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Counterion-binding and related phenomena in sodium alginate-sodium chloride-water ternary systems: A conductometric study



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A R T I C L E I N F O

ABSTRACT

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Keywords: Aqueous sodium alginate-sodium chloride solutions Conductivity scaling model for polyion configuration Counterion-binding Effective monomer charge and size Counterion-binding and related phenomena in aqueous solution of the naturally-occurring anionic polyelectrolyte sodium alginate have been explored in absence as well as in presence of sodium chloride using electrical conductivity as the probe. In particular, the variations of the counterion-binding behavior as functions of polyelectrolyte concentration, added electrolyte concentration, and temperature were investigated. A phenomenological treatment of the data which considered the additivity of salt and polyelectrolyte conductivities taking into account the Debye-Hückel interactions using Manning's theoretical expressions for self-diffusion was performed. The results indicated a marked departure from additivity. The data were, therefore, analyzed on the basis of the de Gennes scaling model for the configuration of a polyion chain in semidilute solutions. Counterion-dissociation reached its maximum in absence of the added salt, whereas counterion-binding reached its maximum in presence of the highest amount of the added salt. In moderately saline media, however, counterion-binding was initially found to increase with polyelectrolyte concentration which then gradually leveled off indicating confinement of counterions within the domains of polyion chains at higher polyelectrolyte concentrations. Results indicated the existence of alginate ions as flexible chains in aqueous solutions. A subtle balance of the influences of the effective monomer charge and the effective monomer size played a pivotal role the polyion mobility. Possible conformational changes of the polyion chains caused by dilution led to changes in hydrodynamic resistance in the investigated solutions. The results also provided important insight as to the influence of the alterations of the hydration behavior of the counterions and the relative permittivity of the media on counterion-binding in the investigated systems.

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1. Introduction

Alginates are naturally-occurring water-soluble polysachharides found abundantly in the cell walls of brown algae [1–3]. Alginates are linear polymers of two monomeric units, β -(1–4)-D-mannuronic acid (M) and α -L-guluronic acid (G) (Scheme 1). They can be classified as polyelectrolytes - a special class of polymers - which dissociate in polar media to yield a polyion or macroion and a large number of oppositely charged ions referred to as counterions. Alginates find widespread applications as thickeners, gelling agents, and colloidal stabilizers [4]. The most useful property of these biopolymers is their ability to react with cations to produce gels or insoluble polymers [5,6]. Counterionbinding onto the polyion chains should be taken into account while considering the interaction of alginates with other cations. Elucidation of the interactions in solutions of alginates particularly in presence of cations is, therefore, of utmost importance not only to understand their

* Corresponding author. *E-mail address:* bijan.chem@presiuniv.ac.in (B. Das). mechanism of action in the areas of application, but also to reveal the fundamental chemistry prevailing in these solutions.

The purpose of this study is to explore counterion-binding and transport properties of aqueous solutions of sodium alginate in absence as well as in presence of an added salt with particular reference to the effect of sodium alginate concentration, concentration of the added salt, and temperature using electrical conductivity as the probe. Analyses of the experimental results using the scaling description of Dobrynin et al. [7] helped us recover the extent of counterion-binding and explore the interactions in these systems in a quantitative manner.

2. Experimental

2.1. Materials

Sodium alginate and sodium chloride (NaCl) were purchased from Sigma-Aldrich. The average molecular weight of the sample (108200 g \cdot mol⁻¹) was estimated from the intrinsic viscosity value determined in presence of 0.1 mol \cdot L⁻¹ NaCl aqueous solution at 298.15 K using the Mark-Houwink equation with the constants obtained from the



Scheme 1. Structure of sodium alginate.

literature [8]. The chemicals were dried *in vacuo* for a prolonged period immediately before use.

Triply distilled water with a specific conductance of about 10^{-6} S \cdot cm⁻¹ at 298.15 K was used for the preparation of the experimental solutions.

2.2. Conductance measurements

An Orion (Thermo Fisher, USA) conductivity meter was used to carry out the conductance measurements. The experimental solutions were in a wide mouth test tube fitted with a dip-type cell with a cell constant of 1 cm⁻¹ and having an uncertainty of 0.01%. All measurements were made in a water bath maintained within ± 0.05 K of the temperatures of measurement. Calibration of the conductivity cell was done following the method of Lind and co-workers [9] using aqueous potassium chloride solutions. Specific conductivities of the experimental solutions were always solvent corrected. In all cases, the experiments were performed at least three replicates and the average results were recorded.

2.3. Viscosity measurements

A suspended-level Ubbelohde viscometer was used to measure the viscosities (η) of the liquids. It was kept vertically in a water bath controlled to ± 0.05 K. The viscosity (η) was obtained from the following equation:

$$\eta = (Ct - K/t)\rho \tag{1}$$

where *t* is the time of flow, ρ is the density of the liquid, and *C* and *K* are the two calibration constants characteristic of the viscometer. The values of these constants were determined by using the density and the viscosity values of water, and 2-methoxyethanol [10] and were found to be $C = 1.646 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-2}$ and $K = -0.02332 \text{ cm}^2$, respectively. The values of these constants have also been checked with methanol and acetonitrile [11,12].

The values of the viscosity coefficients (η_0) of water at the experimental temperatures used in this work are listed in Table 1. Also included in this table are the relative permittivities (ε) of water and the limiting equivalent conductivities of sodium ions (λ_c^0) in aqueous solutions from the literature [11,13].

3. Results

3.1. Experimental specific conductivities

The experimental values of the specific conductivities of sodium alginate in absence (κ_{PE}) and those in the presence (κ_{PES}) of varying concentrations of NaCl (0.008, 0.020, and 0.100 mol $\cdot L^{-1}$) in water are depicted as a function of the monovalently-charged groups of sodium alginate per litre (c_{PE}) at 298.15, 308.15, and 318.15 K in Fig. 1. These figures demonstrate a monotonic increase in the specific conductivity values for all the solutions studied. Increasing salinity of the medium is also found to cause an increase in the specific conductivities of the polyelectrolyte-salt solutions as expected.

3.2. Data analyses

Fig. 2 is a representative plot of the difference of the specific conductances of the polyelectrolyte-salt (κ_{PES}) in presence of 0.008 and 0.100 mol \cdot L⁻¹ NaCl and the polyelectrolyte-free salt solutions (κ_S) against polyelectrolyte concentration (c_{PE}) expressed in the number of moles of monovalently-charged groups per unit volume at 298.15 K. Also included in this plot is the variation of the specific conductances of salt-free polyelectrolyte solutions (κ_{PE}) with polyelectrolyte concentration. These plots should coincide irrespective of the amount of the added salt if the additivity equation

$$\kappa_{\rm PF}^{\rm additivity} = \kappa_{\rm PES} - \kappa_{\rm S} \tag{2}$$

holds. It is clear from this figure that the additivity does not hold for the system under investigation, the departure being greater with the higher amount of the added salt.

An analysis of the influence of added salt on the specific conductance of polyelectrolyte solutions considering the Debye-Hückel interaction between the polyion and salt ions was performed following Ander et al. [14,15] with an empirical modified additivity equation

$$\kappa_{\rm PE}^{\rm modified} = \kappa_{\rm PES} - \kappa_{\rm S} \left(D_2 / D_2^0 \right) \tag{3}$$

where D_2 and D_2^0 are, respectively the self-diffusion coefficient of the co-ion in a saltcontaining polyelectrolyte solution and in an infinitely dilute salt solution. The ratio can be calculated by using Manning theory [16] and is expressed as

$$D_2/D_2^0 = 1 - (1/3)\xi(c_{\text{PE}}/c_{\text{S}})[2 + (c_{\text{PE}}/c_{\text{S}})(1 + \pi\xi^{-1})]^{-1}, \xi < 1$$
(4)

$$D_2/D_2^0 = 1 - (1/3)\xi^{-1}c_{\text{PE}}/c_{\text{S}} \left[2 + c_{\text{PE}}/c_{\text{S}}1 + \pi\xi^{-1}\right]^{-1}, \xi > 1$$
(5)

representing the polyions as very dilute non-interacting infinite cylinders in a dielectric continuum in particular below the overlap concentration (c_{PE}). In Eqs. (4) and (5) ξ is the charge density parameter defined as the ratio of the Bjerrum length ($l_B = e^2/kT$) to the separation of the charged sites taken along the axis of the polyion chain (*b*), where *k* is the Boltzmann constant, and *T* the temperature in absolute scale. The value of *b* used for sodium alginate is 5.0 Å [17].

Fig. 2 also compares the $\kappa_{PE}^{modified}$ values calculated on the basis of the modified additivity equation (Eq. (3)) with those calculated from simple additivity for sodium alginate

Table 1

Physical properties of water and the limiting ionic equivalent conductivities of sodium ion in water at 298.15, 308.15, and 318.15 K [11,13].

T/K	η_0 /P	3	λ_c^0 /S·cm ² ·eqv ⁻¹
298.15	0.008903	78.30	50.10
308.15	0.007194	74.82	61.54
318.15	0.005963	71.51	73.73



Fig. 1. Specific conductivities (κ_{PE} or κ_{PES}) of aqueous sodium alginate solutions as a function of polyelectrolyte concentration (c_{PE}) at different temperatures in absence (blue), and in the presence of 0.008 mol·L⁻¹ NaCl (red), 0.020 mol·L⁻¹ NaCl, (black), 0.100 mol·L⁻¹ NaCl (pink). Symbols represent experimental values at 298.15 K (circles), 308.15 K (squares) and 318.15 K (triangles), whereas the lines are used to guide the eye.

solutions in presence of different amounts of the added salt *e.g.*, in presence of 0.008 and 0.100 mol \cdot L⁻¹ NaCl at 298.15 K. Although there is some improvement, the modified additivity does not hold for the present system. The departure from the modified additivity is found to be greater with the higher amount of the added salt.

The primary reason for the change in the conductance of the polyion seems to be due to the change in the overall conformation of the alginate ions (*i.e.*, they exist as flexible chains), which is largely different from an infinite cylinder as assumed in the Manning's theory applicable for dilute solutions. The polyelectrolyte solutions investigated here are essentially in the semidilute regime thus making the application of this theory inappropriate. Further, changed polyion-solvent frictional resistance in salt solutions might also influence the contribution of the polyion to the conductance (see sec. 4.4).

Dobrynin et al. [7] put forward a new theory referred to as the scaling theory for polyelectrolyte solutions which considers the flexibility of the polyion chains in semidilute solutions above c_{PE}^* . This has been successfully exploited by Colby et al. [18] to derive an expression of the specific conductivity of a salt-free semidilute polyelectrolyte solution (κ_{PE}) taking into account the frictional resistance of the polyion moving through the solvent.

According to this theory, the polyion chains are modeled as a random walk of N_{ξ} correlation blobs of diameter ξ_0 , each of which containing g monomers. The electric charge on each monomer is $q_{\xi} = zefg$ (*z* being the valency of the counterion and *e* the charge on an electron). The total charge on the complete chain, with a contour length of $L = N_{\xi}\xi_0$, is $Q_P = N_{\xi}q_{\xi} = zefgN_{\xi}$, where *f* is the fraction of free counterions in polyelectrolyte solution in absence of a salt. The strong electrostatic interactions within the correlation blobs



Fig. 2. Comparison of the experimental specific conductivities (κ_{PE}) of aqueous salt-free sodium alginate solution with those calculated from the additivity equation (Eq. (2)) and those calculated from the modified additivity equation considering the Debye-Hückel interaction between the polyion and salt ions (Eq. (3)) for different concentrations of the added salt (NaCl) at 298.15 K.

stretches the polyion chain to a fully extended conformation of g_e electrostatic blobs of diameter ξ_e .

On the basis of this model, Colby et al. [18] derived the following equation for the specific conductivity of a polyelectrolyte solution (κ_{PE}) in absence of an added salt

$$\kappa_{\rm PE} = f c_{\rm PE} [\lambda_{\rm c}^0 + \left(\left(c_{\rm PE} \xi_0^2 e^2 f \right) / (3\pi\eta_0) \right) \ln(\xi_0 / \xi_e)] \tag{6}$$

where λ_c^0 is the limiting equivalent conductivity of the counterions, and η_0 the coefficient of the viscosity of the medium, and the second term within the square brackets on the right hand side is the equivalent conductivity of the polyion (λ_P).

Addition of a salt to a polyelectrolyte solution causes an alteration in the polyioncounterion interactions, and this, of course, leads to a different extent of counterionbinding [19]. Let the changed fraction of free counterions in polyelectrolyte-salt solutions be *f*. The effective specific conductivity due to the polyelectrolyte when present along with a simple salt can then be given by

$$\kappa_{\text{PE}(\text{eff})} = \int c_{\text{PE}} \left(\lambda_{\text{c}}^{\text{U}} + \lambda_{\text{p}} \right)$$
(7)

The total specific conductivity (κ_{PES}) of a polyelectrolyte-salt solution will, therefore, be the sum of the specific conductivity of the simple salt in the absence of a polyelectrolyte and the effective specific conductivity due to the polyelectrolyte in the presence of a simple salt and is given by

$$\kappa_{\text{PES}} = \kappa_{\text{S}} + f' c_{\text{PE}} \left(\lambda_{\text{c}}^{0} + \lambda_{\text{p}} \right) \tag{8}$$

In Eq. (9), the value of f' takes care of the changed polyion-counterion interactions as influenced by the added salt. This approach has been found to be very successful to describe the electrical conductivity of polyelectrolyte + salt [20–22].

3.3. Evaluation of the fraction of free counterions

Specific conductivity-concentration data of salt-free polyelectrolyte solutions were analyzed on the basis of Eq. (7), while those of polyelectrolyte-salt solutions using Eq. (8). The values of the diameters of the electrostatic blob (ξ_e) and the correlation blob (ξ_0) appearing in Eq. (7) depend upon the solvent quality. Because water is a good solvent for sodium alginate, the following expressions for ξ_e and ξ_0 have been used as given by Ref. [18].

$$\xi_{e} = b \left(\xi f'^{2} \right)^{-(3/7)} \tag{9}$$

$$\xi_0 = (c_{\rm PE}b)^{-(1/2)} \left(\xi f^{\prime 2}\right)^{-(1/7)} \tag{10}$$

The fractions of free counterions have been evaluated from the measured specific conductivity vs. sodium alginate concentration data using Eq. (6) or (8), and (9) and (10). The fractions of free counterions thus obtained have been demonstrated as a function of polyelectrolyte concentration at 298.15, 308.15, and 318.15 K in Fig. 3. It is worth noting that

0.50 0.45 ø ń 0.40 0.35 R 0.30 0 0.02 0.04 0.06 0.08 0.10 $c_{\rm PE}^{}$ / eqv·L⁻¹

Fig. 3. Fraction of free counterions (*f*) in aqueous sodium alginate solutions as a function of polyelectrolyte concentration (c_{PE}) at different temperatures in absence (blue), and in the presence of 0.008 mol·L⁻¹ NaCl (red), 0.020 mol·L⁻¹ NaCl, (black), 0.100 mol·L⁻¹ NaCl (pink). Symbols represent experimental values at 298.15 K (circles), 308.15 K (squares) and 318.15 K (triangles), whereas the curves are used to guide the eye.

Tuffile and Ander [23] reported the fractions of free counterions in aqueous solutions at 298.15 K for four selected concentrations. The *f* values were found to be around 0.57 independent of concentration within the range 0.001–0.015 eqv·L⁻¹. These values are higher than those reported here (0.42–0.44). This may be ascribed to a difference in the methods of analysis of the experimental data. Tuffile and Ander [23] analyzed their data on the basis of the Manning counterion-condensation theory [24–27] of polyelectrolyte solutions available at that time. This theory has, later, shown to have a serious shortcomings in respect of not considering the flexibility of the polyion chains in semidilute solutions where polyion-polyion interactions are absent. This theory is strictly applicable only to infinitely dilute solutions which cannot be attained experimentally [28,29], and the quantitative conclusions drawn from this theory cannot recover the actual behavior in a solution of definite concentration. In view of the above, it is, thus, not possible to compare the results obtained here with those reported by Tuffile and Ander [23].

4. Discussion

4.1. Effect of concentrations of polyelectrolyte and added salt on counterion-binding

The fractions of free counterions in aqueous sodium alginate solution in absence of NaCl are found to be almost independent of polyelectrolyte concentration (cf. Fig. 3). In presence of 0.008 and 0.020 mol \cdot L⁻¹ NaCl, however, the variations of the fractions of free counterions with polyelectrolyte concentration is slightly higher (see Fig. 3). Interestingly again, the fractions of free counterions remain almost invariant with polyelectrolyte concentration in presence of the highest amount of the added salt (0.100 mol \cdot L⁻¹) to aqueous alginate solutions (cf. Fig. 3). These observations indicate that counterion-dissociation reaches a maximum in absence of an added salt in aqueous sodium alginate solutions. Addition of a salt to the sodium alginate solutions causes more counterions to bind to the alginate chains. The extent of counterionbinding is found to increase as the concentration of the added salt increases, which reaches a maximum in presence of a large excess of the added salt. In presence of 0.008 and 0.020 mol \cdot L⁻¹ NaCl solution at a particular temperature the fractions of free counterions were found to initially increase with polyelectrolyte concentration and then gradually level off (cf. Fig. 3). In salt-free solutions, the chain charges are not screened, and hence the intra-chain charge-repulsion stretches the polyions to the maximum extent over the concentration region studied here. This makes the effective charge on a polyion chain independent of the polyelectrolyte concentration. For sodium alginate solutions in presence of the highest amount of the added salt, the chains maintain a compact conformation confining a certain fraction of the counterions throughout the investigated concentration range, thus rendering the effective polyion charge invariant with concentration. In presence of 0.008 and 0.020 mol \cdot L⁻¹ NaCl, however, the initial increase in the fraction of counterions with polyelectrolyte concentration might be attributed to an increase in the relative permittivity of the medium due to the polarizability of polyelectrolytes [30,31]. The increase in the relative permittivity will cause a reduction in the Bjerrum length, a parameter which sets the scale for the distance between dissociated counterions and the polyion chain [24,30,32]. So, there would be more unbound counterions as the polyelectrolyte concentration increases. At higher polyelectrolyte concentrations, polyion chains interpenetrate forming a domain with a certain (constant) fraction of the counterions inside it resulting in an invariance of the effective charge on the polyion chain.

4.2. Effect of temperature on counterion-condensation

The fraction of free counterions in sodium alginate solutions in absence as well as in presence of the highest amount of the added salt (0.100 mol·L⁻¹ NaCl) is found to be almost independent of temperature (Fig. 2). Several effects may contribute to the value of the fraction of free counterions, and three different effects may be considered as being important: (i) an elevation of temperature induces more counteriondissociation, (ii) an increase in temperature causes gradual dehydration of the counterions and the polyionic sites resulting in an increase of counterion-binding on the polyion chain as the electrostatic attraction between the dehydrated ionic species with higher surface charge density improves upon temperature-elevation, and (iii) decreasing relative permittivity of the medium with increasing temperature (*cf.* Table 1) might cause greater counterion-binding at higher temperatures. The results of the present study indicate a mutual cancellation of effect (i) by the combined effects of (ii) and (iii) leading to an invariance of the fraction of free counterions in the case of aqueous sodium alginate solutions both in absence and in presence of 0.100 mol·L⁻¹ NaCl. In presence of moderate concentrations of added NaCl (0.008 and 0.020 mol·L⁻¹), a decrease in the fraction of free counterions in the low polyelectrolyte concentration region with increasing temperature may be attributed to initial coiling of the polyion chains, thus confining more counterions. In the higher polyelectrolyte concentration region, however, saturation of polyion coiling commensurate with the added salt concentration results in temperature-independent counterion-binding.

4.3. Effect of polyelectrolyte concentration, temperature, and added salt concentration on polyion equivalent conductivity

Fig. 4 demonstrates the influences of the concentration of the added salt and the experimental temperature on the variation of the polyion equivalent conductivity (λ_P) as a function of polyelectrolyte concentration.

A careful perusal of the influences of polyelectrolyte concentration, added salt concentration, and temperature on polyion equivalent conductivities provided an important insight into the relative role of the effective monomer charge and the effective monomer size in determining the polyion equivalent conductivities.

4.3.1. Effect of concentrations of polyelectrolyte on polyion equivalent conductivity

The λ_P values are found to be reduced at the highest polyelectrolyte concentrations to an extent of approximately 27–37% from their corresponding values at the lowest concentrations investigated. This supports our previous contention from an analysis of the conductivity data on the basis of the additivity and modified additivity rules (*cf.* sec. 3.2). Since the fractions of free counterions do not change with concentration in polyelectrolyte solutions in absence of a salt and in those containing highest amount of the added salt, the number of ions will remain the same because 1 g equivalent would produce the same number of ions at all dilutions. The interionic attraction between the oppositely charged ions, however, increases with increasing polyelectrolyte



Fig. 4. Polyion equivalent conductivity (λ_P) in aqueous sodium alginate solutions as a function of polyelectrolyte concentration (c_{PE}) at different temperatures in absence (blue), and in the presence of 0.008 mol·L⁻¹ NaCl (red), 0.020 mol·L⁻¹ NaCl, (black), 0.100 mol·L⁻¹ NaCl (pink). Symbols represent experimental values at 298.15 K (circles), 308.15 K (squares) and 318.15 K (triangles), whereas the lines are used to guide the eye.

concentration, which effectively reduces the speed of the ions and hence the polyion equivalent conductivity. The observed dependence of the polyion equivalent conductivity in these two solutions can be interpreted if both the effective monomer size and effective monomer charge are simultaneously taken into consideration. In presence of the two intermediate salt concentrations, as the effective charge on the polyion chains increases, the chains expand with the initial increase in the concentration of the polyelectrolyte. It may be noted while increasing effective monomer charge should cause an increase in the polyion equivalent conductivity, an increase in the monomer size should result in a reduction in the mobility, and it is the subtle balance between these opposing effects which decides the observed mobility in the present aqueous sodium alginate-NaCl solutions. The results obtained thus indicate clearly that the size effect predominates over the charge effect, and that these two effects get closer the higher the polyelectrolyte concentration.

4.3.2. Effect of concentrations of added salt on polyion equivalent conductivity

The polyion equivalent conductivity in any given concentration of sodium alginate solution is found to decrease with increasing concentration of added NaCl at a given temperature. This is a general feature for all the systems studied. An increase in the added salt concentration induces more counterion-binding to the polyion chain. Moreover, increasing salt concentration causes more effective screening of the chain charges and hence more coiling of the polyion chains. Both these effects cause a reduction in the mobility of the polyions at higher salt concentrations.

4.3.3. Effect of temperature on polyion equivalent conductivity

An increase in temperature results in a significant enhancement of the polyion mobility in a given polyelectrolyte solution with a given amount of the added salt. Since the effective charge on the polyion chains does not vary much with temperature (*cf.* sec. 4.2), the observed mobility enhancement could be attributed to an enhanced speed of the ions at higher temperatures.

4.4. Effect of polyelectrolyte concentration, temperature, and added salt concentration on the friction coefficient of the monomer with the solvent media

The monomer friction coefficient provides a measure of the friction between a monomer unit of the polyion and the solvent and can be estimated from the following expression [33].

$$f_{\rm PW} = \left(|z_{\rm P}| f F^2 \right) / \lambda_{\rm P} \tag{11}$$

where z_P is the number of elementary charges on the monomer unit of the fully dissociated polyion, *F* the Faraday constant ($F = eN_A$, N_A being the Avogadro number), and the other symbols bear their usual significance. The results are demonstrated in Fig. 5 where the effect of the concentration of the added salt and the temperature on the variation of the coefficient of friction (f_{PW}) as a function of polyelectrolyte concentration (c_{PE}) are depicted.

4.4.1. Effect of polyelectrolyte concentration on the friction coefficient of the monomer with the solvent media

Fig. 5 demonstrates that the monomer-solvent friction coefficient ($f_{\rm PW}$) values increase significantly with increasing polyelectrolyte concentration (the increment being around 46–71% over the concentration range investigated here). This observation may be attributed to a greater frictional resistance experienced by the monomer units for their movement in a solution with higher polyelectrolyte concentration than in dilute solutions.



Fig. 5. Friction coefficient of the monomer with the solvent media (f_{PW}) in aqueous sodium alginate solutions as a function of polyelectrolyte concentration (c_{PE}) at different temperatures in absence (blue), and in the presence of 0.008 mol·L⁻¹ NaCl (red), 0.020 mol·L⁻¹ NaCl, (black), 0.100 mol·L⁻¹ NaCl (pink). Symbols represent experimental values at 298.15 K (circles), 308.15 K (squares) and 318.15 K (triangles), whereas the lines are used to guide the eye.

4.4.2. Effect of concentration of the added salt on the friction coefficient of the monomer with the solvent media

It can be inferred from the coefficients of friction of the alginate ion with the solvent molecules (Fig. 5) that the possible conformational changes of the polyion chains caused by dilution lead to changes in hydrodynamic resistance, thus supporting our earlier contention (*cf.* sec. 3.2). The effects become more prominent as the concentration of the added salt is increased at a given temperature. The friction coefficients of the monomer units have been found to decrease with increasing amount of the added salt NaCl over the entire polyelectrolyte concentration range studied. Addition of NaCl to a polyelectrolyte solution with a given concentration causes a reduction in the effective polyion charge (*cf.* sec. 4.1) and in the monomer size (*i.e.*, coiling of the polyion chains), and this results in a concomitant decrease in the friction coefficient of the monomer units with the solvent molecules.

4.4.3. Effect of temperature on the friction coefficient of the monomer with the solvent media

An elevation of temperature is found to reduce the frictional resistance of the monomers with the solvent molecules in a specified polyelectrolyte solution in absence as well as in the presence of the added salt (Fig. 5). Since the extent of counterion-binding does not vary with temperature the effective charge and effective size of the monomer units remain invariant with temperature, and hence these could not contribute to the changed values of the monomer-solvent friction coefficients. The observed weakening in the frictional resistance might, therefore, be attributed to the less viscous medium at higher temperatures exerting lower friction.

5. Conclusions

A comprehensive understanding of the factors affecting the dissociation of counterions in aqueous sodium alginate solutions investigated here revealed the nature of the interactions prevailing in these polyelectrolyte solutions. Since in polyelectrolyte gels, counterion-dissociation leads to gel swelling, it is hoped that the information obtained might help modulate the properties of gels of alginates in particular, and other potential gel-forming bio-polyelectrolytes in general. This study signifies the importance of conductometry in conjunction with a judicious choice of an appropriate theoretical model to elucidate the behavior of polyelectrolyte solutions.

Conflicts of interest

There are no conflicts to declare.

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