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Salt-induced counterion condensation and related phenomena in sodium carboxymethylcellulose–sodium halide-methanol-water quaternary systems

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Abstract

Polyion-counterion interactions in sodium carboxymethylcellulose (NaCMC) in methanol-water media have been investigated conductometrically with reference to their variations with polyelectrolyte concentration, relative permittivity and the type and concentration of added electrolytes. The specific conductance data in polyelectrolyte-salt solutions were analyzed using an equation recently developed by us following the scaling description for the configuration of a polyion chain according to Dobrynin *et al*. Excellent quantitative agreement between the experimental results and those obtained with the new equation developed was observed. The results demonstrate that approximately 43-59% of the counterions remain free and that there has been a suppression of counterion dissociation in presence of a salt in any given mixed solvent medium, the extent of which increases with increasing salt concentration. NaCl was found to be slightly more efficient than NaBr in suppressing the counterion-condensation in NaCMC-methanol-water systems. An increase in the amount of methanol in the media causes a reduction in the fraction of free counterions. The results further demonstrate that the monomer units experience more frictional resistance as the methanol content of the mixture increases or as the concentration of the added electrolytes increases. The results were discussed in terms of various interactions prevailing in these systems.

1. Introduction

Polyelectrolytes constitute a special class of polymers which usually contain a large number of affixed charged groups on the polymeric chain compensated by oppositely charged counterions making the whole entity electrically neutral. Dissolution of polyelectrolytes in polar solvents, *e.g.*, water, causes dissociation of the counterions, leaving a charged chain, referred to as the polyion, behind. The counterions and polyions are subject to the long-range Coulomb interaction leading to a variety of effects absent in uncharged polymers solutions. The study of polyelectrolyte solutions has, therefore, been an outstanding problem in polymer science for the last decades from an experimental as well as a theoretical point of view.[1-5] The widespread interest in the area of polyelectrolytes stems from the important roles they play in everyday life. For example, most of the biopolymers such as DNA or RNA as well as almost all proteins are polyelectrolytes. On the other hand, synthetic polyelectrolytes are used in a very wide range of technical applications such as water purification, stabilization of gels, or superabsorbers.[1,2,5-7] In majority of the cases, polyelectrolytes are present along with electrolytes. A preliminary understanding of the influence of electrolytes on the physical properties of polyelectrolytes is, therefore, really only the first step toward understanding the effects of solution conditions on biological as well as industrial systems. Despite significant theoretical and experimental efforts, many properties of polyelectrolyte solutions are still poorly understood compared to those of solutions of neutral polymers.[5,8-12]

The transport properties, which can be conveniently studied by the electrical conductivity, are of central importance in accounting for the solution behavior of polyelectrolytes because electrical conductivity takes into account the movement of any charged entity present in the system under the influence of an externally applied electric field.

A survey of the literature indicated that although within a limited concentration range the polyelectrolyte solution conductivity could be described by the Manning counterion condensation model, the failure of this model is now well known.[13-23] A new model for the electrical conductivity of polyelectrolyte solutions without added salt has been proposed by Colby *et al*.[24] and this approach has been found to be useful to describe the conductivity of polyelectrolyte solutions.

Although the polyelectrolyte conductivities have been well understood in salt-free solutions[24] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al*.,[25] the situation was quite unsatisfactory for salt-containing polyelectrolyte solutions for a long time. Very recently, we have been successful to provide a quantitative description of the electrical conductivities of polyelectrolyte solutions in the presence of an added electrolyte[26,27] using the scaling description of Dobrynin *et al*.[25] The interactions between the polyion and the counterions will be modified in the presence of an electrolyte which will result in a different level of counterion condensation, and this has been considered in this approach while modifying the model for the electrical conductivity of polyelectrolyte solutions without added salt proposed by Colby *et al*.[24] (*cf*. section 2). This opens up an excellent opportunity to study the interactions prevailing in polyelectrolyte-salt solutions, in general, and in biopolymer-salt (*e.g.*, protein-salt, DNA-salt etc.) solutions, in particular, in a quantitative manner.

We have earlier studied the polyion-counterion condensation behavior of an anionic polyelectrolyte sodium carboxymethylcellulose (NaCMC) in methanol-water mixed solvent media using electrical conductivity,[28] which provided important information as to the fraction of free counterions and polyion-counterion interaction of NaCMC in the mixed solvent media as well as their variations with the dielectric constant of the media and the temperature. Addition of salt ions to a polyelectrolyte solution is expected to modify the Coulombic interaction between the polyion and its counterions, and hence modify the extent of counterion condensation. With the availability of a new approach to analyze quantitatively the electrical conductivity data in polyelectrolyte-salt solutions, it is a good idea to study here how polyion-counterion interactions in a mixed solvent media vary with the type and concentration of added salt since these variations would alter the electrostatics and hence the interactions prevailing in these solution which would help shed more light on these interactions in NaCMC solutions in particular, and in polyelectrolyte solutions in general.

2. Theory

Very recently, a convenient approach has been put forwarded by us[26,27] to analyze the conductivity of polyelectrolyte solutions in the presence of an added electrolyte following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*[24] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[25] This approach has been extensively tested with data on sodium polystyrenesulfonate (NaPSS)-NaCl in 2-ethoxyethanol-water mixed solvent media,[26] as well as on NaCMC-NaCl in acetonitrile-water at different temperatures.[27] The data set used considered a number of parameters *e.g.*, relative permittivity of the medium, temperature and concentration of the added salt. Moreover, three decades of concentration of the polyelectrolyte were covered. Very good quantitative agreement with only one adjustable parameter (fraction of free counterions) has been observed.

Here we briefly review the model to describe the conductivity behavior of polyelectrolyte in salt solutions.

In semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0, each of them containing g monomers. Each blob bears an electric charge $q_\xi = zefg$ (z being the counterion valence and e is the electronic charge) and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge $Q_p = N_\xi q_\xi = zefgN_\xi$, where f is the fraction of free counterions. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e. This means that for length scales less than ξ_0, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0, the electrostatic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0.

Following Colby *et al.*,[24] the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

$$\kappa_\mathrm{p} = fc\left[\lambda_c^0 + \frac{c\xi_0^2 e^2 f}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_\mathrm{e}}\right)\right] \qquad (1)$$

where c is the number density of monovalent charged groups, λ_c^0 the limiting equivalent conductivity of the counterions and η_0 the coefficient of the viscosity of the medium.

The interactions between the polyion and the counterions will be modified in the presence of an electrolyte which will result in a different level of counterion condensation, *i.e.*, in a different value of f (designated as f'). The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt can be expressed as

$$\kappa_\mathrm{p(eff)} = f'c\left[\lambda_c^0 + \frac{c\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_\mathrm{e}}\right)\right] \qquad (2)$$

Thus the total specific conductivity (κ) of a polyelectrolyte solution with added simple electrolyte should be equal to 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

$$\kappa = \kappa_{\mathrm{S}} + f^{'} c \left[\lambda_c^0 + \frac{c \xi_0^2 e^2 f^{'}}{3\pi \eta_0} \ln\left(\frac{\xi_0}{\xi_{\mathrm{e}}} \right) \right] \tag{3}$$

On the right hand side of the above equation, the second term within the square brackets is actually the polyion equivalent conductivity designated by λ_{p}. This equation [Eq. (3)] has one adjustable parameter $f^{'}$ and this could be obtained by the method of least-squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in presence of a salt to Eq. (3) using the measured specific conductance (κ_s) of the salt in the absence of the polyelectrolyte. This value of $f^{'}$ takes care of the changed polyion-counterion interactions under the influence of the added salt. The second term in Eq. (3) is the actual contribution of the polyelectrolyte species towards the total specific conductivity in the presence of an added salt.

3. Experimental

3.1 Materials

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance of about 10^{-6} S cm^{-1} at 308.15 K was used for the preparation of the solvent mixtures.

NaCMC employed in this investigation was purchased from Aldrich Chemical Company, Inc. The sample had an average molecular weight (M_{w}) of 90,000 Da, degree of polymerization of and a degree of substitution of 0.70. The chemical structure of the NaCMC sample used in this study is depicted in Scheme 1. The average molecular weight of the sample was estimated from the intrinsic viscosity value determined in 0.2 mol L^{-1} NaCl aqueous solution at 298.15 K using the Mark-Houwink equation with the constants obtained from the literature.[29] The degree of substitution was determined by a conductometric procedure as described by Eyler *et al*.[30] These values agree well with those declared by the producer. NaCl and NaBr were of Fluka puriss grade. These were dried *in vacuo* for prolonged period immediately before use.

3.2 Solutions

The binary methanol-water solvent mixtures were prepared by volume. Three sets of binary solvent systems of methanol and water, having volume fractions of methanol (v) of 0.1, 0.2, and 0.3, have been chosen as the solvent media for the present study. Freshly distilled solvents were always used and the solvent mixtures were prepared immediately prior to use.

3.3 Viscosity measurements

The kinematic viscosities (μ) were measured by means of a suspended level Ubbelohde viscometer. The viscometer was kept in a vertical position in a water thermostat controlled to ±0.01 K. The kinematic viscosity (μ) and the absolute viscosity (η) are given by the following equations:

$$\mu = Ct - K/t \tag{4}$$

$$\eta = \mu\rho \tag{5}$$

where t is the efflux time, ρ is the density, and C and K are the characteristic constants of the viscometer. The values of the constants C and K, determined by using the density and the viscosity values of water and 2-methoxyethanol,[31] were found to be 1.646×10^{-5} cm^2 s^{-2} and

-0.02331647 cm^2, respectively. The calibration constants were also checked with methanol.[32] The estimated error of the viscosity measurements was ± 0.05%.

3.4 Conductance measurements

Conductance measurements were carried out on an Orion (Thermo Fisher) conductivity meter with the solutions taken 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%. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer. The cell was calibrated by the method of Lind and co-workers[33] using aqueous potassium chloride solutions. Due correction was made for the specific conductivity of the solvent by subtracting the specific conductivity of the relevant solvent medium (κ_0) from those of the polyelectrolyte solutions (κ). In all cases, the experiments were performed at least in three replicates and the results were averaged.

4. Results and discussion

4.1 Physical properties of the solvent mixtures

The physical properties of methanol-water mixtures used in this study at 308.15 K, namely the measured values of the coefficients of viscosity (η_0), and the literature[34] relative permittivities (ε), are reported in Table 1. Also included in this table are the limiting equivalent conductivities of the counterion (Na$^+$), λ_c^0 in methanol-water mixtures with volume fractions of methanol (v) of 0.1, 0.2, and 0.3 taken from the literature.[34]

4.2 Experimental specific conductivities

The experimental values of the specific conductivities (κ) of NaCMC in the presence of varying concentrations of NaCl and NaBr (0.0001, 0.0010, and 0.0100 mol L^{-1}) in methanol-water mixtures containing 0.1, 0.2, and 0.3 volume fractions (v) of methanol have been depicted as a function of the moles of monomers per litre *i.e.*, monomol L^{-1} (c_p) at 308.15 K in Figs. 1, 2, and 3 respectively. From these figures, it is apparent that for all the solutions studied the specific conductivities increase with polyelectrolyte concentration. Addition of salt increases the specific conductivities of the polyelectrolyte-salt solutions as expected. The specific conductivities of the polyelectrolyte-salt systems are, in general, found to decrease with increasing amount of methanol in the mixed solvent media at constant salinity. Further, the specific conductivities of the polyelectrolyte-salt solutions investigated are always found to be greater in presence of NaBr than in presence of NaCl.

4.3 Fraction of free counterions

We have employed Eq. (3) for the analysis of the present conductivity data. The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) appearing in Eq. (3) depend upon the quality of the solvent and are, for poor solvents, given by[24]

$$\xi_e = b\left(\xi f'^2\right)^{-1/3} \tag{6}$$

$$\xi_0 = (cb)^{-1/2}\left(\xi f'^2\right)^{-1/3} \tag{7}$$

with the charge density parameter ξ defined as

$$\xi = \frac{e^2}{\varepsilon kTb} \tag{8}$$

where b is the spacing between the charged groups taken along the axis of the polyion chain, k the Boltzmann constant, and T the temperature in absolute scale. The value of b is obtained as the ratio of the segment length (5.15 x 10^{-8} cm) to the degree of substitution of 0.70, which is 7.36 x 10^{-8} cm for the polyelectrolyte under investigation. The ξ values in the three mixed solvent media can then be obtained from Eq. (8) using the b value and the values of the relative permittivities in solvent mixtures, and these are included in Table 1.

For good solvent cases, on the other hand, these are given by[24]

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

$$\xi_0 = (cb)^{-1/2}\left(\xi f'^2\right)^{-1/7} \tag{10}$$

For the present system, good solvent correlations are always found to provide a better description of the experimental results.

The specific conductivity values of the polyelectrolyte-salt system as a function of $c_{\rm p}$ in a given solvent medium and for a given salt concentration were fitted to Eq. (3) by the method of least-squares. The best-fitted f' values along with the standard deviations are reported in Table 2. In Figs. 1-3, we compare the calculated specific conductivities using the f' values reported in Table 2 with those obtained experimentally. From the standard deviations recorded in Table 2, as well as from an inspection of these figures, it is directly evident that the method of analysis described above reproduced the experimental results quite satisfactorily. The present experimental results, thus, provide a further support in favor of the validity of the model for the conductivity of polyelectrolyte-salt solutions proposed recently by us.[26,27]

The results obtained herein will now be discussed to derive important information as to the influence of added salt on the counterion condensation behavior in polyelectrolyte solutions.

Table 2 demonstrates that approximately 43-59% of the counterions remain free in the systems under investigation.

We have earlier reported[28] the fractions of free counterions in NaCMC solutions in methanol-water mixtures under salt-free situations. The fractions of free counterions are found be 0.61, 0.59, and 0.55 in methanol-water mixed solvent media with v = 0.1, 0.2, and 0.3, respectively at 308.18 K. The present results (*cf.* Table 2) thus indicate a suppression of the dissociation of the counterions in presence of a salt in any given mixed solvent medium, the extent of which increases with increasing salt concentration. This is in complete accordance with the Le Chatelier's principle, the equilibrium

$$\text{Free polyion site} + \text{Na}^{+} \Leftrightarrow \text{Combined site} \qquad (11)$$

for the process of binding of the counterions onto to polyionic sites being gradually shifted to the right with the increase in the concentration of the added sodium salt.

NaCl is found to be slightly more efficient than NaBr in suppressing the counterion-condensation of NaCMC in the media investigated. This observation indicates that more sodium ions are available for binding onto the polyion chain in sodium chloride solutions than in sodium bromide solutions having same concentration. Chloride ion due to its greater charge to radius ratio compared to the bromide ion is expected to be more solvated in solutions. This makes the effective size of the chloride ion bigger than that of the bromide ion in solutions resulting in a greater electrostatic attraction between sodium and bromide ions than that between sodium and chloride ions and hence in a more availability of sodium ions in NaCl solutions.

An increase in the amount of methanol in the methanol-water mixtures has also shown to cause a reduction in the fraction of free counterions. This might be ascribed to the changing interaction between the polyion and the counterions with varying relative permittivity of the medium. Strengthening of the polyion-counterion with decreasing relative permittivity of methanol-water mixtures upon gradual addition of methanol to water brings about the weakening of the counterion dissociation and hence a reduction in the fraction of free counterions as the medium gets richer in methanol.

4.4 Polyion equivalent conductivity

Fig. 4 demonstrates the influences of medium, concentration of the added salts as well as their nature on the variation of the polyion equivalent conductivity (λ_{p}) as a function of polyelectrolyte concentration (c_{p}). The λ_{p} values are found to be reduced at the highest concentrations to an extent of approximately 22-35% from their corresponding values at the lowest concentrations investigated. Since the fractions of free counterions do not change with concentration for the present system, the number of ions will remain the same for one gram equivalent would produce the same number of ions at all dilutions. The interionic attraction between the oppositely charged ions, however, increases with increasing polyelectrolyte concentration, which effectively reduces the speed of the ions and hence the polyion equivalent conductivity.

It is directly evident from Fig. 4 that the polyion equivalent conductivity decreases with increasing methanol content of the mixed solvent media. More counterion condensation onto the polyion chain with decreasing relative permittivity of the medium (*cf.* 4.3) causes a reduction in the effective charge (effect 1) and hence a contraction of the polyion coil (effect 2). Decreasing relative permittivity, on the other hand, is expected to increase the intrapolyionic repulsion leading to a stretching of the coil (effect 3). The first and the third effects should result in a lower polyion mobility, while the second in a higher mobility as the medium becomes richer in methanol. The present results demonstrate the predominance of the combined influence of the first and the third effects over the second.

Also displayed in Fig. 4 are the variation of the polyion equivalent conductivity in NaCMC solutions as a function of the polyelectrolyte concentration (c_p) in a given methanol–water mixture in presence of varying concentration of NaCl at 308.15 K. This is a general feature for all the systems studied. An increase in the added salt concentration induces more counterion condensation onto 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 reduce the mobility of the polyions at higher salt concentrations.

Polyion equivalent mobility increases in going from NaCl solutions to NaBr solutions (Fig. 4). This is a consequence of more counterion condensation on polyion chains in presence of NaCl than in presence of NaBr as pointed out above (*cf*. section 4.3).

4.5 The coefficient of friction between the polyion and the solvent (f_ps) and its variation with polyelectrolyte concentration, solvent medium and temperature

The 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:[35]

$$f_\mathrm{ps} = \frac{|z_\mathrm{p}| f F^2}{\lambda_\mathrm{p}} \qquad (12)$$

where z_p is the number of elementary charges on the monomer unit of the completely dissociated polyion, F the Faraday constant ($F = eN_\mathrm{A}$, N_A being the Avogadro number), and the other symbols have their usual significance.

The results are summarized in Fig. 6 where the influences of medium, concentration of the added salts and their nature on the variation of the coefficient of friction (f_ps) as a function of polyelectrolyte concentration (c_p) have been depicted. The significant increase in the (f_{ps}) values with polyelectrolyte concentration (around 32-55% over the concentration range investigated) may be attributed to greater frictional resistance experienced by the monomer units for movement in a more populated solution than in dilute solutions.

We can see from the coefficients of friction of the carboxymethylcellulose ion (Fig. 5) that the possible conformational changes of the molecules caused by dilution lead to changes in solvodynamic resistance. The effects become more prominent as the medium becomes richer in the organic solvent at a given salt concentration, or as the concentration of the added salt is increased in a given medium. An increase in the friction coefficients with increasing methanol content of the mixture over the entire polyelectrolyte concentration range for a given NaCMC-salt system reflects bigger sizes of the monomer units as the medium becomes richer in the organic cosolvent.

The friction coefficients of the monomer units are also found to increase with the increasing addition of any given salt over the entire polyelectrolyte concentration range in a given mixed solvent medium thus indicating bigger sizes of the monomer units at higher salt concentrations. A comparison of the present f_{ps} values in NaCMC-salt solutions with those reported earlier in salt-free NaCMC solutions revealed that addition of salt reduces the monomer sizes in salt solutions. This is in complete agreement with our earlier inference on the coiling of the polyions in presence of a salt based on the polyion conductivity values.

4.6 Comparison with available literature data

There are very few reports on the conductivity behavior of polyelectrolyte solutions in presence of an added salt.[26,27,36-41,43] Although the fractions of free counterions in salt-containing polyelectrolyte solutions are available,[26,27,41,43] there are, so far, no report on the friction coefficient in polyelectrolyte-salt solutions with the exception of our earlier two reports,[26,27]

Bordi *et al*.,[41] however, reported the fraction of free counterions in aqueous sodium polyacrylate-NaCl solution as a function of polyelectrolyte concentration in presence of varying ratio of the polyelectrolyte concentration to the salt concentration (X). The fraction of free counterions, for all the three values of the ratio X investigated (0.1, 1, and 10), shows a marked increase with polyelectrolyte concentration, followed by an approximately constant value and then a pronounced decrease, at higher polyion concentration. The invariance of the fraction of free counterions over a certain polyelectrolyte concentration range in presence of a salt is particularly noteworthy. In the present study, the excellent description of the conductivity data by the model with a single value of the fraction of free counterions is, thus, in agreement with this observation by Bordi *et al*.[41] Analyses of the conductivity data by Colby *et al*.[24] as well as the osmotic pressure data by Bordi *et al*.[42] of aqueous NaPSS and sodium poly(2-acrylamido-2-methylpropanesulfonate), although in the absence of added salt, also evidenced such an invariance of the fraction of free counterions with certain polyelectrolyte concentration. Bordi *et al*.[41] reported a decrease in the fraction of free counterions in aqueous sodium polyacrylate solutions as the concentration of the added salt increases. A similar behavior has also been observed in the present investigation (*cf*. Table 2).

Vuletić *et al*.[43] in their study on the dilute aqueous solutions of rodlike polyions (150 base-pair long DNA fragments) in presence of very low concentration of added monovalent salt ([salt] < 0.00005 mol L^{-1}) quantified the fraction of free counterions. Conductivity measurements of these solutions for DNA base pair concentration range $0.015 \le c_p \le 8$ mM were complemented by fluorescence correlation spectroscopy (FCS) measurements of the DNA polyion diffusion coefficient $D_p(c_p)$. The fractions of free counterions were found to be in the range 0.40 - 0.60. The results were related to the gradual denaturation of DNA with the decrease in DNA concentration in the very low salt environment. It is interesting to note that the fractions of free counterions in the investigated aquo-methanolic NaCMC-NaCl solutions in the present study were found to vary in the range 0.43 - 0.58.

We investigated earlier the conductivity behavior of NaCMC in three different acetonitrile-water mixtures containing 0.1, 0.2, and 0.4 volume fraction of acetonitrile in presence of 0.01, 0.001, and 0.0001 mol L^{-1} NaCl at 308.15 K.[27] The specific conductances and the fractions of free counterions in NaCMC-NaCl in methanol-water mixtures reported in the present study are always found to be significantly higher than those reported in acetonitrile-water mixtures. In view of the similarity of the charge density parameters of NaCMC in methanol-water and acetonitrile-water[27] mixtures, it may be concluded that the specific interactions between the polyion and counterions in these two mixed solvent media play a decisive role.

Our earlier reported specific conductances and the fractions of free counterions in NaPSS-NaCl solutions in 2-ethoxyethanol-water mixtures[26] are found to be smaller than the corresponding values reported in this article. The results indicate more counterion condensation in NaCMC-NaCl-2-ethoxyethanol-water systems than those in NaCMC-NaCl-methanol-water driven by higher charge density parameters in the former system[44] than in the later over specific interactions.

5. Conclusions

Counterion condensation behavior in NaCMC solutions in methanol-water mixed solvent media have been investigated conductometrically in presence of varying concentrations of two electrolytes, namely NaCl and NaBr. Analyses of the specific conductivity data in polyelectrolyte-salt solutions have been performed with an equation recently developed by us following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a polyion chain according to Dobrynin *et al*. (*Macromolecules*, 1995, **28**, 1859-1871). The agreement between the experimental results and those obtained with the new equation developed is excellent. The results demonstrate that approximately 43-59% of the counterions remain free in the systems under investigation. The added salts are found to suppress the dissociation of the counterions in any given mixed solvent medium, the extent of which increases with increasing salt concentration. NaCl was found to be slightly more efficient than sodium bromide in suppressing the counterion-condensation in NaCMC-methanol-water systems. An increase in the amount of methanol in the methanol-water mixtures has also shown to cause a reduction in the fraction of free counterions. The counterion condensation processes are found to be spontaneous for the present polyelectrolyte-salt systems over the entire concentration range and the process becomes less spontaneous as the polyelectrolyte concentration increases while it becomes more spontaneous as the medium gets richer in methanol. The results further demonstrate that the monomer units experience more frictional resistance in solutions as the methanol content of the mixture increases or as the concentration of the added electrolytes increases.

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Table 1 Properties of methanol-water mixtures containing 0.10, 0.20 and 0.30 volume fractions (v) of methanol, the charge density parameters (ξ) and the corresponding limiting ionic equivalent conductivities of sodium ion (λ_c^0) at 308.15 K

v	η_0 (mPa s)	ε	ξ	λ_c^0 (S cm^2 eqv^{-1})
0.10	0.8665	71.57	1.0321	58.12
0.20	1.0218	68.14	1.0841	53.32
0.30	1.1418	64.25	1.1497	49.76

Table 2 The fractions of free counterions ($f^{'}$) and the standard deviations (σ) of fit for the experimental specific conductance for NaCMC in methanol-water mixed solvent media with varying volume fractions of methanol (v) in presence of NaCl and NaBr at 308.15 K as obtained according to Eq. (3)

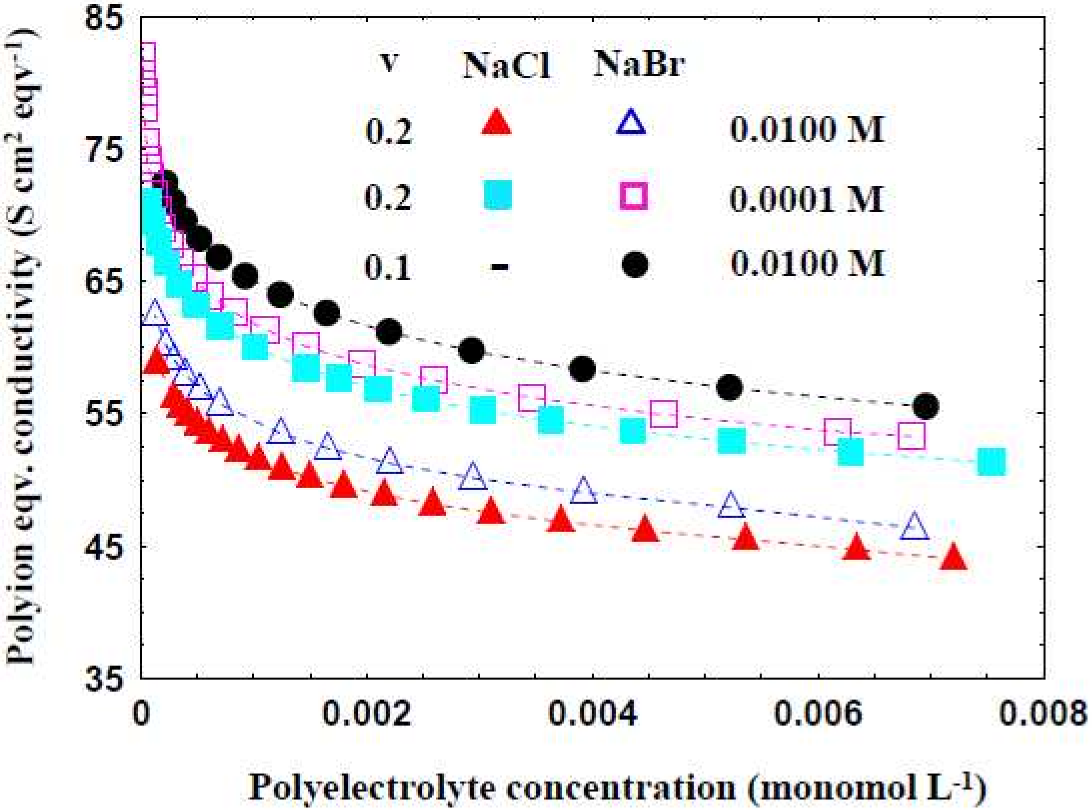
v	Added Salt	[Salt]/ mol L^{-1}	$f^{'}$	σ x 10^5
0.1	NaCl	0.0001	0.575	1.00
		0.0010	0.568	2.12
		0.0100	0.500	1.46
0.2	NaCl	0.0001	0.532	1.07
		0.0010	0.508	0.87
		0.0100	0.474	1.60
0.3	NaCl	0.0001	0.493	0.31
		0.0010	0.470	0.72
		0.0100	0.435	2.18
0.1	NaBr	0.0001	0.588	0.68
		0.0010	0.571	1.04
		0.0100	0.510	1.34
0.2	NaBr	0.0001	0.544	0.43
		0.0010	0.524	1.24
		0.0100	0.493	0.72
0.3	NaBr	0.0001	0.521	0.22
		0.0010	0.510	0.53
		0.0100	0.441	0.68

Graphical Abstract

Salt-induced counterion condensation and related phenomena in sodium carboxymethylcellulose–sodium halide-methanol-water quaternary systems

Bijan Das and Amritendu Chatterjee

Transport and frictional behaviour of sodium carboxymethylcellulose dissolved in methanol-water mixed solvent media with varying volume fraction (v) of methanol have been investigated conductometrically with special reference to their variations as functions of polyelectrolyte concentration, relative permittivity of the medium and the type and concentration of added electrolytes.



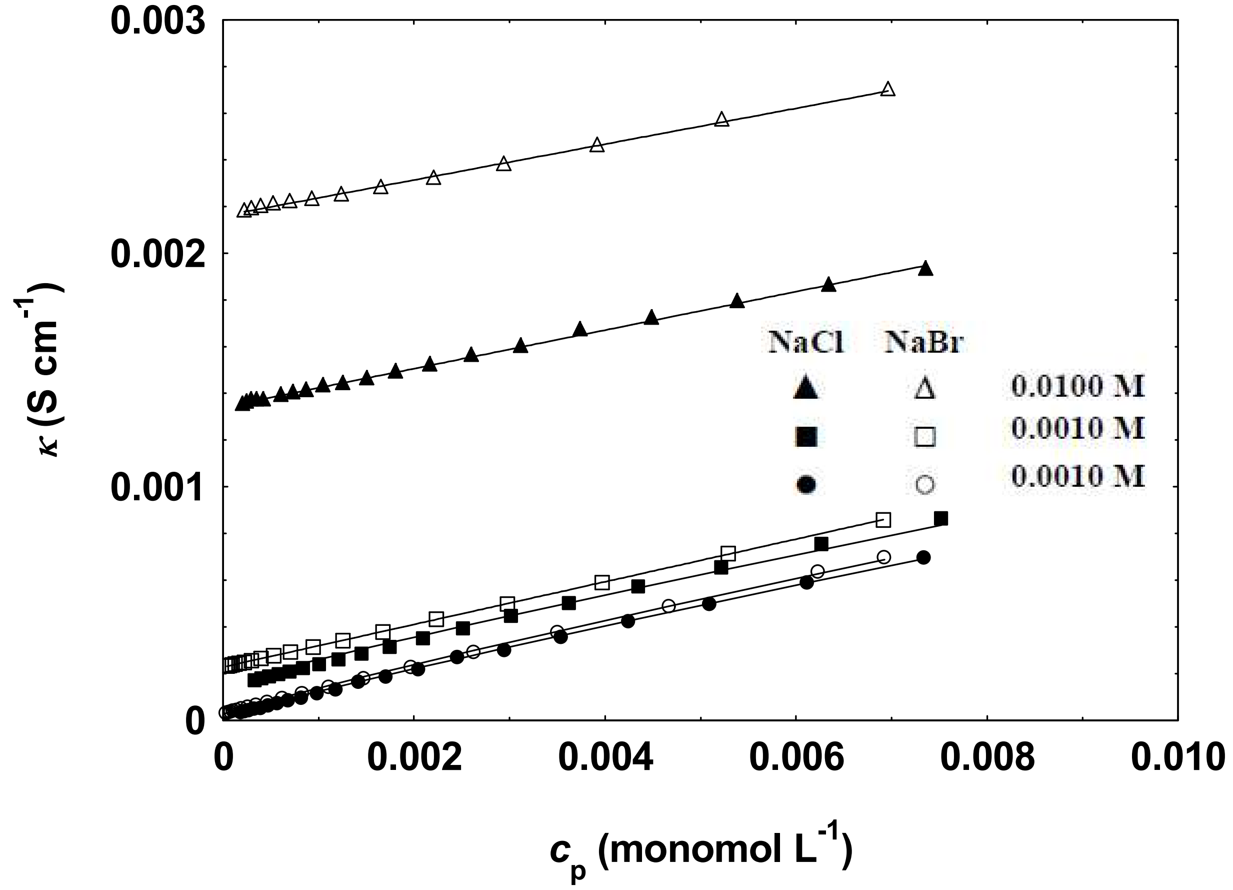


Fig. 1. Specific conductivities (κ) of NaCMC as a function of polyelectrolyte concentration (c_p) at 308.15 K in a methanol-water mixture with 0.1 volume fraction (v) of methanol. Symbols represent experimental values in presence of varying salt concentrations, whereas the lines are according to Eq (3).

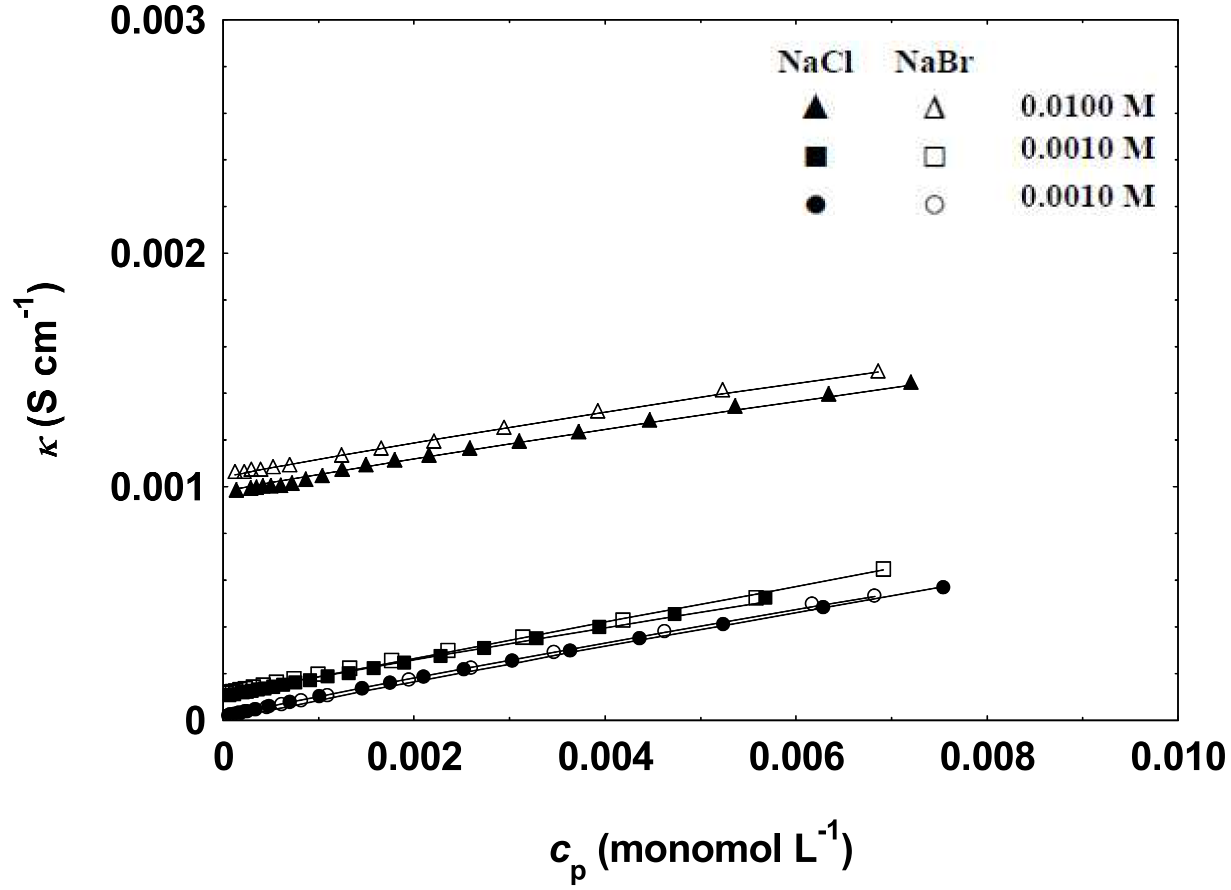


Fig. 2. Specific conductivities (κ) of NaCMC as a function of polyelectrolyte concentration (c_p) at 308.15 K in a methanol-water mixture with v = 0.2. Symbols represent experimental values in presence of varying salt concentrations, whereas the lines are according to Eq (3).

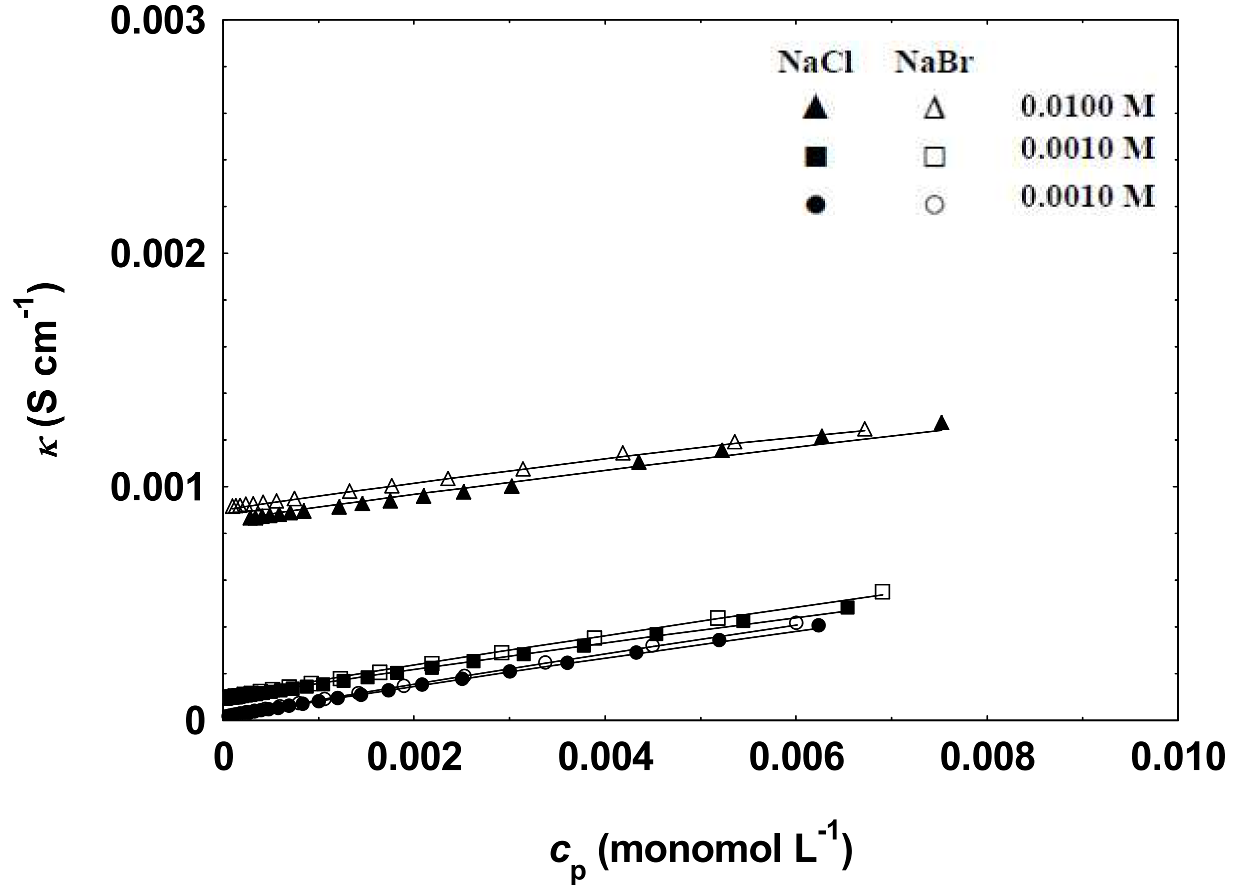


Fig. 3. Specific conductivities (κ) of NaCMC as a function of polyelectrolyte concentration (c_p) at 308.15 K in a methanol-water mixture with v = 0.3. Symbols represent experimental values in presence of varying salt concentrations, whereas the lines are according to Eq (3).

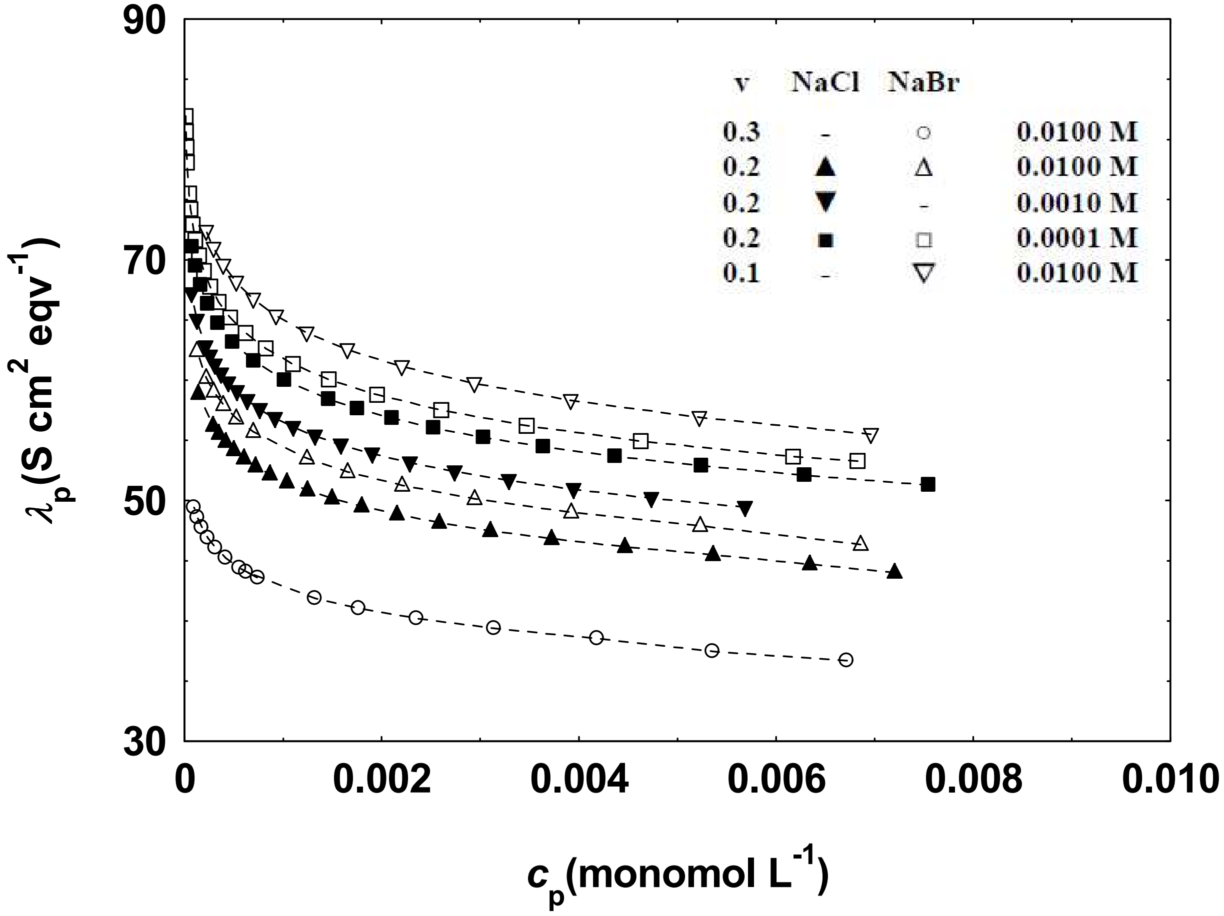


Fig. 4. Variation of the polyion equivalent conductivity in NaCMC solutions as a function of the polyelectrolyte concentration (c_p) at 308.15 K in presence of varying salt concentrations in methanol-water mixtures with varying volume fractions of methanol (v).

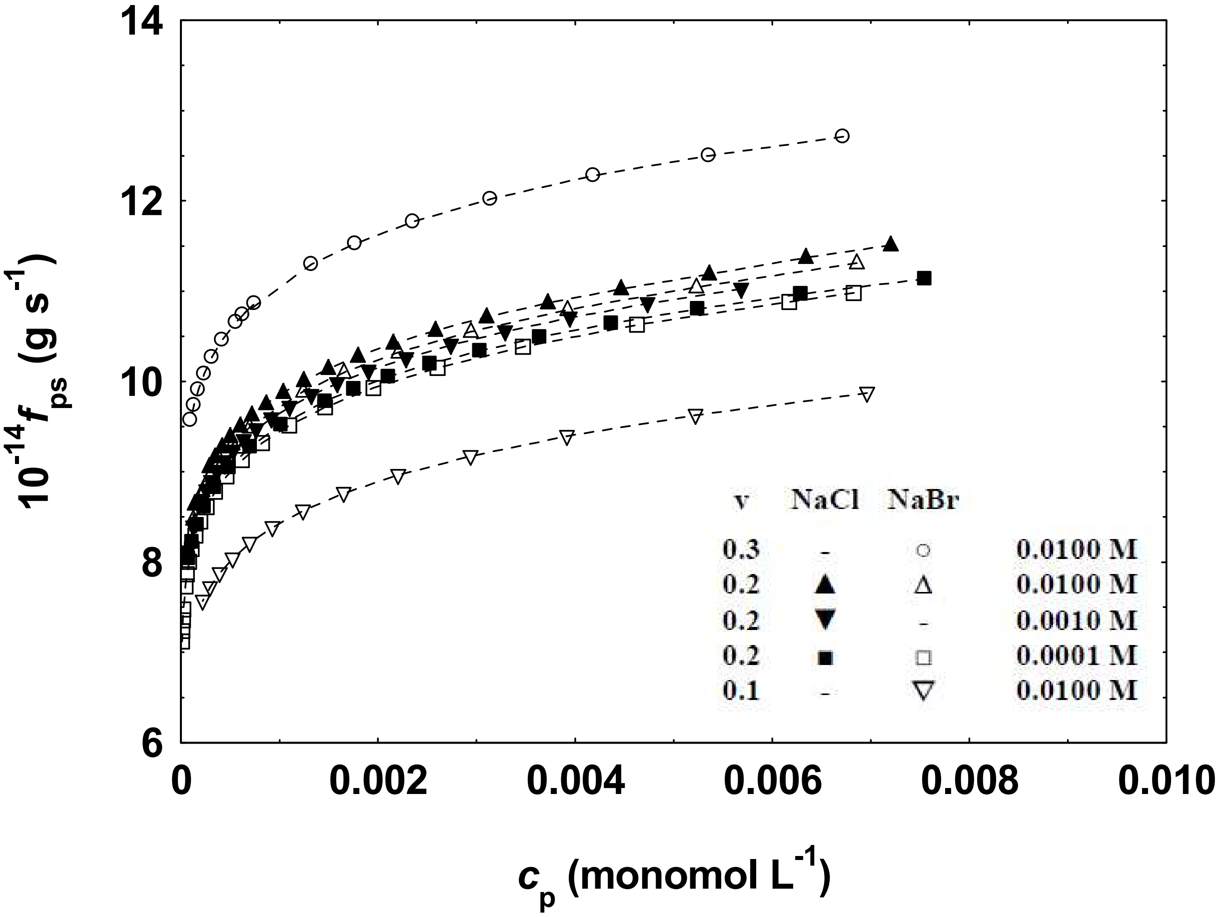
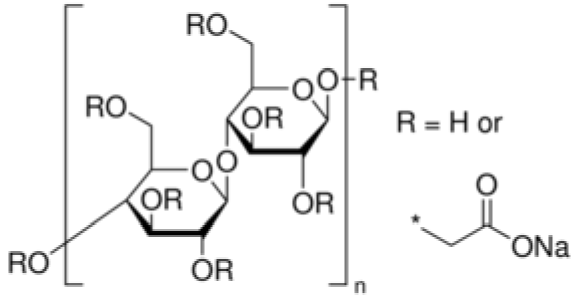


Fig. 5. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) in NaCMC solutions as a function of the polyelectrolyte concentration (c_p) at 308.15 K in presence of varying salt concentrations in methanol-water mixtures with varying volume fractions of methanol (v).



Scheme 1. Chemical structure of NaCMC.