clarify the effects of NaCl salt on the polychain behaviour of alginate in aqueous solution. It is shown in Table 1 that the intrinsic viscosity values of alginate decrease with increasing concentration (c_s) of the added salt, NaCl, which are quite similar to those usually observed when a simple salt is added to a polyelectrolyte solution. These results are in good agreement with those reported in the literature (Smidsrod and Haug, 1968, Smidsrod, 1970). The values of intrinsic viscosity of alginate, $[\eta]$, at various NaCl concentrations allow to determine the parameter, $[\eta]_\infty$, the intrinsic viscosity extrapolated to infinite ionic concentration c_s from the equation:

$$[\eta] = [\eta]_\infty + Kc_s^{-1/2} \qquad (3)$$

This variation is well consistent with that predicted from the model proposed by Odijk (1977), Odijk (1979a).

From the results of intrinsic viscosity obtained, we are able to estimate viscosity–average molecular weight, M_v, according to the Mark–Houwink equation:

$$[\eta] = KM_v^\alpha \ (\text{ml g}^{-1}) \qquad (4)$$

where the proportionality of K is characteristic of the polymer and solvent, and the exponent η is as a function of the shape of the polymer in the solvent. The relation between $[\eta]$ and M_v of $[\eta] = 2 \times 10^{-3} \times M_v^{0.97}$ has been reported for alginate samples of M/G = 1.3 in 0.1 mol l^{-1} NaCl aqueous solution at 30°C. This gives a value of about 5.7×10^4 for M_v of the alginate sample, which is confirmed to be greatly different compared to the weight-average molecular weight of $M_w = 2.1 \times 10^5$ measured with permeation chromatography calibrated by pullulan standard samples. The causes (Varum et al., 1991, Wang et al., 1993, Wang et al., 1994) of the difference between the two values are considered to due to the great difference of the chain conformation between the two polymers, alginate and pullulan. Pullulan chains are considered to be much more flexible than the alginate chains. Since then the molecular weight of alginate determined by using a chromatography system calibrated by pullulan is obtained largely than it is to be.

From Table 1, it is clear that the Huggins constant k'' increases from 0.27 to 0.51 when ionic strength increases, whereas the Kraemer constant k'' varies in the range of −0.08 to −0.11. The significance of k' has been well investigated both theoretically (Simha, 1950) and experimentally (Gragg and Sones, 1952, Gragg and Fern, 1953). It can be reviewed as a measure of polymer–solvent and polymer–polymer interactions, or practically as a parameter indicating the relative effectiveness of various solvents for a given polymer and is almost independent of molecular weight for linear polymers. For many polymers in good solvents, the value of k' is known to be 0.4 ± 0.1. For alginate solutions, ranges of 0.28–2.8 (Makie et al., 1979) and 0.33–0.54 (Yamakawa and Fujii, 1974, Hild and Rempp, 1981, Rinaudo and Graebling, 1986) have been reported for k', depending on the compositional and sequential structure of the samples, and ionic strength of the solvents.

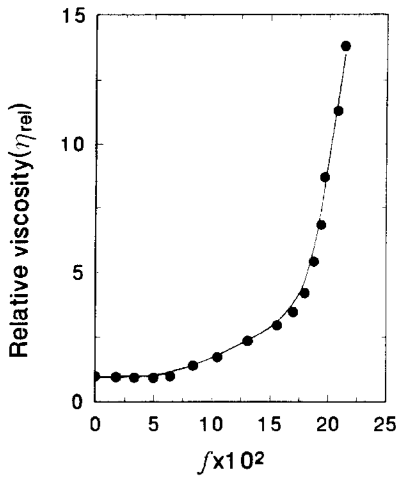

Fig. 1. Variations of relative viscosity (η_{rel}) of alginate solutions *versus* molar fraction of cupric cation, f

Sol–gel transition of alginate solutions in its dilute regime by addition of cupric ions in the absence of a second salt

In this study, cross-linker density is considered as the factor which controls the sol–gel transition. We defined the molar ratio f = [divalent cation]/[residues of alginate] to describe the fraction of cross-linked monomers with the assumption that the ratio f is proportional to the cross-linker density (Zheng and Zhang, 1996, Zheng et al., 1996). The gelation point corresponds to the amount $f = f_c$ of cross-links, where an infinite cluster is formed. Fig. 1 shows the variations of relative viscosity of the cupric-induced alginate solutions with the fraction of cross-links, f. It was shown that for the region of f lower than 0.2, the increase of solution viscosity is not obvious at all, and even shows a somewhat decreasing tendency. It was interpreted by the formation of intramolecular cross-linkings of alginate clusters, which give rise to a contractive effect of polychain conformation and results in a viscosity decrease, and even precipitation of polymers while intermolecular cross-linkings giving birth to polymer networks which are considered as the main factors for gel formation of a polyelectrolyte solution mostly cannot

Table 1.
Intrinsic viscosity ($[\eta]$), Huggins constant (k') and Kraemer constant (k'') of alginate solutions at different NaCl concentrations

	c_{NaCl}(mol l^{-1})						
	0.01	0.02	0.05	0.10	0.20	0.50	∞
$[\eta]$ (ml g^{-1})	166	142	123	116	112	104	94.6
k'	0.310	0.367	0.453	0.420	0.431	0.430	—
$-k''$	0.098	0.144	0.101	0.105	0.118	0.116	—

be formed. However, the real story is not so simple. As we can see in Fig. 2, a monotonous increase of intrinsic viscosity of alginate during the sol–gel transition was shown with increasing f, indicating that intermolecular cross-linkings are formed preferentially even when the solution is far away from its gel point. As far as the fully extended alginate chain in its dilute region is concerned, it seems reasonable to assume that the complex formation of intramolecular cross-linkings is less probable due to the restriction of the skeleton of alginate chain in the absence of added salt. On the other hand, however, the intermolecular cross-linkings can be inferred to form overwhelmingly. Both intra- and intermolecular cross-linkings occur simultaneously in a chemical sense when cupric cation is introduced to the solution, yet in a physical sense, we can infer that the formation of intermolecular cross-linkings is dominant on the whole region of sol–gel transition, while the formation of intramolecular cross-linking clusters is not large at all.

It has been clearly stated that there exist three forms of cupric cations in equilibrium in the solution: free ions, monosubstituted ions carried by the alginate chain, and cross-linked ions present in intra- and inter-chains. Since the intramolecular cross-linking cannot be well formed due to the fully extended chains, the decrease of solution viscosity in the low f region may be well explained by the assumption that a great deal of cupric cations in the solution exist as monosubstituted forms carried by alginate chains. The introduction of cupric chloride increased ionic strength in the polyelectrolyte solution system, which invariably brings about a viscosity decrease of the samples. The explanation is consistent with the suggestion proposed by Smidsrod and Haug (1965a), Smidsrod and Haug (1965b). On the other hand, the viscosity of the alginate solution increases very rapidly with increasing f in the higher f region, indicating that the large formation of intermolecular cross-linkings is the dominant factor deciding the physical properties of the solution.

Since the alginate concentration of 0.5 g/100 ml of this study is well within the dilute domains of aqueous solution, and the fraction of cross-links near its gel point is more than 0.2, the connectivity transition of our system can be reasonably described by an aggregation process which generates a non-equilibrium ensemble leading to a sol–gel transition, where reactive monomers diffuse and collide, thus irreversibly bonding to form dimers, trimers, and eventually large clusters, rather than a percolation process (Meakin, 1988), characterizing the colloidal networks formed in polyelectrolyte solutions in its semi-dilute region where bonds are randomly placed with probability. However, for the aggregation growth phase in dilute solutions, it eventually crosses over to the critical growth characteristic of a connectivity transition, when the fractal aggregates fill the solution volume: the so-called semi-dilute point where the virtually immobilized dense aggregates may be thought of as huge 'monomers' that randomly bond to the neighboring monomers to produce a gel. This irreversible connectivity near gel threshold can be well described by percolation on large length scales, as has been pointed out by Martin and Wilcoxon (1989).

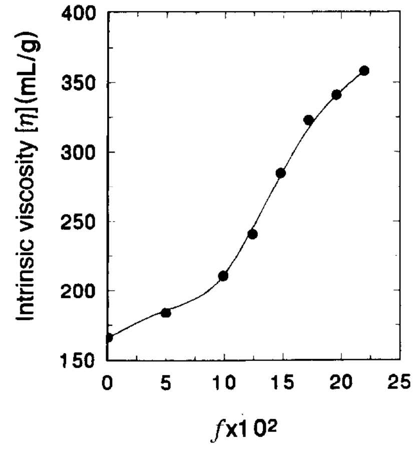

Fig. 2. The intrinsic viscosity, $[\eta]$, plotted against cupric fractions for 0.5 g/100 ml aqueous alginate solutions in sol–gel transition

The critical behaviour of relative viscosity in the vicinity of gel point is described with a power-law relation as shown by the equation:

$$\eta_{\mathrm{rel}} \propto (f_c - f)^{-\kappa} \qquad (5)$$

Here κ is the critical exponent for relative viscosity. Various attempts have been made to estimate the exponent. Theoretical values ranges from 0 to 1.3 (Stockmayer, 1943, Stauffer, 1985) obtained from the three-dimensional percolation theory. So far, experimental measurements of the exponent divergence seem to fall into two camps, with values near either the dynamic scaling prediction of 1.3 or the electric analogy prediction of 0.75. Verification of the 1.3 prediction seems to come from a number of measurements on metal–alginate solutions.

In order to determine the value of f_c, we adopted a procedure used by Takigawa et al. (1990) in which Eq. (5) was rewritten in a linear form as follows:

$$-\eta_{\mathrm{rel}}^{-1}(\mathrm{d}\eta_{\mathrm{rel}}^{-1}/\mathrm{d}f)^{-1} = (f_c - f)/\kappa \qquad (6)$$

The procedure of determination of f_c has been described in previous papers (Takigawa et al., 1990a), using a linear plot between $\eta_{\mathrm{rel}}^{-1}(\mathrm{d}\eta_{\mathrm{rel}}^{-1}/\mathrm{d}f)^{-1}$ against f, the value of f_c can be determined from the intercept on the abscissa which gives the value of f_c to be about 2.4×10^{-1}. Since the measurement of viscosity quite close to the gelation threshold is difficult, as it has been pointed out by Stauffer et al. (1982), the error in estimation is within 5%.

Effects of sodium ions on the association of cupric-induced sol–gel transition in alginate solutions

Fig. 3 shows the variations of relative viscosity of cupric-induced alginate solutions *versus* the cross-linking fraction at different concentrations of sodium chloride. Various series of relative viscosity variations with the cross-linking fraction confirmed that the introduction of a second salt affects sol–gel transition of alginate solutions. The results of Fig. 3 are the following:

(1) At different NaCl concentrations of Cu–alginate solutions, different trends of viscosity variations with increasing fraction of cross-links, *f*, were obtained. At low NaCl concentrations, the increase of relative viscosity of the solutions with *f* in low *f* region is more obvious than that of Cu–alginate solutions without the salt, NaCl. This result implies that the formation of intermolecular cross-linkings seems easily to occur for alginate solutions with a certain amount of salt.

(2) When the NaCl concentration in the mixture is higher than 0.2 M, however, the increase of solution viscosity with increasing *f* is slowed down in the low *f* region, and for alginate solutions with $C_{\mathrm{NaCl}} = 0.4$ M, an increase of viscosity cannot be observed. Even greater concentration of NaCl will bring about precipitation, which makes the viscosity measurements difficult. This result qualitatively shows that high salt concentration is unfavorable for formation of intermolecular cross-linkings and for gel formation of alginate solutions as well.

(3) With increasing fraction of cross-links, *f*, viscosity increases to a maximum value for alginate solutions containing varying amounts of NaCl. Further addition of cupric cation leads to a decrease of viscosity, eventually followed by precipitation. The concentration of Na^+ present in the solutions markedly influences both viscosity and the amount of cupric cations necessary to acquire the maximum viscosity. It simply corresponds to the fact that the lower the Na^+ concentration is, the higher the cupric concentration required to bring about its maximum viscosity.

The above results obtained from our experiment may be roughly explained in terms of added salt effects on the polyelectrolyte chain conformation, which plays an important role in the cross-linking modes between alginate chains via cupric cations. It is well known that a highly charged polyelectrolyte chain in a salt-free aqueous solution will be nearly fully stretched due to strong electrostatic repulsions, which are screened out with the increase of added salt concentration. The charge of an added salt affects the polychain flexibility and subsequently the complex formation mechanism between monomers. According to n.m.r. spectroscopic and rheological studies (Wang et al., 1993, Wang et al., 1994), the interaction between cupric cations and alginate monomers is characterized by a simple complex formation in which the carboxyl groups in both manuronate and guluronate residues are considered to coordinate to cupric cation. An exchange between bound and free cupric ions exists in the system. For dilute alginate solutions in the lower *f* region, and in the absence of a second added salt, it is assumed that cross-linking formation, especially for intramolecular cross-linkings, seems less likely to occur due to the fully stretched chain conformation and high electrostatic energy along the alginate chain.

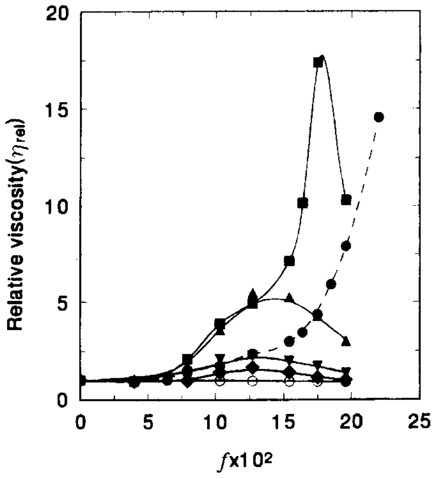

Fig. 3. Variations of relative viscosity (η_{rel}) of alginate solutions *versus* molar fraction of cupric cation, *f*, in the presence of various amounts of NaCl added. Various symbols refer to NaCl concentration (mol l^{-1}) as: (●) 0.00; (■) 0.01; (▲) 0.05; (▼) 0.10; (♦) 0.20; (○) 0.50

When NaCl concentration is gently increased, however, the charge along alginate chain is, to a degree, screened. It has qualitatively and, to a certain extent also semiquantitatively, been borne out by experimental results, mainly with the help of dynamic light scattering and time-dependent electric birefringence measurements on sodium poly(styrensulfonate) in aqueous solutions containing NaCl, that the behaviour of these poly(styrensulfonate) solutions for $c_s > 10^{-2}$ mol l^{-1} is qualitatively different in dilute and semidilute aqueous solutions (Odijk, 1983). The quite flexible chain conformation, and to a great extent also stretched, in the presence of a little amount of simple salt will certainly serve the formation of complexes between alginate monomers. The interaction modes of intra- and intermolecular cross-linkings were suggested to occur simultaneously when divalent cations were added to a solution of alginate (Kasahara, 1958a, Kasahara, 1958b). Both the intra- and intermolecular cross-linkings are chemically equivalent. In a physical sense, however, it was generally believed that the intramolecular cross-linking has a contractive effect on the polychain conformation which leads to a decrease of solution viscosity, while the intermolecular cross-linking generates three-dimensional networks: the main factor for gel formation. In view of the added salt effects on the association of cupric-induced alginate solutions between functional groups, the present viscosity measurements suggest that the quite flexible alginate chain facilitates the formation of intermolecular cross-linkings via cupric ion, which brings about an increase of solution viscosity rather than the formation of intramolecular cross-linkings. The conclusion also supports the suggestion that intramolecular cross-linkings are difficult to obtain in the dilute solution with very low salt concentration, where polychains are, to a great extent, extended; whereas the intermolecular cross-linking may be formed preferentially.

With increasing NaCl concentrations in cupric-induced alginate solutions, however, the increase of solution viscosity with increasing cupric concentration is slowed down, and for alginate solutions with $C_{\mathrm{NaCl}} = 0.4$ mol l^{-1}, an increase of viscosity is not observed. The reason for which may be due to the fact that, with increasing salt

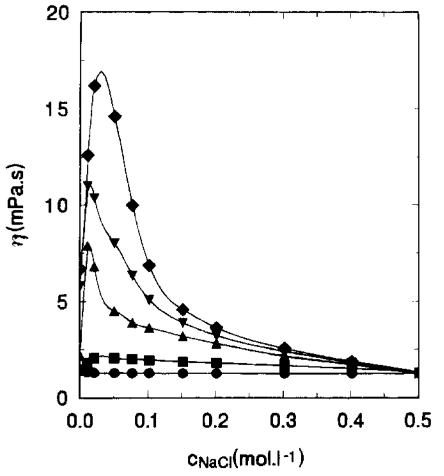

Fig. 4. Viscosity of cupric-induced alginate solutions plotted against NaCl concentration. Various symbols refer to a cupric cation, *f*, of: (●) 1.99×10^{-2}; (■) 7.69×10^{-2}; (▲) 11.4×10^{-2}; (▼) 13.4×10^{-2}; (◆) 15.9×10^{-2}

concentrations, NaCl, the flexibility of the alginate chain increases as well, and eventually the chain behaves as a neutral polymer chain in its θ solvents. The flexible chain in its dilute solution doubtlessly makes the intramolecular cross-linking occur overwhelmingly, while the formation of intermolecular cross-linking is very difficult both thermodynamically and kinetically. The increase of solution viscosity with increasing amount of cupric cation is thus weakened.

Considering that cation exchange leads to a liberation of sodium ion when cupric chloride is added to a solution of sodium alginate, the added salt concentrations for alginate aqueous solution in this study, c_s, equals $c_{NaCl} + 2c_{CuCl_2}$. To further investigate the added salt influence on the interaction mechanisms between alginate chains via cupric cation, the variations of solution viscosity *versus* c_s at constant cupric concentrations were examined. Analyses of the influences of added salt on the solution viscosity are presented in Fig. 4. It was found that, for alginate solutions without cupric ions, and even when the cupric concentration is considerably low, similar to those usually observed for a polyelectrolyte solution in the presence of a simple salt, the solution viscosity decreases with increasing concentration of NaCl. This result confirmed that, for alginate solutions with very low cupric concentrations, the chain behaves as if it were alone, which was suggested by Takigawa et al. (1990b) by the determination of intrinsic viscosity for poly(vinyl alcohol) solutions. The same conclusion has also been achieved by Daoud (1979) for the gelation process of a neutral polymer in its θ solvents. With increasing fraction of cross-links, *f*, however, very different trends of viscosity variations with increasing NaCl concentrations were obtained. A maximum viscosity was found existing for each curve, and the c_s of each curve corresponding to the maximum viscosity falls in the range of 0.02–0.05 mol l^{-1}. The conclusion can be drawn from this figure that an optimum salt concentration exists for an alginate gelation system where a maximum viscosity is reached at a constant cupric concentration. This conclusion qualitatively indicates that gel formation cannot be well carried out for alginate solutions either in the dilute region without salt, or in solutions with high salt concentrations. This result coincides with the conclusion drawn by Odijk (1979b): they state clearly that the behaviour of a polyelectrolyte chain in a solution with c_s in the range of 10^{-2} mol l^{-1}, can neither be strictly assumed as one without added salt nor be strictly considered as a neutral polymer in a good solvent. The behaviour of the polyelectrolyte chain is qualitatively different when it is in its dilute aqueous solutions and when in a solution with an excess of added salt.

CONCLUSION

The above evidence proves unambiguously that salt effects play an important role in the sol–gel transition of alginate solutions induced by cupric cation: the role of which is different according to the salt concentration in the samples. For alginate solutions with $c_s < 10^{-2}$ mol l^{-1}, it improves the formation of intermolecular cross-linkings. The samples then exhibit a rapid viscosity increasing trend with increasing salt concentration. Added salt shows a promoted role for gel formation of alginate solutions. By contrast, for alginate solutions with high salt concentration, the case is not quite the same. High c_s makes the polyelectrolyte chain flexible and thus enables intramolecular cross-linking occur overwhelmingly in its dilute solution. Solution viscosity decreases rapidly with increasing salt concentration. An optimum salt concentration was found existing in the range of 10^{-2} mol l^{-1} where the viscosity of alginate solution gives a maximum value at a constant cupric concentration.

REFERENCES

Daoud, M. (1979) J. Phys. (Paris), **40**, L201.
Gragg, L.H., Fern, G.R.H. (1953) J. Polym. Sci., **10**, 185.
Gragg, L.H., Sones, R.H. (1952) J. Polym. Sci., **9**, 585.
Grasdalen, P., Larsen, B., Smidsrod, O. (1979) Carbohydr. Res., **68**, 23.
Grasdalen, P., Larsen, B., Smidsrod, O. (1981) Carbohydr. Res., **89**, 179.
Haug, A., Larsen, B., Smidsrod, O. (1966) Acta Chem. Scand., **20**, 183.
Haug, A., Larsen, B., Smidsrod, O. (1967) Acta Chem. Scand., **21**, 691.
Haug, A., Larsen, B., Smidsrod, O. (1974) Carbohydr. Res., **32**, 217.
Hild, G., Rempp, P. (1981) Pure Appl. Chem., **53**, 1541.
Huggins, M. (1942) J. Am. Chem. Soc., **64**, 2716.
Kasahara, F. (1958) Kogyo Kagaku Zasshi, **61**, 1282.
Kasahara, F. (1958) Kogyo Kagaku Zasshi, **61**, 1285.
Kohn, R., Larsen, B. (1972) Acta Chem. Scand., **26**, 2455.
Kraemer, E.O. (1938) Ing. Eng. Chem., **30**, 1200.
Larsen, B., Smidsrod, O., Haug, A. (1970) Acta Chem. Scand., **24**, 726.
Makie, W., Nor, R., Sellen, D.B. (1979) Biopolymers, **19**, 1839.
Mackie, W., Noy, R., Sellen, D.B. (1980) Biopolymers, **19**, 1839.
Martin, J.E., Wilcoxon, J.P. (1989) Phys. Rev., **A39**, 252.
Meakin, P. (1988) Phase Transit., **12**, 336.
Odijk, T. (1977) J. Polym. Sci., **15**, 477.
Odijk, T. (1979) Biopolymers, **18**, 3111.

Odijk, T. (1979) Macromolecules, **12**, 688.

Odijk, T. (1983) Chem. Phys. Lett., **100**, 145.

Rinaudo, M., Ravanat, G. (1980) Macromol. Chem., **181**, 1059.

Rinaudo, M., Graebling, D. (1986) Polym. Bull., **15**, 253.

Simha, R. (1950) J. Collid. Sci., **5**, 386.

Smidsrod, O. (1970) Carbohydr. Res., **13**, 359.

Smidsrod, O. (1974) Faraday Disscus. Chem. Soc., **57**, 263.

Smidsrod, O., Haug, A. (1965) Acta Chem. Scand., **19**, 329.

Smidsrod, O., Haug, A. (1965) Acta Chem. Scand., **19**, 341.

Smidsrod, O., Haug, A. (1968) Acta Chem. Scand., **22**, 797.

Smidsrod, O., Haug, A. (1972) Acta Chem. Scand., **26**, 2063.

Smidsrod, O., Haug, A. (1972) Acta Chem. Scand., **26**, 2563.

Stauffer, D. (1985). *Intruduction to Percolation Theory* (124 pp.). London: Taylor and Francis.

Stauffer, D., Coniglio, A., Adam, M. (1982) Adv. Polym. Sci., **44**, 103.

Stockmayer, W.H. (1943) J. Chem. Phys., **11**, 45.

Takigawa, T., Urayama, K., Masuda, T. (1990) Chem. Phys. Lett., **174**, 259.

Takigawa, T., Urayama, K., Masuda, T. (1990) J. Chem. Phys., **93**, 7310.

Varum, K.M., Martinsen, A., Smidsrod, O. (1991) Food Hydrocol., **5**, 363.

Wang, Z., Zhang, Q., Konno, M. (1992) Chem. Phys. Lett., **186**, 463.

Wang, Z., Zhang, Q., Konno, M. (1993) Biopolymers, **33**, 703.

Wang, Z., Zhang, Q., Konno, M. (1993) Biopolymers, **34**, 737.

Yamakawa, H., Fujii, M. (1974) Macromolecules, **7**, 128.

Yokio, H., Kawata, S., Iwaizumi, M. (1986) J. Am. Chem. Soc., **108**, 3358.

Yokio, H., Kawata, S., Iwaizumi, M. (1986) J. Am. Chem. Soc., **108**, 3361.

Zheng, H. (1997) Carbohydr. Res., **302**, 97.

Zheng, H., Zhang, Q. (1996) J. Chem. Phys., **105**, 7746.

Zheng, H., Jiang, K., Zhang, Q. (1996) Chem. Phys., **211**, 507