

Chapter 2

Thermodynamic, Transport and Frictional Properties in Semidilute Aqueous Sodium Carboxymethylcellulose (NaCMC) Solution

2.1 Introduction

Polymers with repeat units bearing an electrolyte group are referred to as polyelectrolytes. These groups dissociate in polar solvent media, conferring charges to the polymers to yield a multivalent polyion and a large number of counterions of opposite charge. The strong electric field causes a distinct correlation of the counterions with the polyion thus leading to what is commonly known as the "condensation" of a certain fraction of the counterions onto the polyion. The concept of counterion-condensation, which is central to the solution behaviour of polyelectrolytes, was originally introduced by Oosawa's two-phase model.^{1,2} This idea was later fully exploited by Manning who derived the well-known limiting laws for salt-free solutions of linear polyelectrolytes.³⁻⁶ In particular, Manning derived limiting laws for a number of thermodynamic and transport properties of polyelectrolytes in solution *e.g.*, osmotic coefficient, electrophoretic mobility, equivalent conductivity etc. It must, however, be kept in mind that these laws apply only to infinitely dilute solutions which cannot be attained experimentally.

The Manning model has been recently successfully extended by Colby and co-worker^{7,8} to describe the dielectric and conductometric behaviour of flexible polyelectrolyte systems having finite concentrations on the basis of the scaling picture for the chain conformation of a polyelectrolyte in solution. The predictions for the conductivity of semidilute polyelectrolyte solutions have been compared with the experimental data and found to provide satisfactory descriptions.^{7,13}

A survey of the literature indicated that the influences of polyelectrolyte concentration, polyelectrolyte molecular weight, medium, and temperature on counterion-condensation in salt-free polyelectrolyte solution have been fairly investigated.⁷⁻¹⁸

Another important parameter, namely the degree of substitution of the polyelectrolyte sample defined as the average number of dissociable groups per monomer unit in a polyion, should have a profound influence on the counterion-condensation behaviour. This can be conceived if one considers the charge density parameter of a polyelectrolyte defined through the ratio of the Bjerrum length (λ_B) to the contour distance per unit charge (b):

$$\xi = \frac{\lambda_B}{b} \quad (1)$$

The Bjerrum length $\lambda_B = e^2/\epsilon k_B T$ is the length scale where the Coulomb interaction energy between two elementary charges and the thermal energy are equal (e is the elementary charge, ϵ the relative permittivity of the solvent medium, k_B the Boltzmann constant and T the temperature in absolute scale). With the variation of the degree of substitution, the value of b will vary which, in turn, will result in a changed charge density parameter value. The extent of counterion-condensation onto the polyion chain should also be affected. This aspect, however, has not been fully explored, in particular, with respect to its temperature dependence till date despite its importance in the elucidation of the interactions prevailing in polyelectrolyte solutions. This prompted us to undertake a comprehensive program to investigate the counterion-condensation phenomena in aqueous solution of NaCMC with varying degrees of substitution. Furthermore, the influences of polyelectrolyte concentration, and temperature will also be taken into consideration. Electric conductivity has been employed as a convenient probe to quantify the fractions of free counterions as it measures the contribution of every charged entity present in a solution under the influence of an external electric field.

The polyelectrolyte chosen in this study is an important industrial polymer with a wide range of applications in detergents, textiles, paper, food, drugs, and oil well drilling operations.^{19,20} As shown in Fig. 2.1, carboxymethylcellulose is a derivative of cellulose with carboxymethyl groups ($-\text{CH}_2\text{COOH}$) substituting some of the hydroxyl groups ($-\text{OH}$) of cellulose. The degree of substitution indicates the average number of carboxymethyl groups in a monomer unit, which significantly affects the properties of carboxymethylcellulose. The degree of substitution can vary from 0 to 3. The hydrogen ions in the carboxymethyl groups are generally substituted by the alkali ions used as catalysts during the synthesis of carboxymethylcellulose from cellulose. Sodium ions are commercially used and thus NaCMC is a cellulose material containing sodium-substituted carboxymethyl groups ($-\text{CH}_2\text{COONa}$).

This chapter has been organized as follows. In the next section, a brief description of the modern theory of electrical conductivity of semidilute polyelectrolyte solution is appended, and a summary of the main prediction of the scaling theories of polyelectrolyte solution according to the model proposed by Rubinstein and co-workers²¹⁻²⁴ is given. The

Experimental section provides a hint to the chemical characterization of the polyelectrolyte samples studied along with an account of the experimental techniques employed. In the Results and Discussion section, the counterion-condensation behaviour of the investigated NaCMC solutions in aqueous media has been assessed with particular reference to its dependence on the degree of substitution of the polyelectrolyte sample, its concentration, and the experimental temperature. We also considered the thermodynamics of counterion-condensation, frictional behaviour of the monomer units and the transference behaviour of the polyion and counterion in this section. Finally, the Conclusions section summarizes the important conclusions derived from the present study.

2.2 Experimental

NaCMC with a molecular weight of 250000 was purchased from Acros Organics. Three polyelectrolyte samples with degrees of substitution of 0.7. (range 0.65-0.90), 0.9 (range 0.80-0.95), and 1.2 (range 1.15-1.45) were used. Since our primary aim was to study the role of the degree of substitution of the polyelectrolyte on its counterion condensation behaviour in solution, we carefully checked the degrees of substitution of the investigated samples using the method described by Eyler *et al.*²⁵ and the values obtained (0.70, 0.92, and 1.23) agreed well with those reported by the manufacturer. The values obtained in this study were used in all calculations.

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

Aqueous solutions of NaCMC were prepared by mass by dissolving appropriate amount of the polyelectrolyte in triply distilled water at room temperature. Sufficient time of gentle stirring was allowed to achieve complete solution.

An Orion (Thermo Fisher, USA) conductivity meter operating at 2 kHz was used for the measurement of the specific conductances of the experimental solutions. The meter used a dip-type cell having a cell constant of 1 cm⁻¹. The conductivity cell was calibrated by the method of Lind and co-workers²⁶ using aqueous potassium chloride solutions. The measurements were performed in a water bath maintained within ± 0.01 K of the desired temperature. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium (κ_0) from those of the

polyelectrolyte solutions (κ). Each measurement was replicated three to four times and the average value was taken.

The properties of water namely the coefficient of viscosity and the relative permittivity values at the experimental temperatures are listed in Table 2.1. While the coefficients of viscosity of water have been measured in this investigation, the relative permittivities were obtained from the literature.²⁷ Also included in this table are the literature values of the limiting equivalent conductivities (λ_c^0) of the counterion (Na^+) in water. Since the λ_c^0 values are available for 308.15, 318.15, and 328.15 K,²⁷ those at 313.15 and 323.15 K were obtained by regressing the λ_c^0 data as a function of temperature in the range 298.15 - 373.15 K from the literature.

2.3 Results and Discussion

2.3.1 Scaling Theory of Electric Conductivity of Semidilute Polyelectrolyte Solution

Scaling concepts, successfully used for uncharged polymers, have been applied to the description of the chain conformation of polyelectrolyte solutions in different concentration regimes by de Gennes *et al.*,^{28, 29} Odijk,³⁰ Grosberg and Khokhlov³¹ and more recently by Rubinstein and co-workers.²¹⁻²⁴

In a semidilute solution of polyelectrolytes, a polyion chain has been considered as an assembly of randomly walking N_ξ correlation blobs each with a size of ξ_0 . Each correlation blob consists of g monomers and carries an electric charge of $q_\xi = |z_c|efg$, z_c being the charge on the counterion. The whole chain which has a contour length of $N_\xi\xi_0$, bears a charge of $|z_c|efgN_\xi$. The strong electrostatic interactions within the correlation blobs cause the chain to attain a completely extended conformation of g_e electrostatic blobs each of size ξ_e .

Based on this model, Colby *et al.*,^{7,8} derived the following expression of the equivalent conductivity of a salt-free solution of a polyion (λ_p)

$$\lambda_p = \frac{F|z_c|efg \ln(\xi_0 / \xi_e)}{3\pi\eta_0\xi_0} \quad (2)$$

where F is the Faraday constant, and η_0 the coefficient of viscosity of the medium.

The equivalent conductivity (Λ) of the polyelectrolyte solution was given by

$$\Lambda = f \left[\lambda_c^0 + \frac{F|z_c|efg \ln(\xi_0 / \xi_e)}{3\pi\eta_0\xi_0} \right] \quad (3)$$

λ_c^0 being the limiting equivalent conductivity of the counterions.

The size of the electrostatic blob (ξ_e) and that of the correlation blob (ξ_0) appearing in Eq. (3) are governed by the quality of the solvent. For poor solvents, these are given by⁷

$$\xi_e \cong b \left(\frac{b}{f^2 \lambda_B} \right)^{1/3} \quad (4)$$

$$\xi_0 \cong (cb)^{-1/2} \left(\frac{b}{f^2 \lambda_B} \right)^{1/3} \quad (5)$$

where c is the number density of monovalent charged groups. Polyelectrolyte concentration may also be expressed in terms of moles of monovalent charged groups per unit volume, $c_p = c/N_A$ with N_A being the Avogadro number).

For good solvents, on the other hand, the values of ξ_e and ξ_0 are given by²⁷

$$\xi_e \cong b \left(\frac{b}{f^2 \lambda_B} \right)^{3/7} \quad (6)$$

$$\xi_0 \cong (cb)^{-1/2} \left(\frac{b}{f^2 \lambda_B} \right)^{1/7} \quad (7)$$

Now, since the specific conductance (κ) of the polyelectrolyte solution is related to the equivalent conductivity through $\kappa = \Lambda c / N_A$, it is given by

$$\kappa = \frac{fc}{N_A} \left[\lambda_c^0 + \frac{F|z_c|efg \ln(\xi_0 / \xi_e)}{3\pi\eta_0\xi_0} \right] \quad (8)$$

As can be seen, the above equation has a single free parameter, the fraction f of free counterions that defines the fraction of the effectively ionized group along the polyion chain, in the scheme of the Manning counterion condensation theory. Whereas the Manning theory applies to a polyelectrolyte solution which is infinitely dilute, Eq. (8) can be applied to more concentrated systems.

2.3.2 Fractions of Free Counterions

The specific conductances of aqueous solutions of three NaCMC samples with degrees of substitution of 0.7, 0.9, and 1.2 at 308.15, 313.15, 318.15, 323.15, and 328.15 K as a function of the polyelectrolyte concentration (c_p) expressed as monomol (defined as the moles of elementary charges on the macromolecular chains,³² which is the ratio of the molar mass of a repeat unit to the degree of substitution) per unit volume of water are depicted in Figs. 2.2(a)-(c). The polymer solutions employed in the present study are essentially in the semidilute regime ($c_p > c_p^* \approx 10^{-5}$ monomol.L⁻¹) where the Manning limiting law does not apply. We, therefore, have taken the recourse of the approach proposed by Colby *et al.*,^{7,8} for semidilute polyelectrolyte solutions, for the analysis of our conductivity-concentration data. For the present polyelectrolyte system, good solvent correlations (*cf.* Eqs. (6) and (7)) were always found to provide an excellent description of the specific conductance vs. polyelectrolyte concentration data according to Eq. (8). In Figs. 2.2 (a) - (c) and, the predictions in accordance with the Colby model (lines) for the entire concentration regime have been compared with the experimental specific conductance data with only one adjustable parameter f . The values of f along with the charge density parameters calculated using a segment length³³ of 5.15×10^{-8} cm considering the appropriate value of the degree of substitution are listed in Table 2.2. The excellent description of the concentration dependence of the experimental specific conductance data for all the systems studied here indicates clearly that the effective charge on the polyion chain is invariant with the polymer concentration within the concentration range under investigation for the present polyelectrolyte system. The independence of the fraction of free counterions with the polyelectrolyte concentration may be interpreted as follows: as the polyelectrolyte concentration increases, the relative permittivity of the medium is known to increase, owing to the polarizability of polyelectrolytes.² While the increase in the effective relative permittivity of the medium is not completely understood yet,³⁴ the experimental evidence is well established.^{2,35} The increase in the relative permittivity of the medium (ϵ) would result

in a decrease in the Bjerrum length. Since the scale for the distance between the dissociated counterions on the polyion chain^{2,3,36} is set by the Bjerrum length, as λ_B decreases, the neighbouring charges on the polyion chain could come closer. This happens when more counterions dissociate leaving more charges on the chain. Thus, there will be more free counterions as the relative permittivity of the medium increases. There is, however, an opposing effect which reduces the fraction of free counterions as the polyelectrolyte concentration increases. An increase in the polyelectrolyte concentration causes gradual coiling of the polyion chain which will lead to a greater confinement of the counterions within the polyion coils. The present observation, thus, indicates a fortuitous cancellation of these two opposing effects aqueous NaCMC solution (see Table 2.2).

The fraction of free counterions is found to be greatly influenced by the degree of substitution of the polyelectrolytes sample. At any given temperature, the fraction of free counterions decreases as the polyelectrolyte degree of substitution is increased. This may be attributed to the greater charge density on the polyion chains with higher degree of substitution which induces more counterion-condensation.

The extent of counterion-condensation, however, remains unaltered with the variation of the temperature for each of these three polyelectrolyte samples. The influence of temperature on counterion-condensation is, at first sight, rather perplexing. Increasing temperature causes a reduction in the relative permittivity of the media with a slow rise in the value of the product of the temperature and the relative permittivity. This would result in a greater polyion charge density [*cf.* Eq. (1)] and hence in a higher level of counterion-condensation at higher temperatures. It should also be kept in mind that elevation of temperature also promotes counterion dissociation. An exact balance of these two effects which act in opposite sense maintains the counterion-condensation value at a constant level within the experimental temperature range.

2.3.3 Polyion Equivalent Conductivities

Polyion equivalent conductivities as a function of the polyelectrolyte concentration are depicted in Figs. 2.3 (a)-(c). For a polyelectrolyte sample with a given degree of substitution at a given temperature, the polyion equivalent conductivity decreases monotonically with concentration. As pointed out earlier, the effective charges on the polyion chains as well as their sizes do not vary with polyelectrolyte concentration and hence would not affect the

polyion equivalent conductivity. Increasing polyelectrolyte concentration, however, increases the density of ions in solution causing an obstruction to the polyion movement and hence a reduction the λ_p value.

A monotonous increase was noted in the λ_p value with temperature when the concentration and the degree of substitution are fixed. Since the effective polyion charge and the polyion size are independent of temperature, these have nothing to do with the observed increase in the λ_p value with temperature. Temperature-induced increase in the speed of the ions in a lower viscous medium at higher temperatures could, therefore, be attributed to the enhancement of the polyion equivalent conductivity as the temperature is elevated.

The polyion equivalent conductivities are found to increase with the degree of substitution of NaCMC for a solution of given concentration at each of the temperature investigated. As the degree of substitution is increased, more counterion-condensation would take place on to the polyion chain as has been evidenced from the decreasing fraction of free counterions for polyelectrolyte samples with higher degrees of substitution. Effective charge on the polyion is thus reduced as the degree of substitution increases. This gradually relieves the intrachain electrostatic repulsion thus causing chain coiling when the degree of substitution is increased. Now, since the polyion equivalent conductivity is known to decrease with decreasing effective polyion charge and increase with decreasing polyion size, the size effect takes the lead here over the charge effect in determining the dependence of the polyion equivalent conductivity on the degree of substitution of the polyelectrolyte sample.

2.3.4 Mobility Ratio

The ratios of the mobility of the polyion to that of the counterion (μ_p/μ_c) have been calculated according to Colby *et al.*,^{7,8} and have been depicted against concentration of NaCMC in Figs. 2.4(a)-(c). At low concentrations, the mobility of the polyion is significantly higher than that of the counterions, indicating that the polyion has a larger contribution to the conductivity than the counterions. The mobility ratio decreases logarithmically with concentration through the term $\ln(\xi_0/\xi_e)$ in Eq. (8), because g/ξ_0 is independent of concentration. Physically, this arises because the polyion inside the correlation volume has friction scaling as $\xi_0/\ln(\xi_0/\xi_e)$, while its charge is simply proportional to ξ_0 . The mobilities of the counterions and the polyion become comparable at high concentrations for the NaCMC

sample with the lowest degree of substitution. The mobility ratios are found to be almost independent of temperature for all the three NaCMC samples with varying degrees of substitution indicating that the mobilities of the polyion and the counterion are increased with temperature to the same extent.

Mobility ratios, however, increase appreciably as the degree of substitution of NaCMC is increased. Increasing degrees of substitution favor less charge and more coiling of the polyion chain. Thus, size effect is, again, proved to be the key factor in determining the dependence of the mobility ratio on the degree of substitution. This again confirms our earlier contention regarding the predominance of the polyion size effect over the charge effect for the present system.

2.3.5 Free Energies of Counterion-condensation

In order to obtain an insight into the spontaneity of the counterion condensation process, an information on the standard state free energies of counterion association (ΔG_A^0) is essential. For this purpose, the values of the association constants (K_A) for the process of condensation of counterion as shown below



were calculated as a function of concentration using the following equation:

$$\ln K_A = \ln \left(\frac{1-f}{f} \right) - \ln(f c_p) \quad (10)$$

The standard state free energies of counterion association (ΔG_A^0) can then be easily obtained from:

$$\Delta G_A^0 = -RT \ln K_A \quad (11)$$

where R is the universal gas constant.

Figs. 2.5(a)-(c) display the variation of ΔG_A^0 values of aqueous solutions of NaCMC with degrees of substitution of 0.7, 0.9, and 1.2 as a function of polyelectrolyte concentration at 308.15, 313.15, 318.15, 323.15 and 328.15 K. The negative ΔG_A^0 values indicate that the counterion-condensation process is spontaneous for the present polyelectrolyte system over

the entire concentration range although the process becomes gradually less spontaneous as the concentration increases. Elevation of temperature makes the process more favourable. The spontaneity of the counterion-condensation process is also found to increase with the degree of substitution of the polyelectrolyte sample indicating ease of counterion-binding as the linear charge density of the polyelectrolyte increases.

2.3.6 Polyion Transference Number

The transference number of the polyion (t_p) has been ascertained from the equivalent conductivity of the polyion obtained earlier (λ_p) and the experimentally determined equivalent conductivity of the polyelectrolyte as a whole (Λ) using the following relationship

$$t_p = \frac{\lambda_p}{\Lambda} \quad (12)$$

In Fig. 2.6 we present the transference number data of the polyion as a function of the polyelectrolyte equivalent concentration for all the three polyelectrolyte samples at 308.15, 313.15, 318.15, 323.15, and 328.15 K. Although polyelectrolyte concentration and the degree of substitution of the polyelectrolyte used significantly affect the polyion transference number values, temperature has almost no influence upon them. The polyion transference number values are found to be greater than unity except above 0.0005 monomol.L⁻¹ for NaCMC with a degree of substitution of 0.7. It is well known that the transference number is strongly dependent on the charge density parameter of the polyion, *i.e.*, the larger the charge density parameter the greater is the transport number. Thus it is not at all unusual to find the polyion transference number values larger than unity,³⁸⁻⁴² indicating that a preponderant proportion of the counterions travels in the same direction as the polyions do. No prior report on the transference numbers on NaCMC is available. The systems investigated earlier include alkali-metal salts of polystyrenesulfonic acid, dextransulfonic acid, and *t*-RNA, and a monotonous decrease in the transference number values with polyelectrolyte concentration was also observed in these systems.³⁷⁻⁴¹

2.3.7. Coefficient of Friction Between a Monomer Unit of the Polyion and the Solvent

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 expression⁴¹

$$f_{pw} = \frac{|z_p| f F^2}{\lambda_p} \quad (13)$$

where z_p is charge on each monomer unit of the completely dissociated polyelectrolyte chain, and the other symbols bear their usual significance. The results are summarized in Figs. 2.7(a)-(c). The friction coefficient values (f_{pw}) are found to decrease with the increase in the degree of substitution of the polyelectrolyte sample at any given temperature. As pointed out earlier higher degree of substitution promotes counterion-condensation leading to a less charged and more coiled polyion as the degree of substitution increases. A smaller entity with lower charge naturally experiences less frictional resistance. The friction coefficients of the monomer units decrease with increasing temperature over the entire polyelectrolyte concentration range for a polyelectrolyte sample with a given degree of substitution thus indicating a reduction in the frictional resistance as the temperature is elevated. Since the effective charge and the size of the polyion chain do not change either with polyelectrolyte concentration or with the temperature provided the degree of substitution remains unaltered, the observed decrease in the monomer friction coefficient values as the temperature is raised might be attributed to a reduction in the viscosity of the medium with temperature.

2.4 Conclusions

Electrical conductivity is a powerful tool to elucidate the polyion-counterion interaction in solutions. A comprehensive investigation on the electrical conductivity data of salt-free aqueous solutions of NaCMC has been presented. A number of parameters *e.g.*, degree of substitution of the polyelectrolyte, concentration of polyelectrolyte, and temperature have been taken into consideration. Use has been made of the current model for the electrical conductivity of semidilute polyelectrolyte solutions which relied on the de Gennes scaling picture of the configuration of a polyion chain in semidilute solutions. An excellent description of the specific conductance *vs.* polyelectrolyte concentration data was achieved with a single value of the fraction of free counterions at each temperature for each degree of

substitution. 36-55% of the counterions were found to remain free in the investigated systems. Temperature and the polyelectrolyte concentration were found to have no influence on counterion-binding onto the polyion chains. The level of counterion-condensation was greatly affected by the degree of substitution of the polyelectrolyte sample, the one with the highest degree of substitution showing the maximum condensation. The counterion-condensation processes were always found to be spontaneous for the present system. The size effect of the polyion has been shown to predominate over the charge effect in governing the polyion mobility. The results demonstrate that the transference numbers of the two more substituted samples (*i.e.*, higher charge densities of polyions) are clearly larger than unity over the entire concentration range studied, decrease monotonously with increasing concentration. The monomer units of the polyion experiences more frictional resistance with the solvent molecules as the polyelectrolyte concentration increases, or as the temperature is lowered, or as the degree of substitution of the polyelectrolyte is reduced. The degree of substitution has always found to have more influence on the thermodynamic, transport and frictional properties reported here than the polyelectrolyte concentration and the experimental temperature.

2.5 References

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TABLE 2.1. The Relative Permittivity (ϵ), and the Coefficient of Viscosity (η_0) of Water as well as the Limiting Ionic Equivalent Conductivity (λ_c^0) of Sodium Counterion at Different Temperatures (T).

$T(K)$	ϵ^a	$\rho\text{ (g.cm}^{-3}\text{)}^a$	$\eta_0\text{ (mPa.s)}^a$	$\lambda_c^0\text{ (S.cm}^2\text{.eqv}^{-1}\text{)}$
308.15	74.82	0.99407	0.7194	61.54 ^a
313.15	73.15	0.99224	0.6531	67.55 ^b
318.15	71.51	0.99206	0.5963	73.73 ^a
323.15	69.91	0.98808	0.5467	80.23 ^b
328.18	68.34	0.98573	0.5044	86.88 ^a

^a Ref. [31].
^b Interpolated values (please see text).

TABLE 2.2. Fraction of Free Counterions (f), the Standard Deviation of Fits (σ) and the Charge Density Parameters (ξ) in Aqueous Solutions of Sodium Carboxymethylcellulose of Different Degrees of Substitution at Different Temperatures (T).

Degree of Substitution	T (K)	ξ	f	$\sigma \times 10^5$
0.7	308.15	1.0	0.55	0.99
	313.15	1.0	0.55	0.86
	318.15	1.0	0.55	0.89
	323.15	1.0	0.55	1.22
	328.15	1.0	0.55	1.61
0.9	308.15	1.3	0.44	1.58
	313.15	1.3	0.44	1.47
	318.15	1.3	0.45	1.27
	323.15	1.3	0.44	1.17
	328.15	1.3	0.44	1.35
1.2	308.15	1.7	0.36	1.31
	313.15	1.7	0.36	1.35
	318.15	1.7	0.36	1.44
	323.15	1.7	0.36	1.63
	328.15	1.7	0.36	2.16

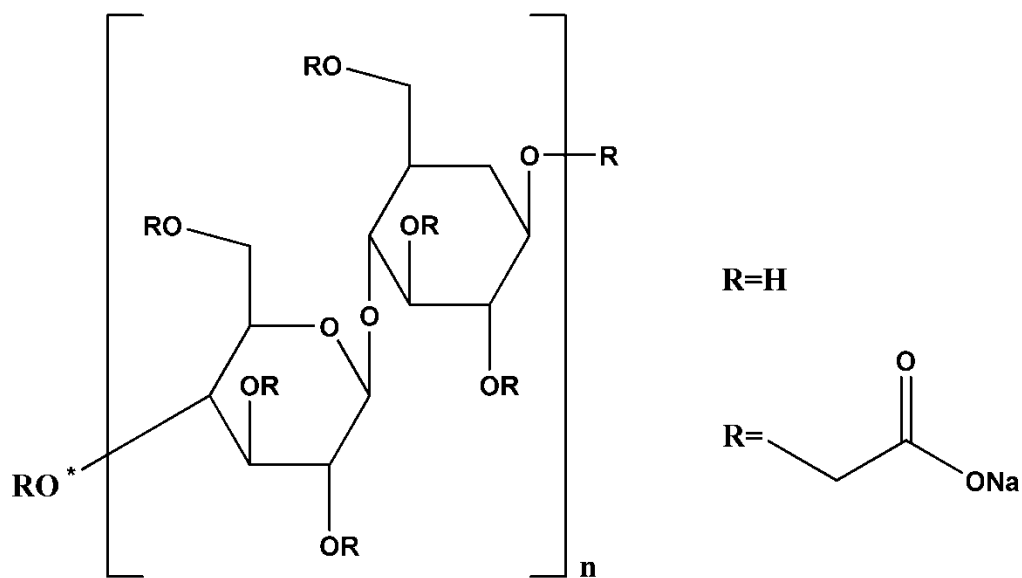


Fig. 2.1. Chemical structure of NaCMC.

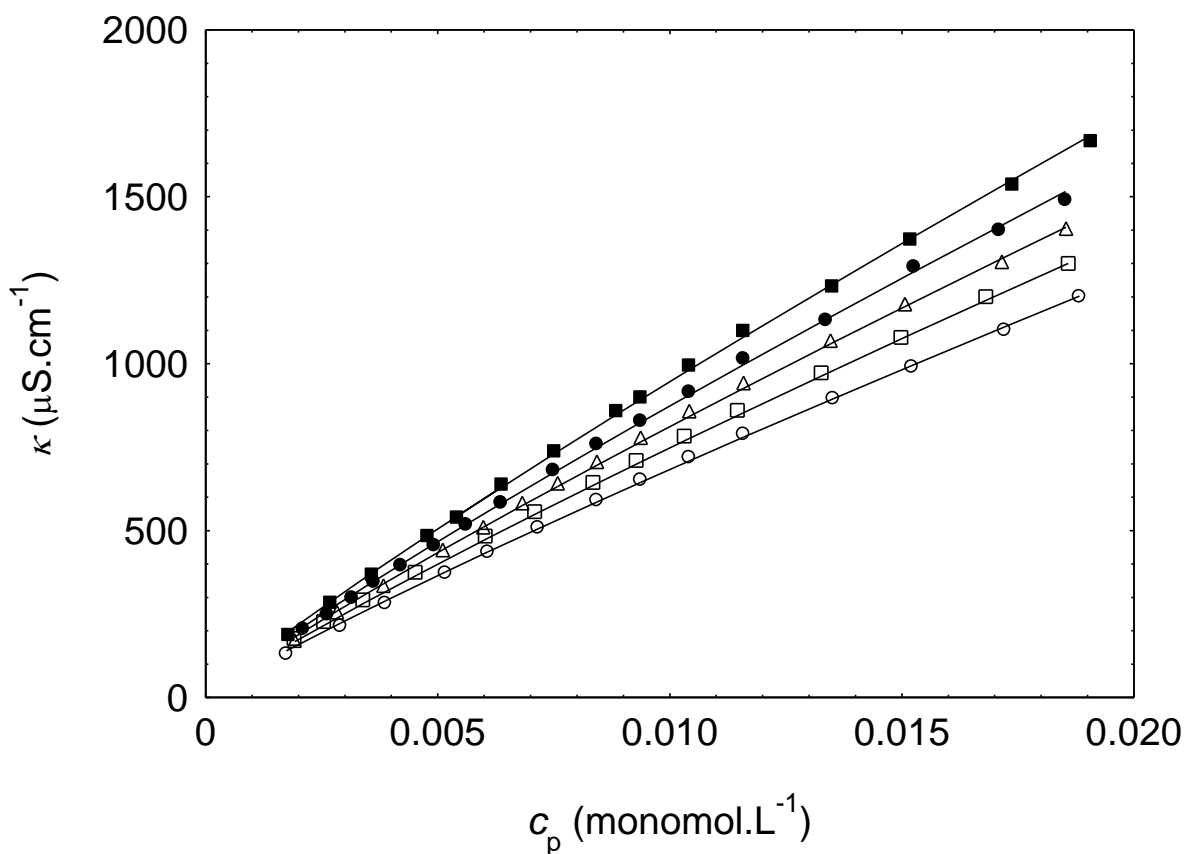


Fig. 2.2(a). Specific conductances of aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.7 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare) along with the calculated values (lines) according to Colby model.

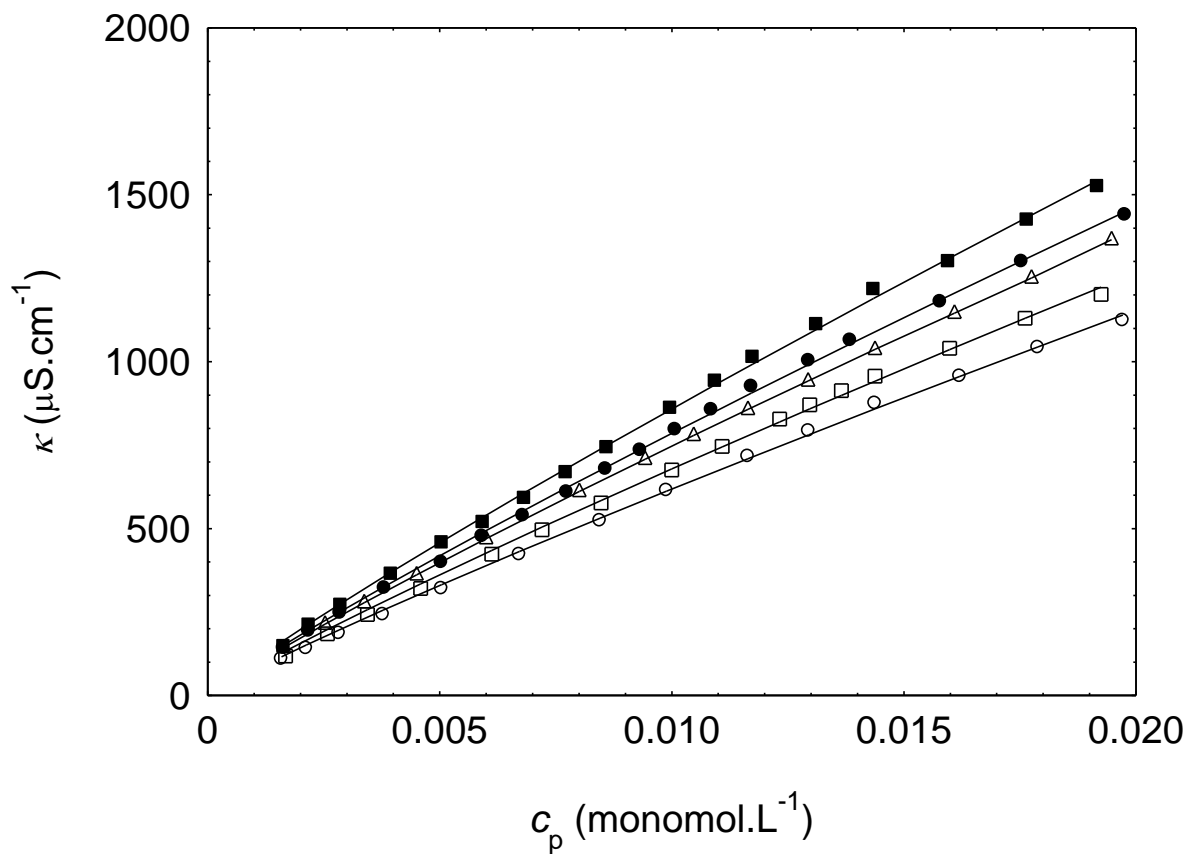


Fig. 2.2(b). Specific conductances of aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.9 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare) along with the calculated values (lines) according to Colby model.

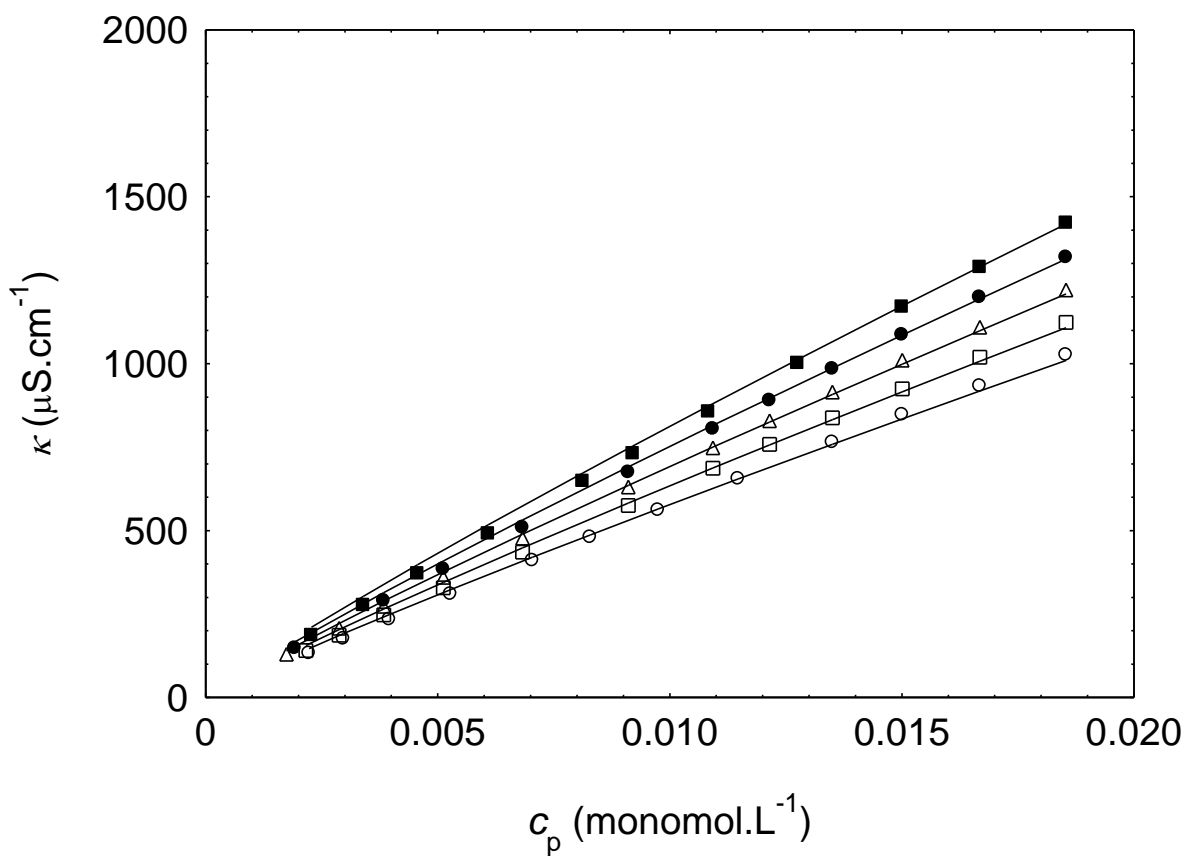


Fig. 2.2(c). Specific conductances of aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 1.2 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (Δ), 323.15 K (●) and 328.15 K (■) along with the calculated values (lines) according to Colby model.

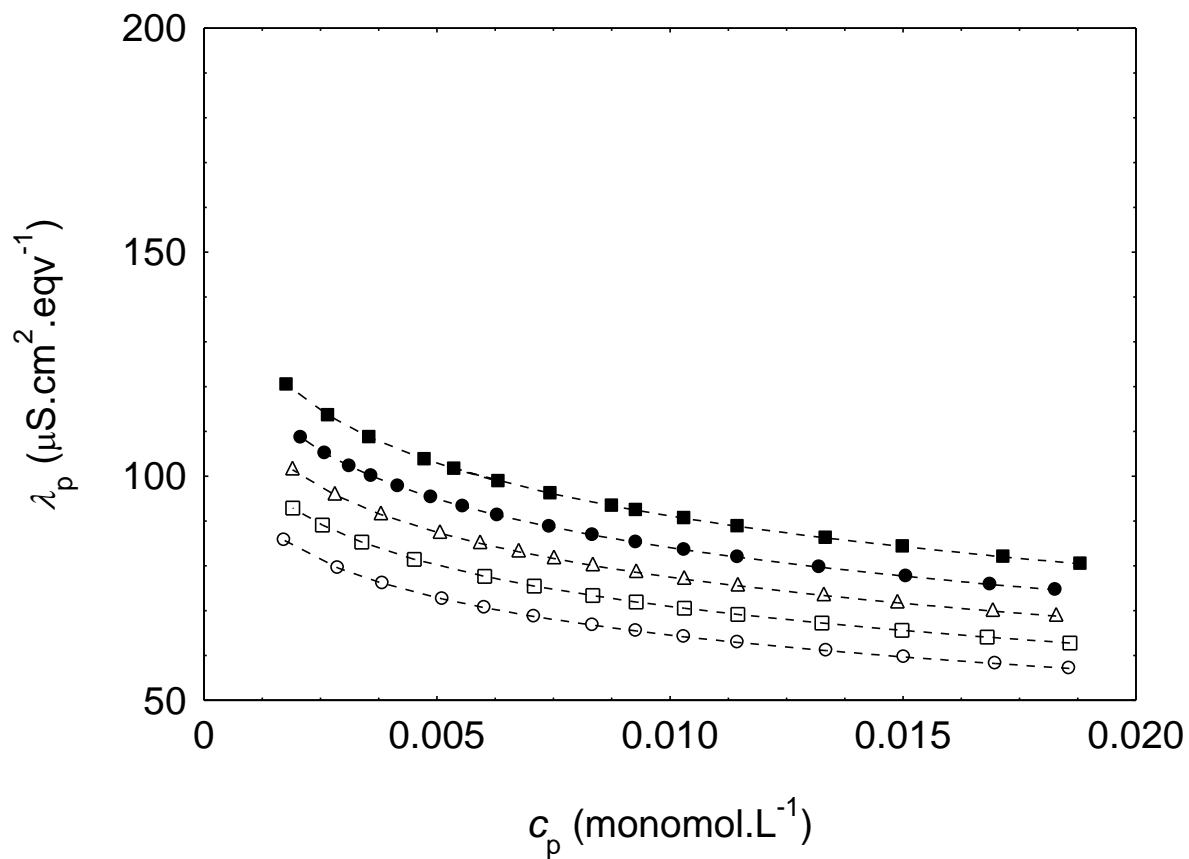


Fig. 2.3(a). Polyion equivalent conductivities in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for the degree of substitution of 0.7 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (Δ), 323.15 K (●) and 328.15 K (■). The dashed lines are used to guide the eye.

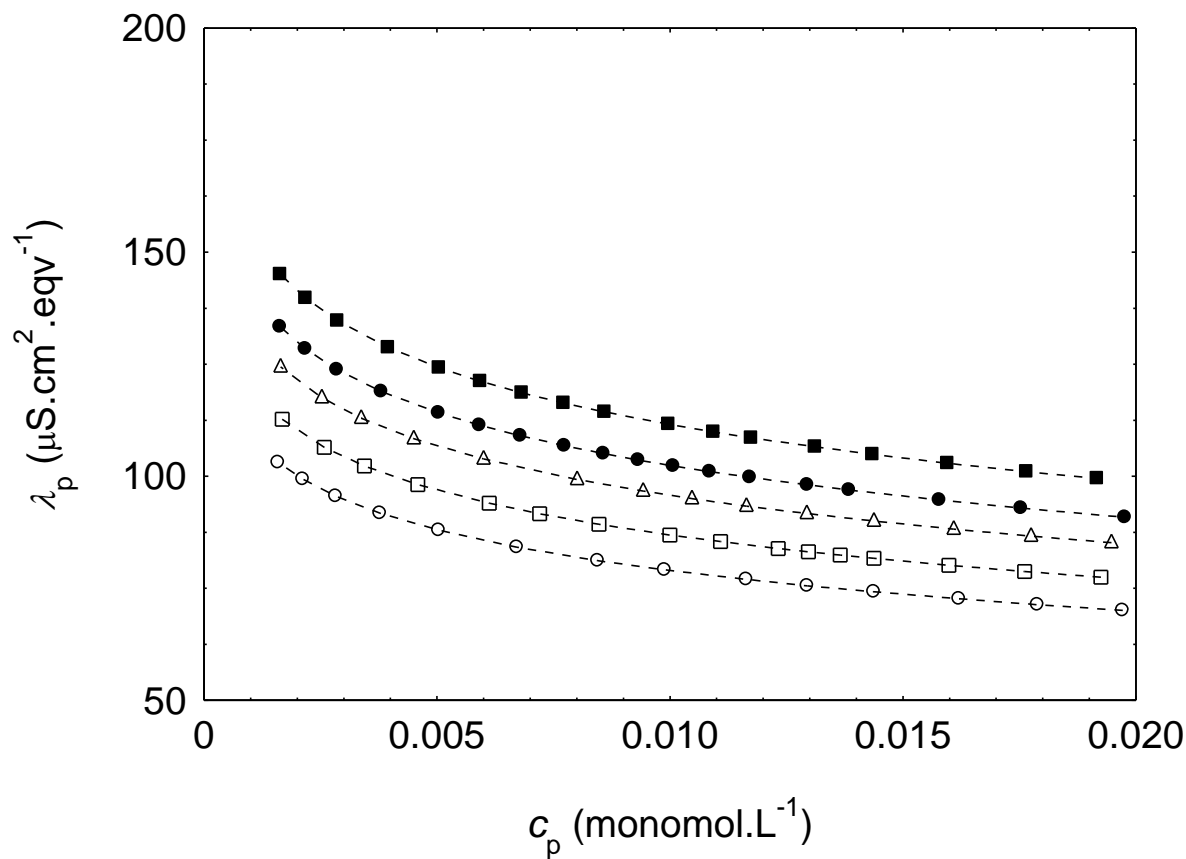


Fig. 2.3(b). Polyion equivalent conductivities in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for the degree of substitution of 0.9 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare). The dashed lines are used to guide the eye.

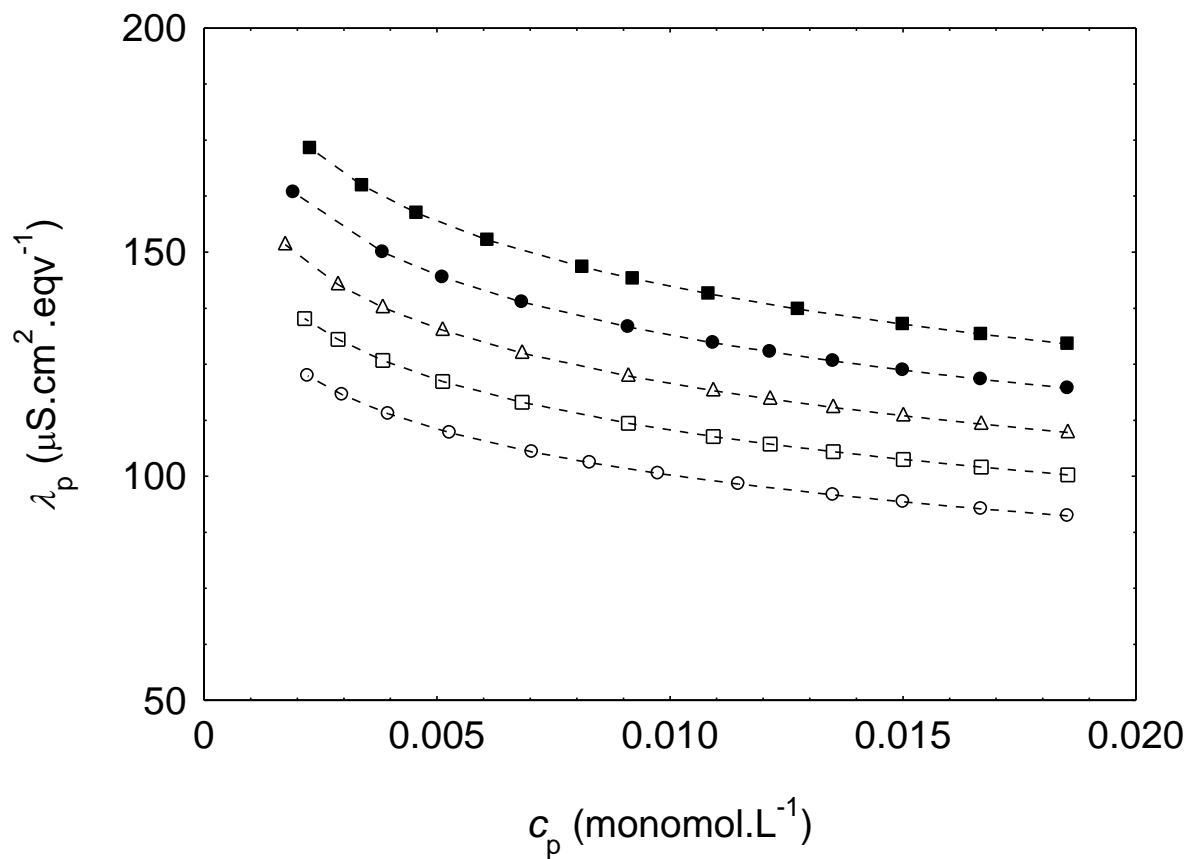


Fig. 2.3(c). Polyion equivalent conductivities in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for the degree of substitution of 1.2 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (△), 323.15 K (●) and 328.15 K (■). The dashed lines are used to guide the eye.

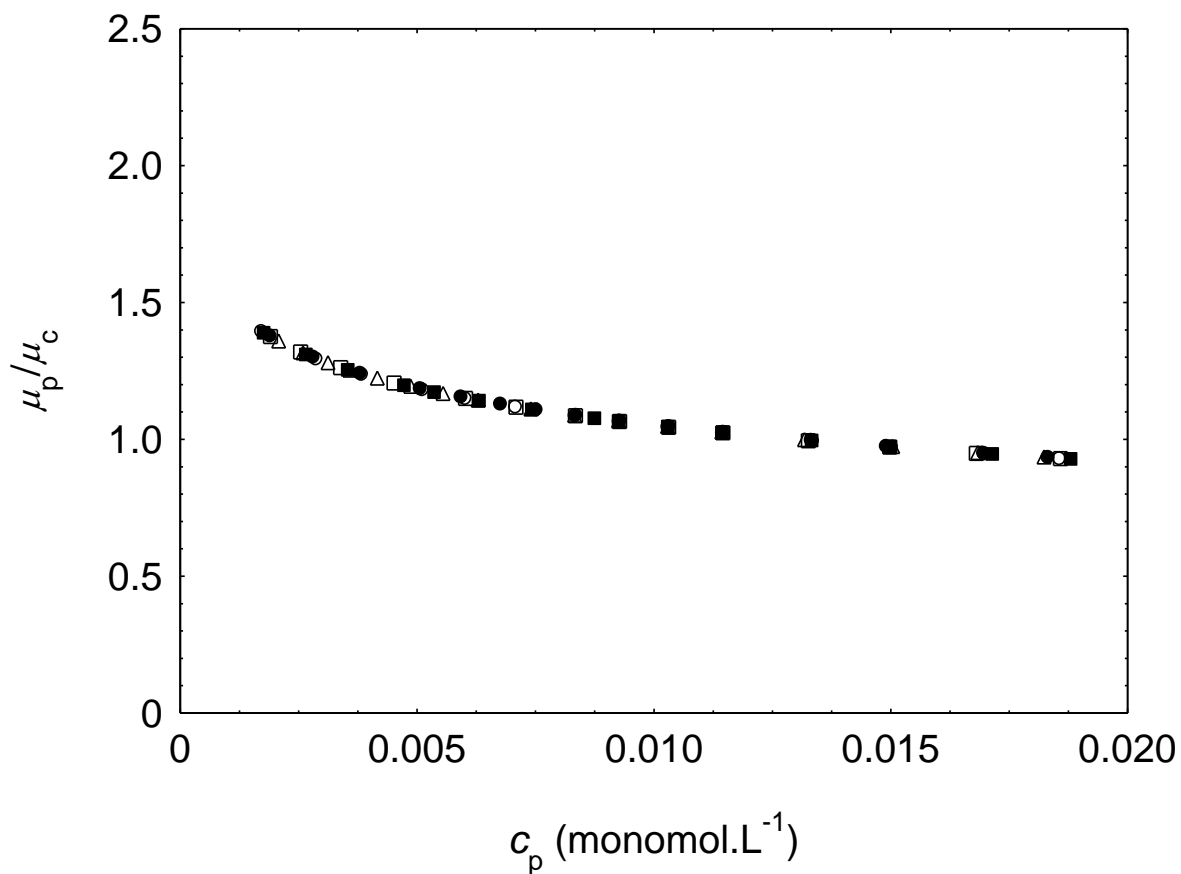


Fig. 2.4(a). Ratio of the mobility of the polyion to the counterion in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.7 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (△), 323.15 K (●) and 328.15 K (■).

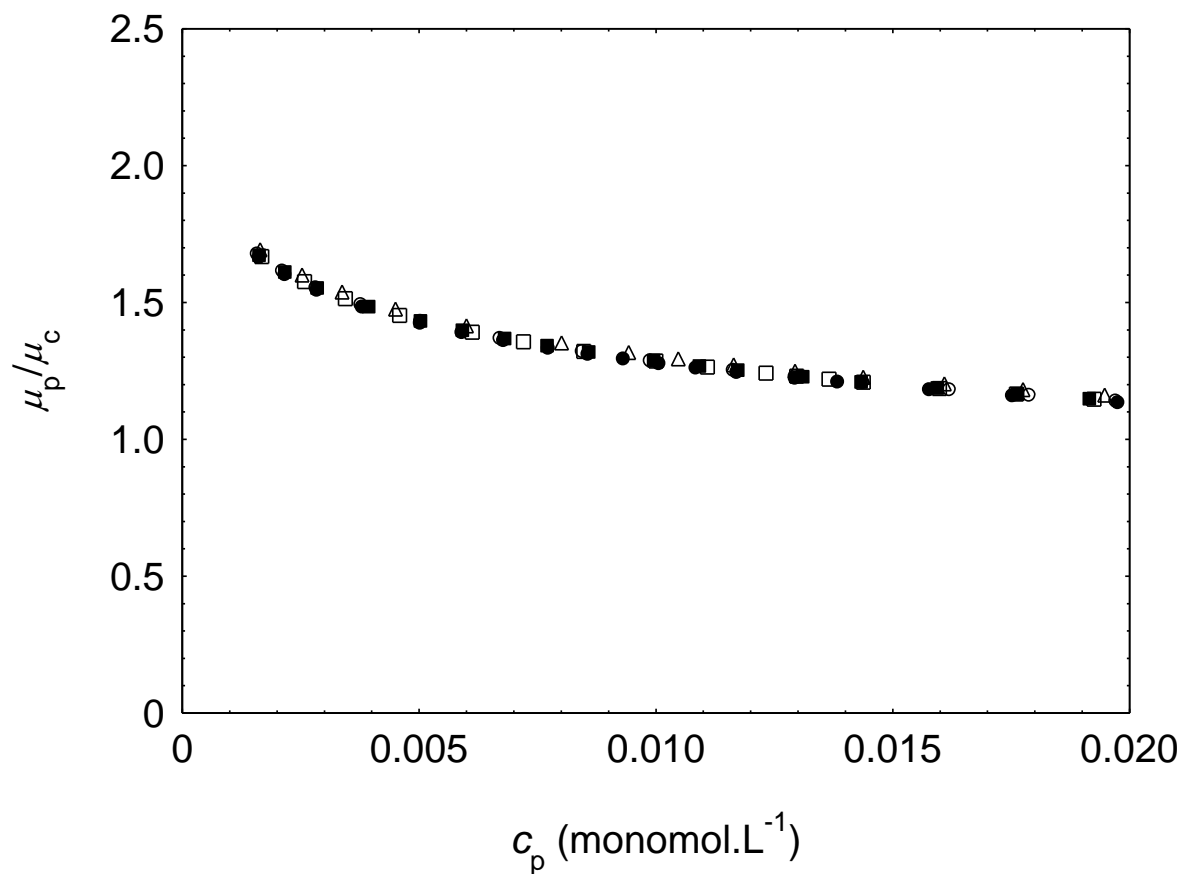


Fig. 2.4(b). Ratio of the mobility of the polyion to the counterion in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.9 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (△), 323.15 K (●) and 328.15 K (■).

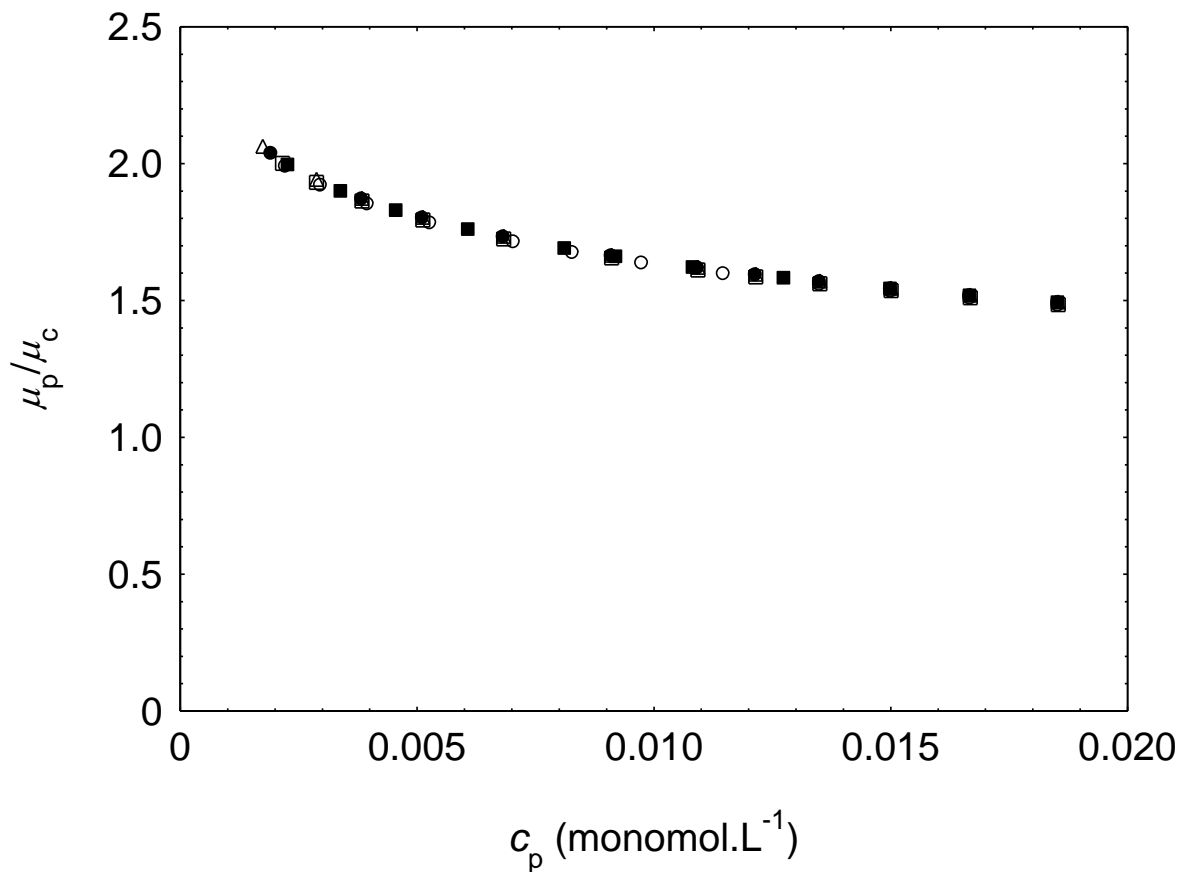


Fig. 2.4(c). Ratio of the mobility of the polyion to the counterion in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 1.2 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (△), 323.15 K (●) and 328.15 K (■).

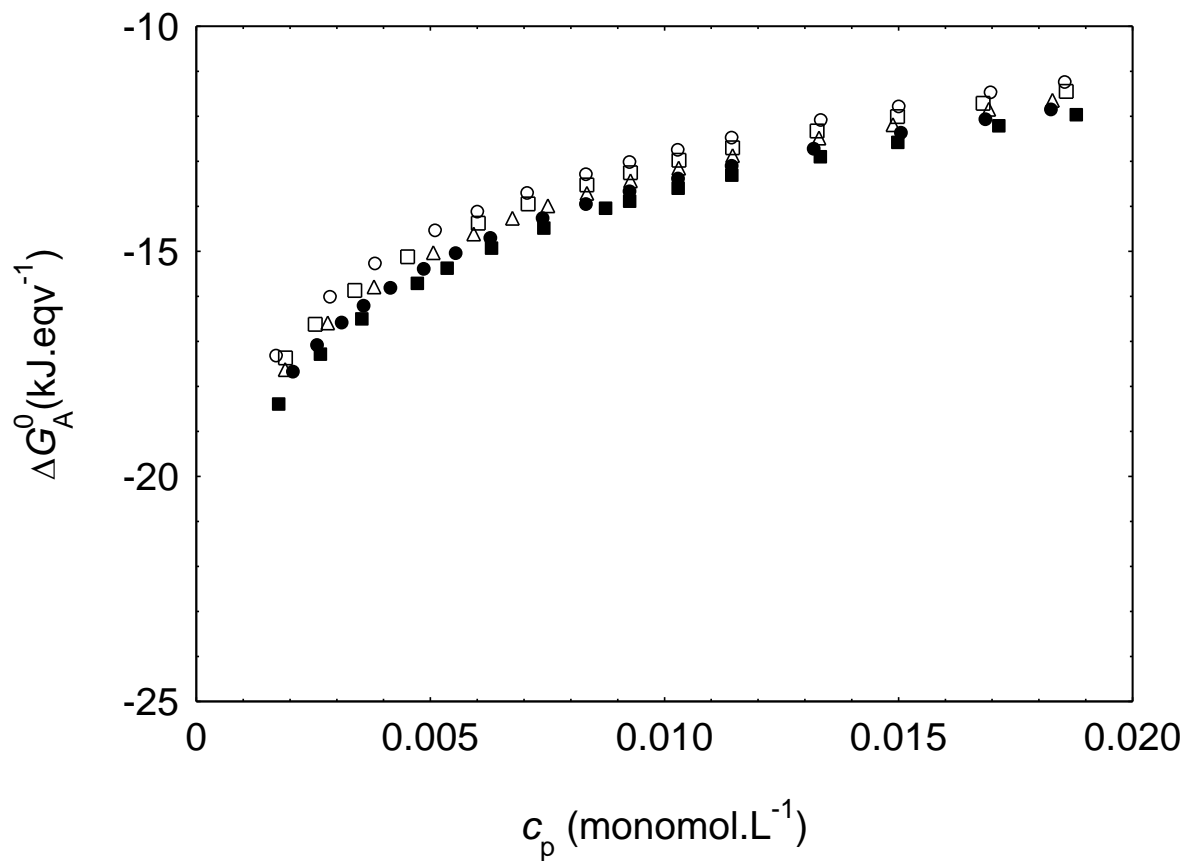


Fig. 2.5(a). Free energies of counterion-condensation in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.7 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare).

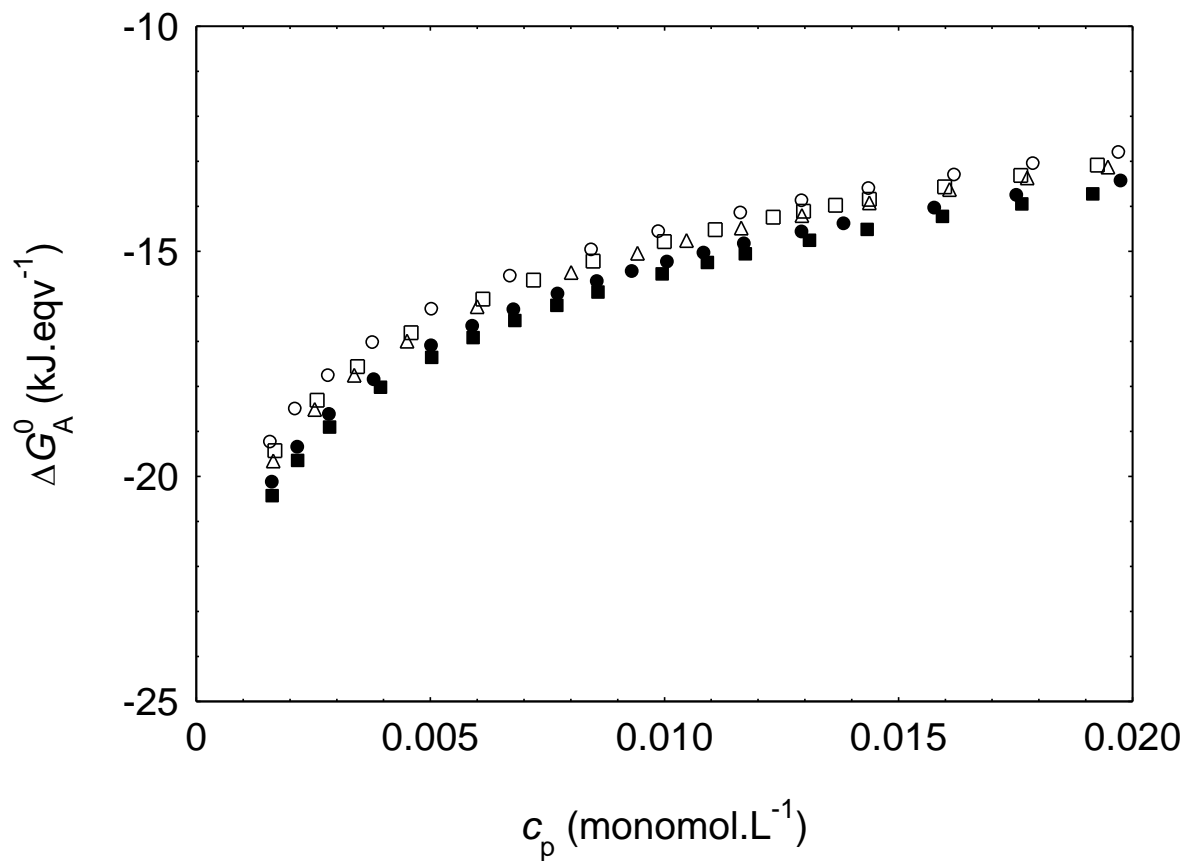


Fig. 2.5(b). Free energies of counterion-condensation in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.9 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare).

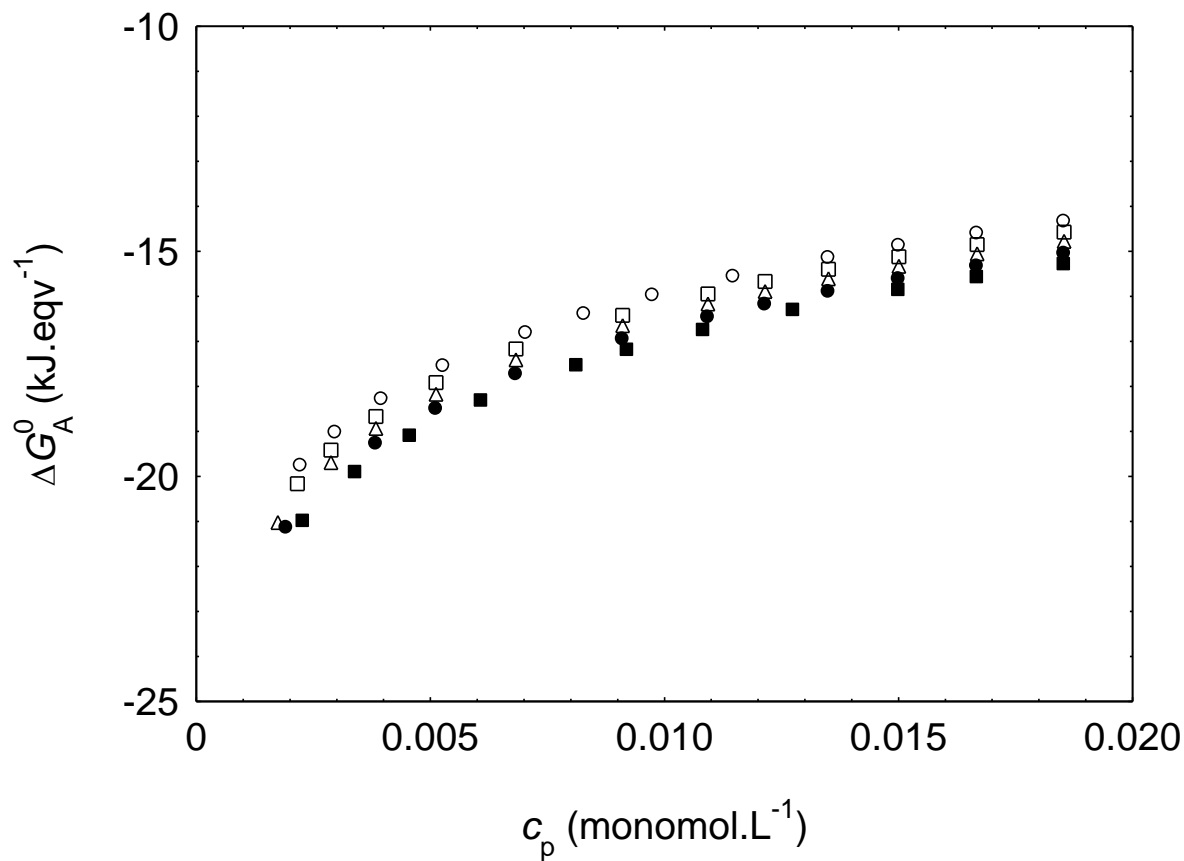


Fig. 2.5(c). Free energies of counterion-condensation in aqueous NaCMC solutions as a function of the polyelectrolyte concentration at different temperatures for a degree of substitution of 1.2 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare).

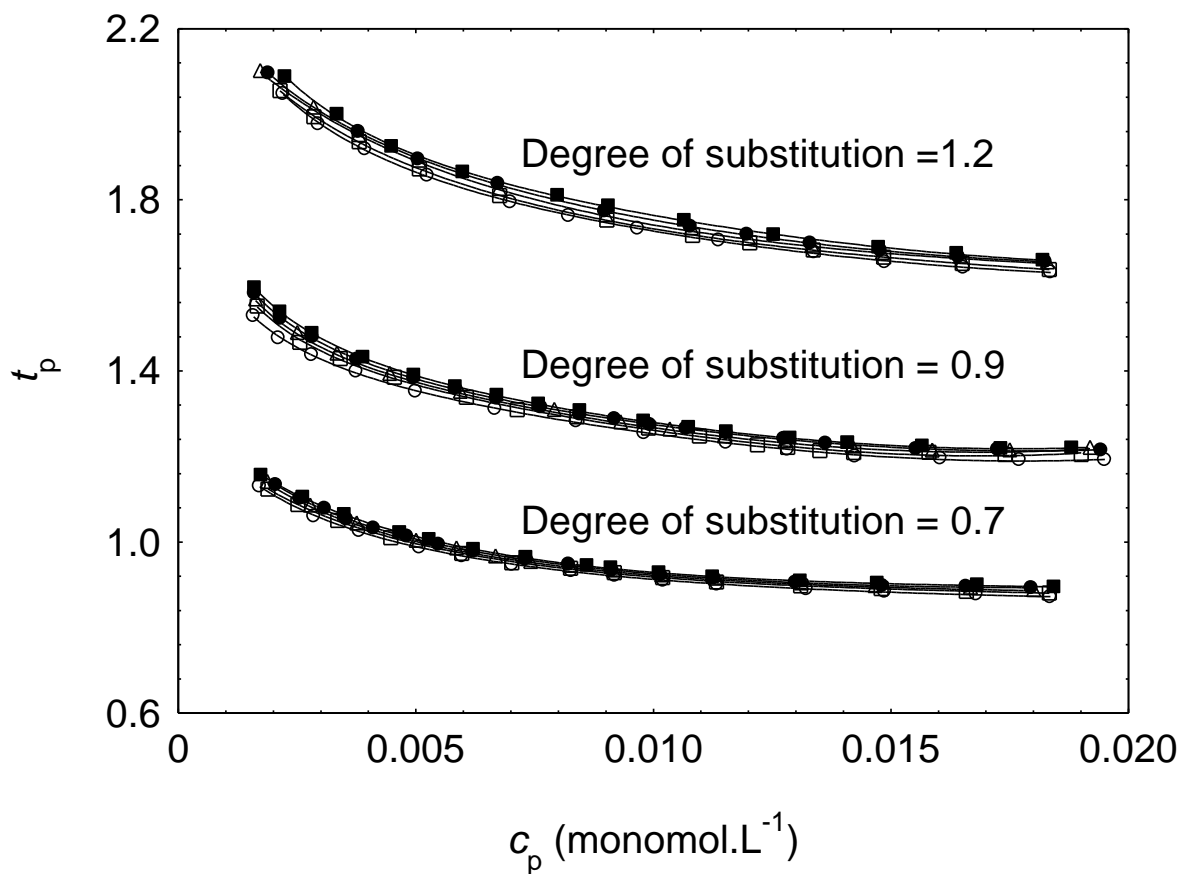


Fig. 2.6. Transference number of the polyion in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for degrees of substitution of 0.7, 0.9, and 1.2 at temperatures 308.15 K (\circ), 313.15 K (\square), 318.15 K (Δ), 323.15 K (\bullet) and 328.15 K (\blacksquare).

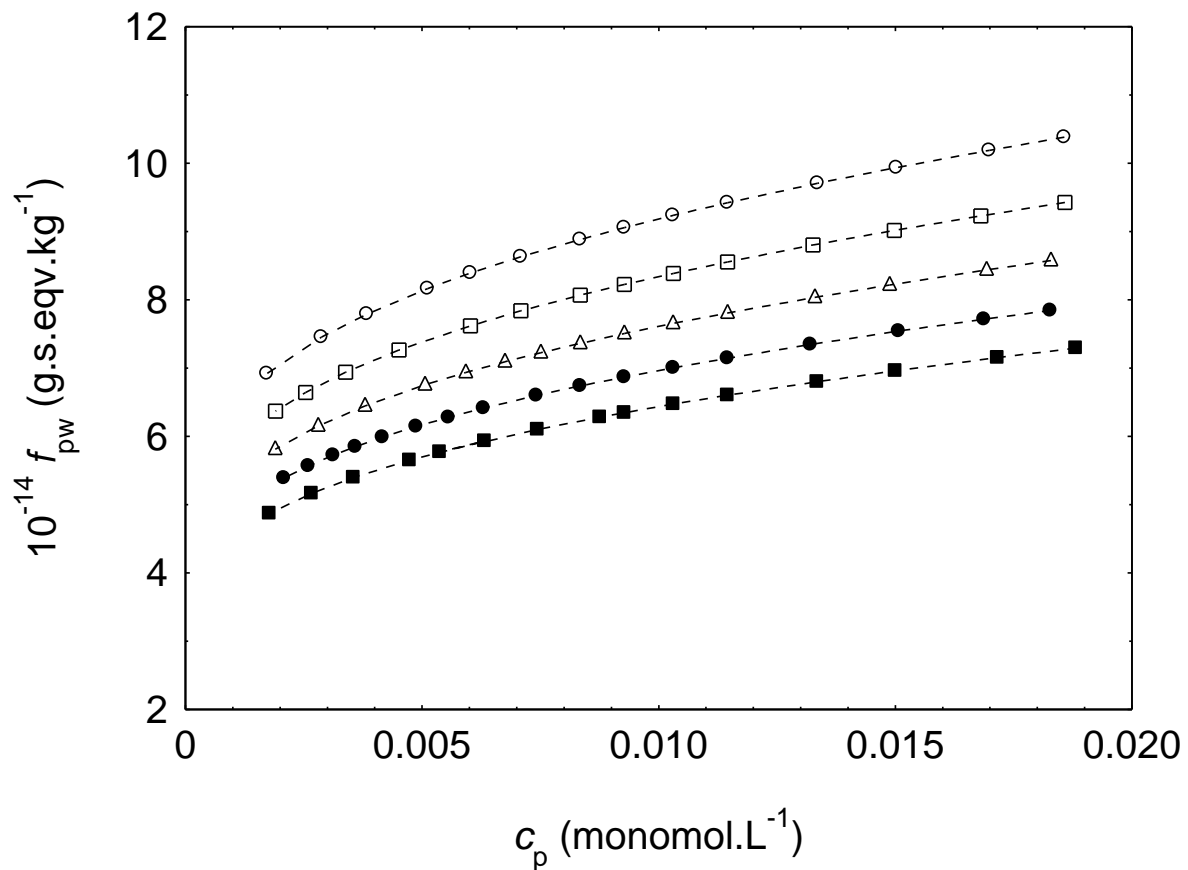


Fig. 2.7(a). Friction coefficient of the monomer with the solvent molecules in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.7 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (Δ), 323.15 K (●) and 328.15 K (■). The dashed lines are used to guide the eye.

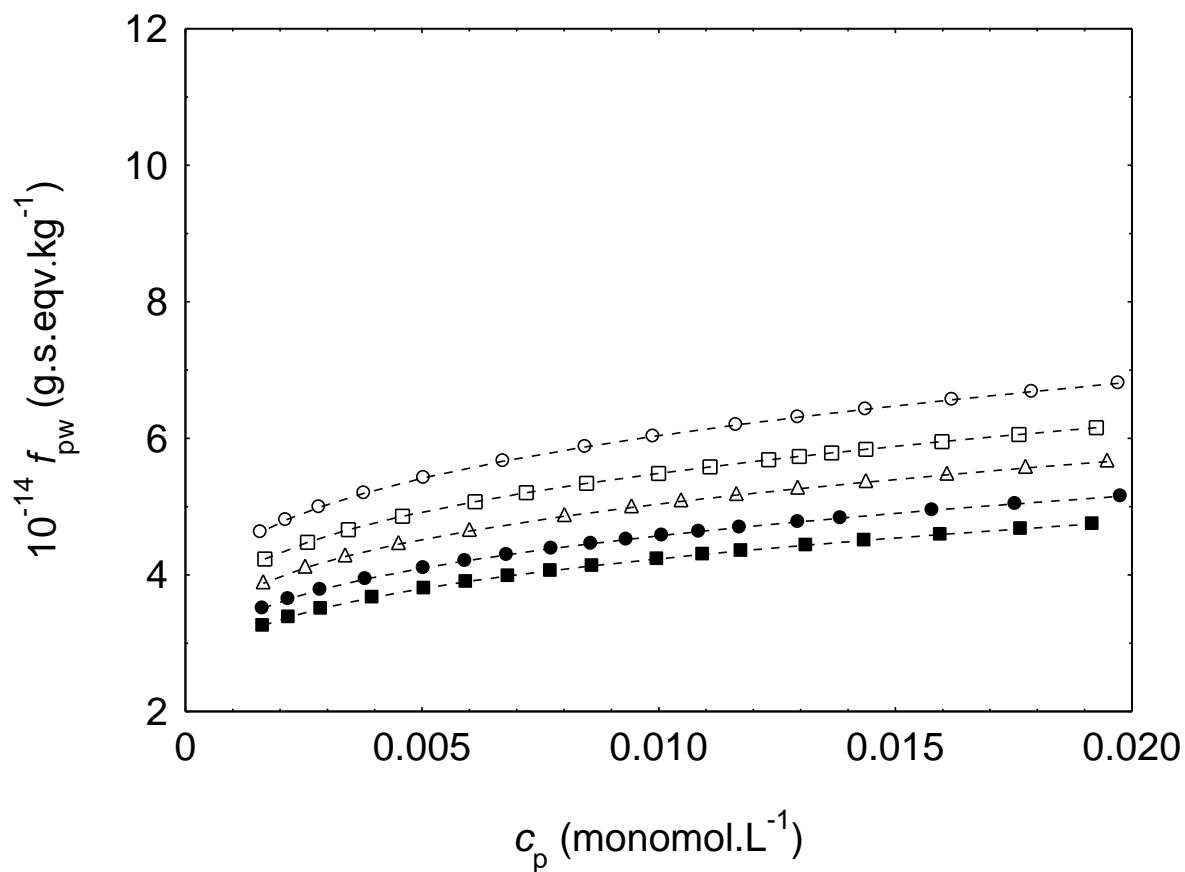


Fig. 2.7(b). Friction coefficient of the monomer with the solvent molecules in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 0.9 at temperatures 308.15 K (○), 313.15 K (□), 318.15 (△), 323.15 K (●) and 328.15 K (■). The dashed lines are used to guide the eye.

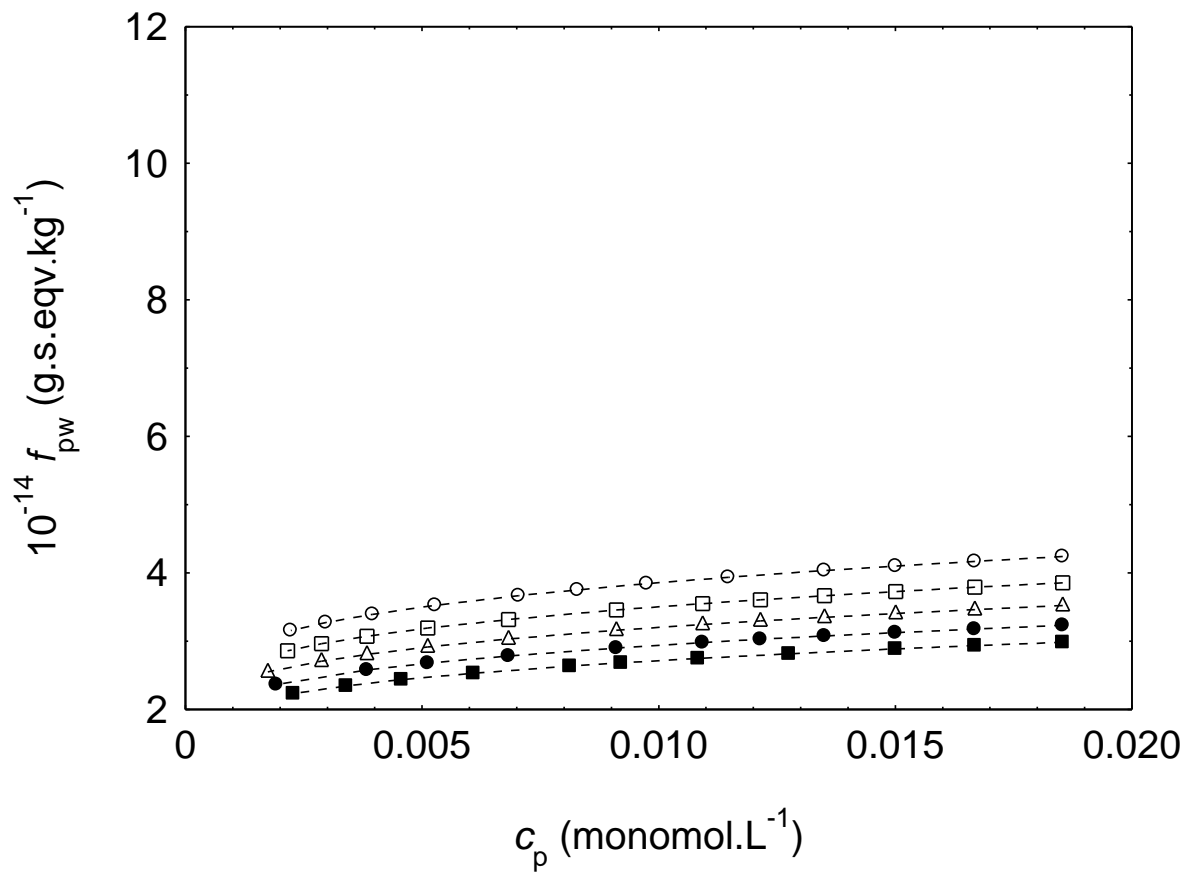


Fig. 2.7(c). Friction coefficient of the monomer with the solvent molecules in aqueous NaCMC solutions as a function of the polyelectrolyte concentration for a degree of substitution of 1.2 at temperatures 308.15 K (○), 313.15 K (□), 318.15 K (Δ), 323.15 K (●) and 328.15 K (■). The dashed lines are used to guide the eye.