Chapter 5

Effect of Salts on the Conductivity of Sodium Carboxymethylcellulose in Methanol-Water Mixed Solvent Media

Introduction

The conductance behaviour of sodium carboxymethylcellulose in methanol-water mixed solvent media in absence of an added salt has been reported in Chapter 4. In this chapter, we report the results of conductivity measurements on the solutions of sodium carboxymethylcellulose in methanol-water solvent mixtures in presence of two 1:1 electrolytes *i.e.*, sodium chloride and sodium bromide. The addition of salts to a polyelectrolyte solution can change the behaviour of polyelectrolytes in solution appreciably essentially because of the changed level of counterion condensation and changed conformation of the polyion chains in salt solution, and hence such study can help obtain deeper insight into the polyion-counterion interactions.

Devore and Manning[1] first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory[2] without much success.

In view of the inadequacy of the Manning theory of the electrical transport of salt containing polyelectrolytes solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the "primitive additivity") of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.[3-7]. Traditionally, this approach takes the form of an assumed additivity of the specific conductances of the polyelectrolyte and the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_{\mathrm{P}} + \kappa_{\mathrm{S}} \qquad (1)$$

where κ_{p} is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_{s} is the specific conductance of the simple salt in the absence of a polyelectrolyte.

However, these investigations[3-7] suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, Eq. (1).

Ander *et al.*[3,4] modified the "primitive" additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa = \kappa_p + \kappa_S\left(\frac{D_2}{D_2^0}\right) \tag{2}$$

where D_2 and D_2^0 are the coion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2 / D_2^0 has been used as a quantitative measure[2] of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s\left(D_2 / D_2^0\right)$.

Although the "modified" additivity has been shown to be somewhat better than the "primitive" one, departures from the experimental results are still prominent.[3-7] Later Bordi *et al.*[8] evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach[9] and compared them with the experimentally determined values. The agreement was rather good, although a quantitative description was not achieved.

Very recently, a simple approach has been put forward by one of us[10] 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.*[9] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[10] This approach has been extensively tested with data on sodium polystyrenesulfonate in the presence of sodium chloride in 2-ethoxyethanol-water mixed solvent media at different temperatures.[11] It has also been tested on sodium carboxymethylcellulose in presence of sodium chloride in acetonitrile-water mixed solvent media.[12] 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 has been observed.

In this chapter, we report the results of conductivity measurements on the solutions of an anionic polyelectrolyte sodium carboxymethylcellulose in the presence of sodium chloride and sodium bromide in methanol-water mixtures. The purpose of this study is to apply this new approach to a different polyelectrolyte-solvent system in order to test its general validity and to examine the influences of the medium and the concentration of the added salt on the counterion-condensation behaviour of the polyelectrolyte in the presence of a salt.

Theory

Here we will briefly describe the model which has recently been introduced by one of us to interpret the conductance behavior of polyelectrolyte in presence of salt.[11,12]

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 (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 uncondensed 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.*,[9] the specific conductivity of a salt-free polyelectrolyte solution (κ_p) is given by

$$\kappa_p = fc\left[\lambda_c^0 + \frac{c\,\xi_0^2 e^2 f}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{3}$$

where c is the number density of monomers, 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 and this 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

$$\kappa_{\mathrm{p(eff)}} = f'c\left[\lambda_c^0 + \frac{c\,\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{4}$$

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

$$\kappa = \kappa_{\mathrm{S}} + f'c\left[\lambda_c^0 + \frac{c\,\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{5}$$

This equation, Eq. (5), has one adjustable parameter f' and this could be obtained by the method of a least squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in presence of a salt to Eq. (5) 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. (5) is the actual contribution of the polyelectrolyte species towards the total specific conductivity in the presence of an added salt.

Experimental

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. The physical properties of the purified solvent was found to be in good agreement with the literature values.[13] Triply distilled water with a specific conductance less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of solvent mixtures. Sodium carboxymethylcellulose employed in this investigation was purchased from Aldrich Chemical Company, Inc. The sample had an average molecular weight (M) of 90,000 and a degree of substitution of 0.7. It was characterized in a similar fashion as described earlier by us.[15] The average molecular weight of the sample was estimated from the intrinsic viscosity value determined in 0.2 M NaCl aqueous solution at 298.15 K using the Mark-Houwink equation with the constants obtained from the literature.[15] *DS* was determined by a conductometric procedure as described by Eyler *et al.*[16] These values agree well with those declared by the procedure. Sodium chloride (Fluka) and sodium bromide (Fluka) were of puriss grade. These were dried *in vacuo* for prolonged period immediately before use.

Conductance measurements were carried out on a Pye Unicam PW 9509 conductivity meter at a frequency of 2000 Hz with negligible polarization effects using a dip-type cell with a cell constant of 1.14 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. The details of the experimental procedure have been described earlier.[17,18] 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 solution (κ).

In order to avoid any moisture pick up the solutions were prepared in a dehumidified room with utmost care. In all cases the experiments were performed in three replicates and the results were averaged.

Results and Discussion

Experimental Specific Conductivity

The specific conductivities of sodium carboxymethylcellulose as a function of the polymer concentration in a given methanol-water mixture with varying amounts of added sodium chloride and sodium bromide are shown in the representative figures (Figs. 1-4). From these figures, it is apparent that for all the solutions studied the specific conductivities increase with polyelectrolyte concentration. The addition of salt increases the specific conductances of the polyelectrolyte-salt system as it should be. The specific conductances of sodium carboxymthylcellulose solutions in any given methanol-water medium are always found to greater in presence of sodium bromide than those measured in presence of sodium chloride. The specific conductances of the polyelectrolyte-salt solution in methanol-water media have been found to decrease with increasing methanol content in the media at constant added salt concentration.

Scaling Theory and the Fraction of Uncondensed Counterions

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) appearing in Eq. (5) depend upon the quality of the solvent and are for poor solvents, given by[12]

$$\xi_e = bf'^{-2}\xi^{-1/3} \tag{6}$$

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

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 polyion chain, k the Boltzman constant, and T the temperature in the absolute scale. The charge density parameters were calculated using a segment length of 5.15×10^{-8} cm, considering a degree of substitution of 0.7.

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

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

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

For the present system, good solvent correlations are always found to provide a better description of the experimental results. In Figs. 1 and 2, the predictions in accordance with the Eq. (5) (dashed lines) have been compared with the experimental specific conductivity data treating the mixed solvent media as a good solvent for sodium carboxymethylcellulose.

The specific conductivity values of the polyelectrolyte-salt system as a function of the polyelectrolyte concentration in a given solvent medium and for a given salt concentration were fitted to Eq. (5) by the method of least-squares analysis. The best-fitted f' values along with the standard deviations are reported in Table 1. In the representative Figs. 1 and 2 we compare the calculated specific conductivities using the f' values reported in Table 1 with those obtained experimentally. From the standard deviations recorded in Table 1, as well as from an inspection of these figures, it is directly evident that the present method of analysis reproduced the experimental results quite satisfactorily. The present experimental results, thus, provide further support in favor of the validity of the model for the conductivity of polyelectrolyte-salt solutions proposed recently by one of us.[11,12]

The results reported in Table 1 demonstrate that a certain proportion of the counterions remain condensed onto the polyion chains in the present system, the fraction of the uncondensed counterions being approximately 43 to 59%. A survey of the literature indicated that, although studies on the electrical conductances for different aqueous polyelectrolyte-salt solutions are available,[3-7,19] in most of the cases the quantification of the countertion condensation was either not attemped[4-7] or was based on Manning counterion condensation model[3,19] which has subsequently been shown to be inappropriate to describe the polyelectrolyte conductivity.[1,21]

Effect of Added Salt Concentration on Counterion Condensation

The fraction of uncondensed counterions has been found to decrease with increasing concentration of the added salts. This indicates that addition of salt to the present polyelectrolyte solutions promotes counterion binding onto the polyion chains. This is clear from the data sets which are given in Table 1.

Effect of Medium on the Counterion Condensation

Measured fraction of uncondensed counterions is found to decrease with increasing methanol content (*i.e.*, with decreasing relative permittivity) of the mixed solvent media over the entire concentration range investigated. Since decreasing relative permittivity should result in a greater interaction between polyion and counterions, the fraction of condensed counterions would increase as the relative permittivity of the medium becomes lower as has been observed in the present study.

Effect of Added Salt Concentration on Polyion Conductivity

Polyion conductivities have been found to decrease with the increase in the added salt concentration for both the salt solutions. As pointed out above, addition of a salt to the present polyelectrolyte system causes more counterion condensation. This obviously reduces the overall charge on the polyion chains and thus a contraction of the polyion coils is expected upon addition of an external salt. Reduced charge on the polyion chains reduces the polyion conductivity, whereas the reduced size of the polyion coils enhances it, and the balance between these two opposing effects controls the polyion conductivity. The present experimental results demonstrate that the charge effect predominates over the size effect for the system under investigation. This phenomena has been represented in Figs. 3 and 4.

Effect of Medium on the Polyion Conductivity

Fig. 5 show that the polyion 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 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 intra-polyionic repulsion leading to a stretching of the coil (effect 3). The first and the third effects should result in 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. These results are in accordance with the previous results obtained by study in absence and presence of added salt.[11,12,20,22-24]

The nature of variations is seen to be similar in absence of any added salt which has been discussed earlier.

The Association Constant (K_A) and the Standard State Free Energies of Counterion Condensation (ΔG_A^0) and their Variation with Polyelectrolyte Concentration, Solvent Medium, and Added Salt Concentration

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 binding of the counterions onto to polyionic sites defined as the equilibrium constant for the reaction

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

have been calculated as a function of concentration from the fractions of uncondensed counterions using the following equation[20]

$$\ln K_A = \ln\left(\frac{1-f}{f}\right) - \ln(fc) \qquad (12)$$

The values of the association constants (K_A) thus calculated have been found to increase with decreasing concentration of the polyelectrolyte. The influences of different variables on K_A have been shown in Figs. 6-8.

The association constant values are found to increase as the methanol-water mixed solvent medium becomes richer in methanol at a constant level of the added salt concentration. These are also found to increase as the concentration of the added salt is gradually increased in a given mixed solvent medium.

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

$$\Delta G_A^0 = -RT \ln K_A \qquad (15)$$

where R is the universal gas constant.

Figs. 9 -11 display the variation of ΔG_A^0 values of sodium carboxymethylcellulose solutions as a function of the polyelectrolyte concentration in three different methanol-water mixtures containing respectively 10, 20, and 30 vol.% of methanol at a particular temperature

(308.15 K) over the entire concentration range investigated. 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 less spontaneous as the concentration increases. Addition of an increasing amount of methanol to the medium makes the counterion condensation process more favourable. Addition of the external salt has, also, been found to increase the spontaneity of counterion condensation.

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[25]

$$f_{\mathrm{ps}} = \frac{|z_{\mathrm{p}}| fF^2}{\lambda_{\mathrm{p}}} \tag{16}$$

where z_p is the number of elementary charges on the monomer unit of the completely dissociated polyion, and the other symbols have their usual significance. The results are summarized in Figs. 12 - 14, which show the dependence of f_{ps} on c in 10, 20, and 30 vol. % methanol-water mixtures at 308.15 K. We can see from the coefficients of friction of the carboxymethylcellulose ion that the possible conformational changes of the molecules caused by dilution lead to change in solvodyanamic resistance. An increase in the friction coefficients with increasing methanol content of the mixture over the entire polyelectrolyte concentration range reflects bigger sizes of the monomer units as the medium becomes richer in the organic cosolvent. An increase in the salt concentration (0.0001 M to 0.01 M) for a particular solvent mixture for sodium chloride and sodium bromide resulted in an increase in the friction coefficients. It has also been seen that addition of sodium bromide lowers the friction coefficient than does the addition of sodium chloride of the same concentration.

Conclusions

An investigation on the electrical conductivity of an anionic polyelectrolyte, sodium carboxymethylcellulose, in methanol-water mixed solvent media containing 10, 20 and 30 vol.% of methanol have been performed in 308.15 K as a function of polymer concentration in presence of added salts (*i.e.*, NaCl , NaBr). The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter developed recently by one of us following the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby *et al.*[9] using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*[10] Excellent agreement between the experimental results and those obtained following this approach has always been observed. The present experimental results, thus, provide a further support in favor of the validity of this model for the conductivity of polyelectrolyte-salt solutions. The influences of polymer concentration, medium, added salt concentration the fraction of uncondensed counterions, polyion conductance, and other thermodynamic parameters have also been discussed from the viewpoints of polyion-counterion interactions, solvation of counterions and the polyionic sites, and counterion dissociation.

References

1. D. L. Devore and G. S. Manning, *J. Phys. Chem.*, **78**, 1242 (1974).
2. G. S. Manning, *J. Chem. Phys.* **51**, 934 (1969).
3. M. Kowblansky and P. Ander, *J. Phys. Chem.*, **81,** 2024 (1977).
4. D. E. Wingrove and P. Ander, *Macromolecules*, **12**, 135 (1979).
5. J. Nagaya, A. Minakata and A. Tanioka, *Langmuir*, **15**, 4129 (1999).
6. A. Minakata, H. Takahashi, T. Nishio, J. Nagaya and A. Tanioka, *Colloids Surf. A*, 209, 213 (2002).
7. J. Nagaya, A. Minakata and A. Tanioka. *Colloids Surf. A*, **148**, 163 (1999).
8. F. Bordi, C. Cametti and T. Gili, *Phys. Rev. E.*, **68,** 011805-1-011805-12 (2003).
9. R. H. Colby, D. C. Boris, W. E. Krause and J. S. Tan, *J. Polym. Sci., Part B, Polym. Phys.*, **35**, 2951 (1997).
10. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28,** 1859 (1995).
11. R. De and B. Das *J. Chem. Eng. Data*, **55**, 2108 (2010).
12. P. Nandi and B. Das, *J. Chem. Eng. Data*, **56**, 2870 (2011).
13. A. Chatterjee and B. Das, *J Chem. Eng Data* **51**, 1352 (2006).
14. R. Sharma, B. Das, P. Nandi and C. Das, *J. Polym. Sci., Part B, Polym. Phys.*, **48,** 1196 (2010).
15. E. Eremeeva and T. O. Bykova, *Carbohydrate Polym.*, **36**, 319 (1998).
16. R. W. Eyler, E. D. Klug and F. Diephius, *Anal. Chem.*, **19**, 24 (1947).
17. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).
18. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99,** 269 (1995).
19. C. Wandrey, *Langmuir*, **15,** 4069 (1999).
20. A. Chatterjee, B. Das and C. Das, *Carbohydrate Polym.*, **87**, 1144 (2012).
21. D. Ghosh, A. Bhattarai and B. Das, *Colloid Polym. Sci.*, **287**, 1005 (2009).
22. P. Nandi and B. Das, *J. Phys. Chem. B.*, **109**, 3238 (2005).
23. R. De and B. Das, *Eur. Polym. J.*, **43**, 3400 (2007).
24. A. Bhattarai, P. Nandi and B. Das, *J. Polym. Res.*, **13**, 475 (2006).
25. I. A. Kuznestov, O. B. Stanislavaskii and I. S. Kudryavtseva, *Russ. J. Phys. Chem.*, **64,** 1091 (1990).

Table 1. Fractions of Uncondensed Counterions (f') for Sodium Carboxymethylcellulose in Methanol–Water Mixed Solvent Media in presence of Salts following the Scaling Theory Approach using Good Solvent Correlation along with the respective Standard deviations (σ)

Vol.% of Methanol	Salt Conc. (Eqv.L^{-1})	f'	σ
	Sodium Bromide (NaBr)		
10	0.01	0.5102	1.34×10^{-5}
	0.001	0.5714	1.04×10^{-5}
	0.0001	0.5882	6.76×10^{-6}
20	0.01	0.4902	7.23×10^{-6}
	0.001	0.5236	1.24×10^{-5}
	0.0001	0.5435	4.33×10^{-6}
30	0.01	0.4405	6.77×10^{-6}
	0.001	0.5102	5.34×10^{-6}
	0.0001	0.5208	2.22×10^{-6}
	Sodium Chloride (NaCl)		
10	0.01	0.5000	1.46×10^{-5}
	0.001	0.5682	2.13×10^{-5}
	0.0001	0.5747	1.00×10^{-5}
20	0.01	0.4739	1.60×10^{-5}
	0.001	0.5076	9.12×10^{-6}
	0.0001	0.5319	1.07×10^{-5}
30	0.01	0.4348	2.18×10^{-5}
	0.001	0.4695	7.62×10^{-6}
	0.0001	0.4926	4.32×10^{-6}

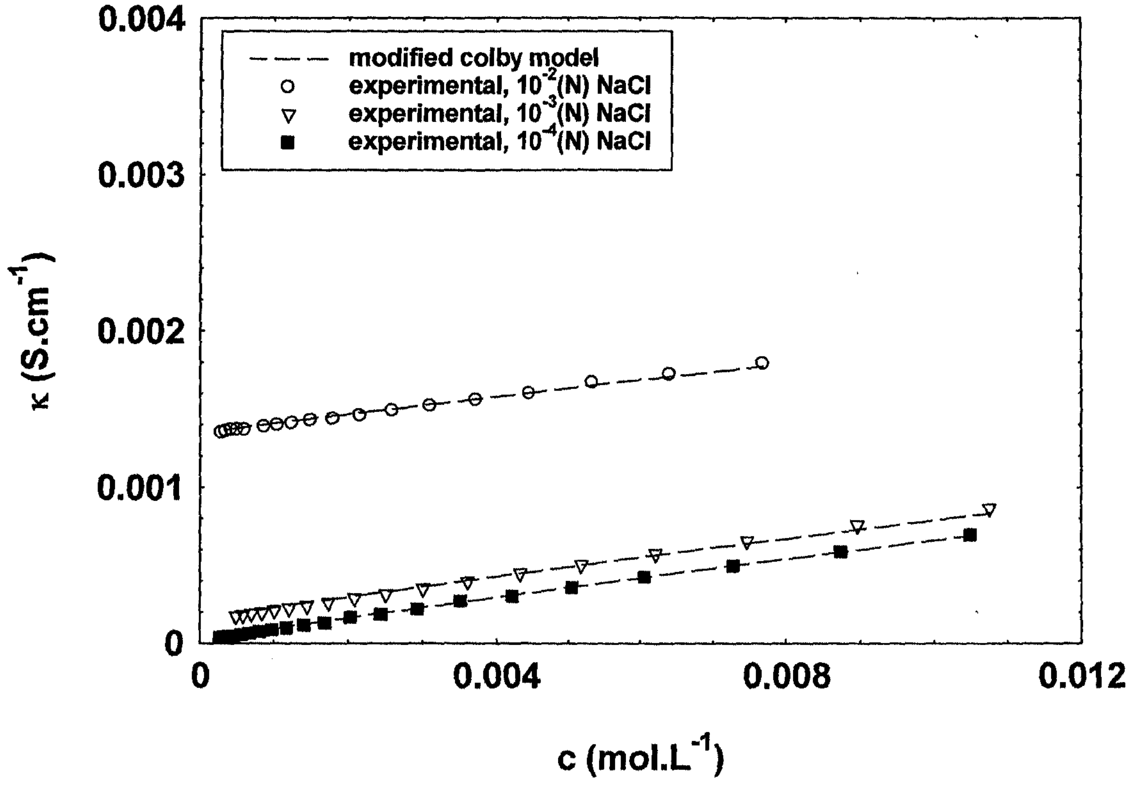

Fig. 1. Variation of the specific conductance (*κ*) of sodium carboxymethylcellulose solution as a function polyelectrolyte concentration in presence of three different added NaCl salt concentration in 10 vol. % methanol-water solvent mixture.

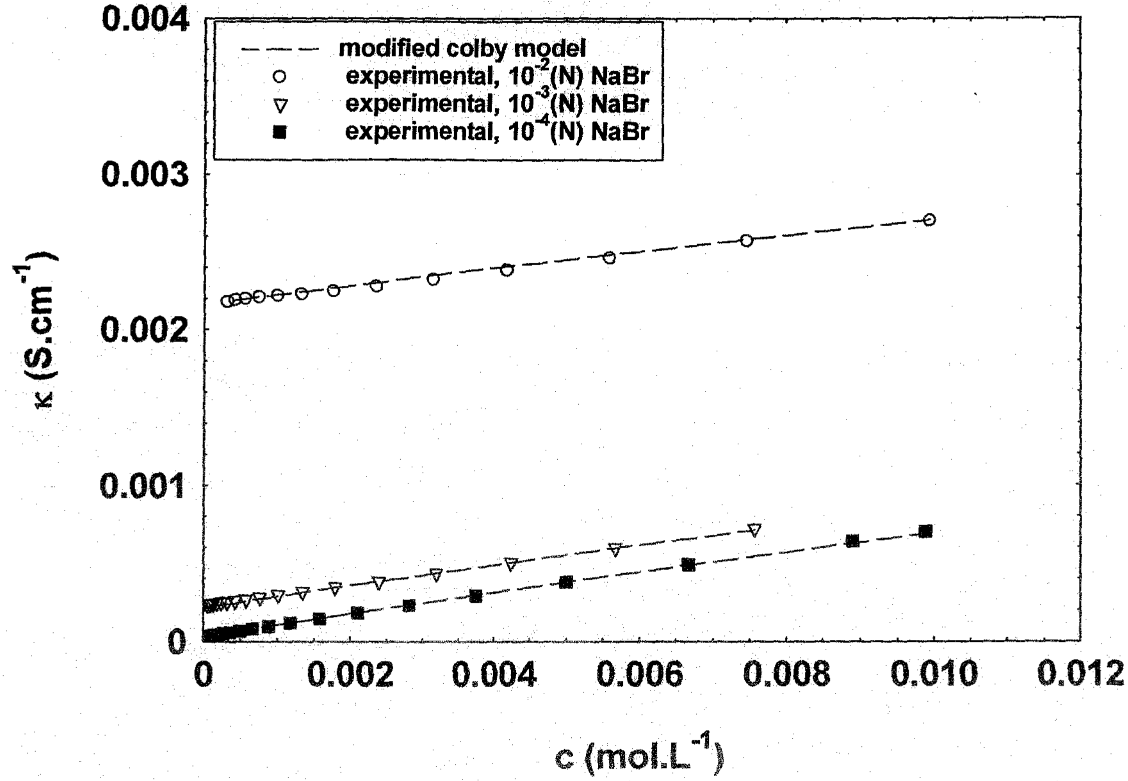

Fig. 2. Variation of the specific conductance (κ) of sodium carboxymethylcellulose solution as a function polyelectrolyte concentration in presence of three different added NaBr salt concentration in 10 vol. % methanol-water solvent mixture.

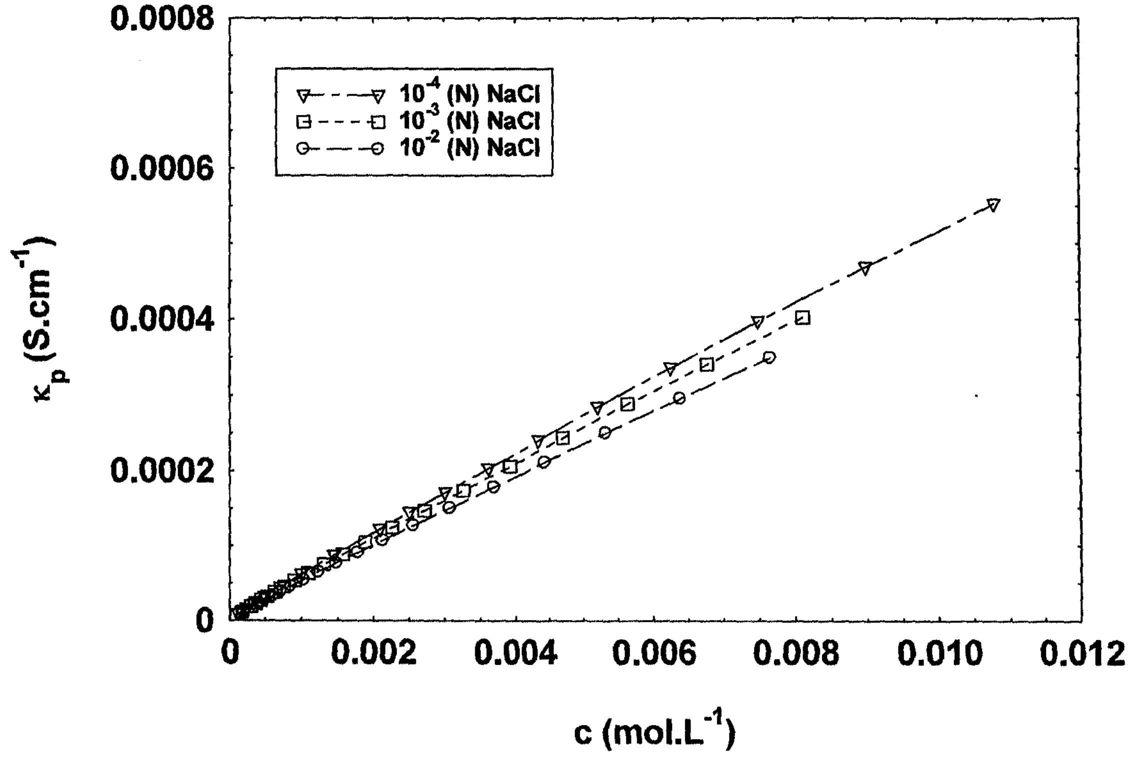

Fig. 3. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

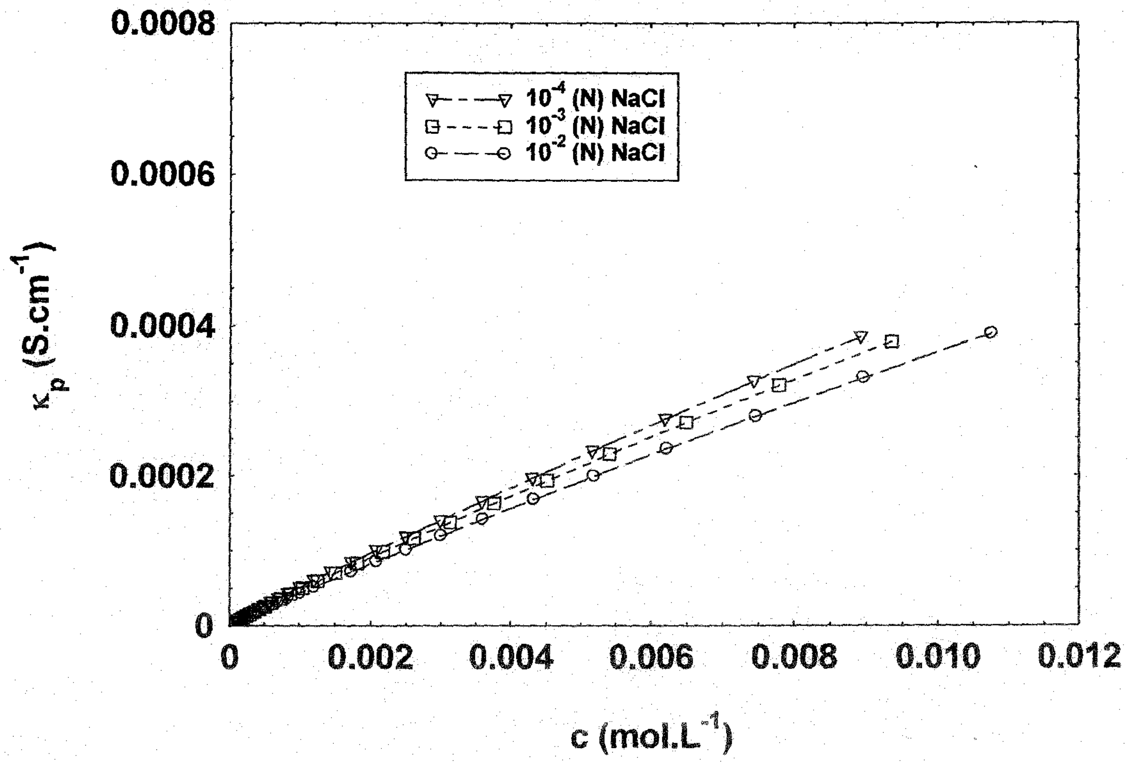

Fig. 4. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 30 vol. % methanol-water mixture.

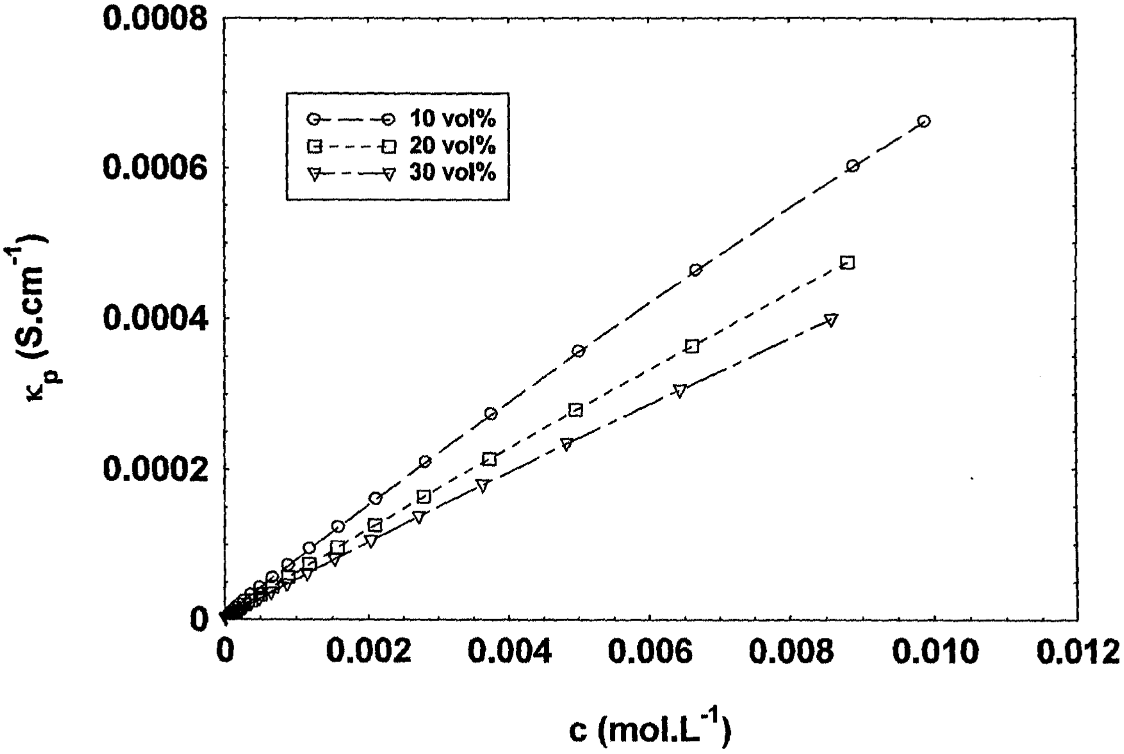

Fig. 5. Variation of the polyion specific conductance (κ_p) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added 10^{-4} (N) NaBr salt concentration in different (10, 20, and 30 vol. %) methanol-water mixtures.

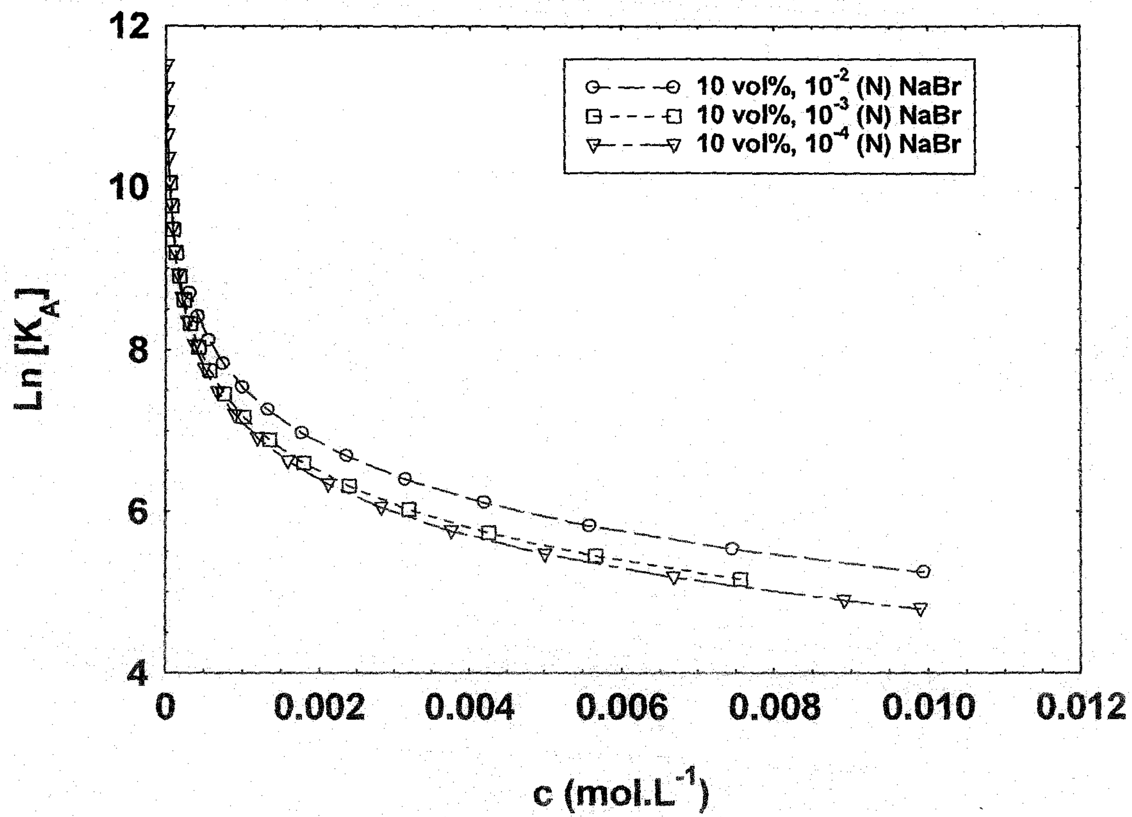

Fig. 6. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of different added NaBr concentration in 10 vol. % methanol-water mixture.

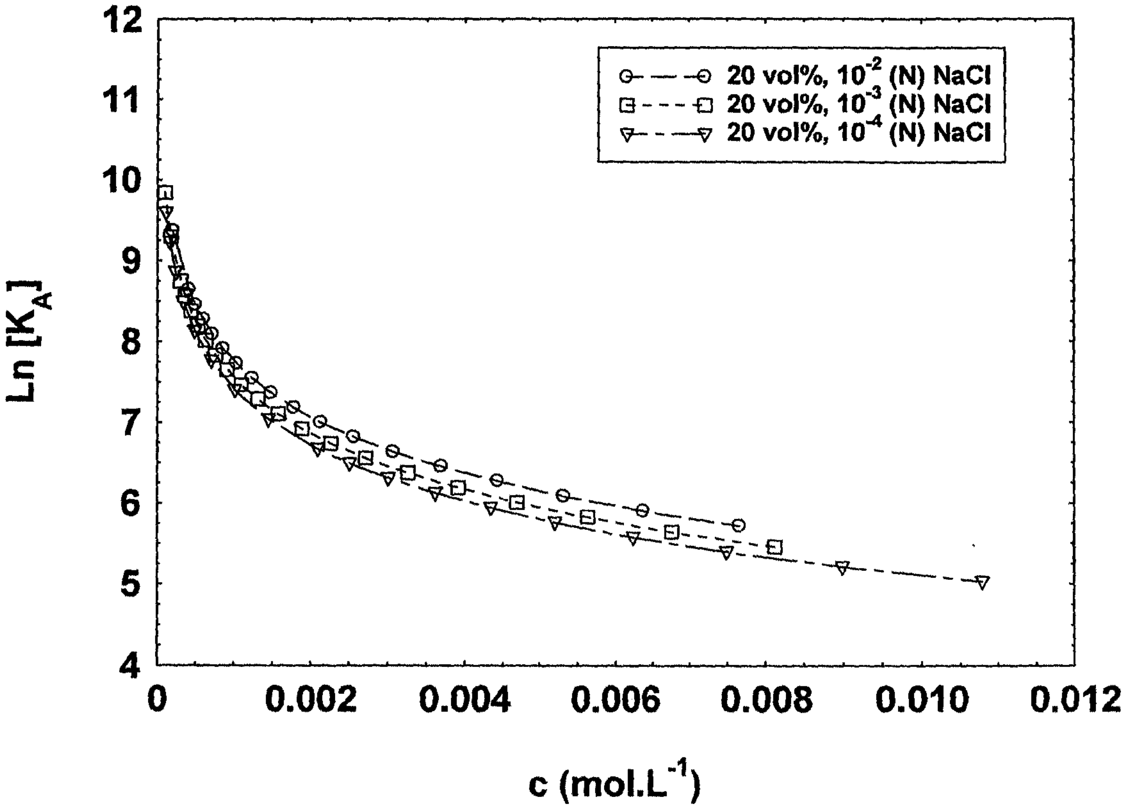

Fig. 7. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

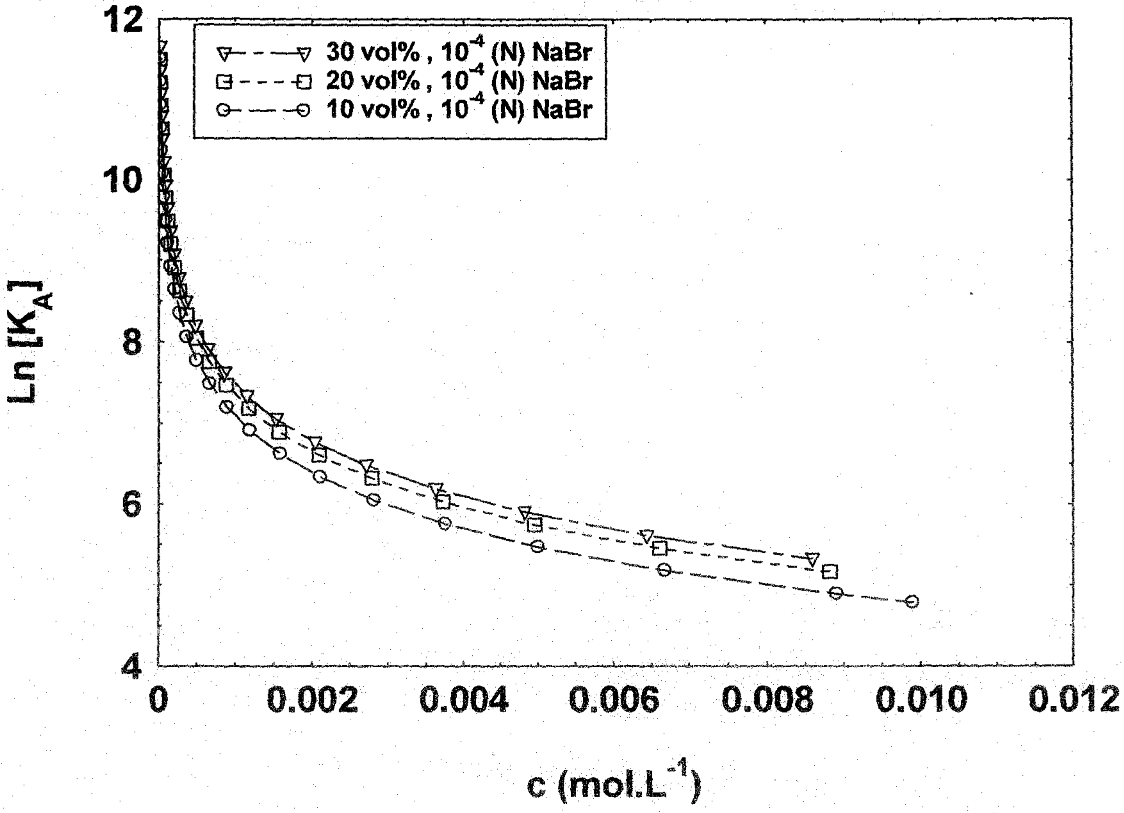

Fig. 8. Variation of association constant of counterion condensation (K_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of 10^{-4} (N) added NaBr salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.

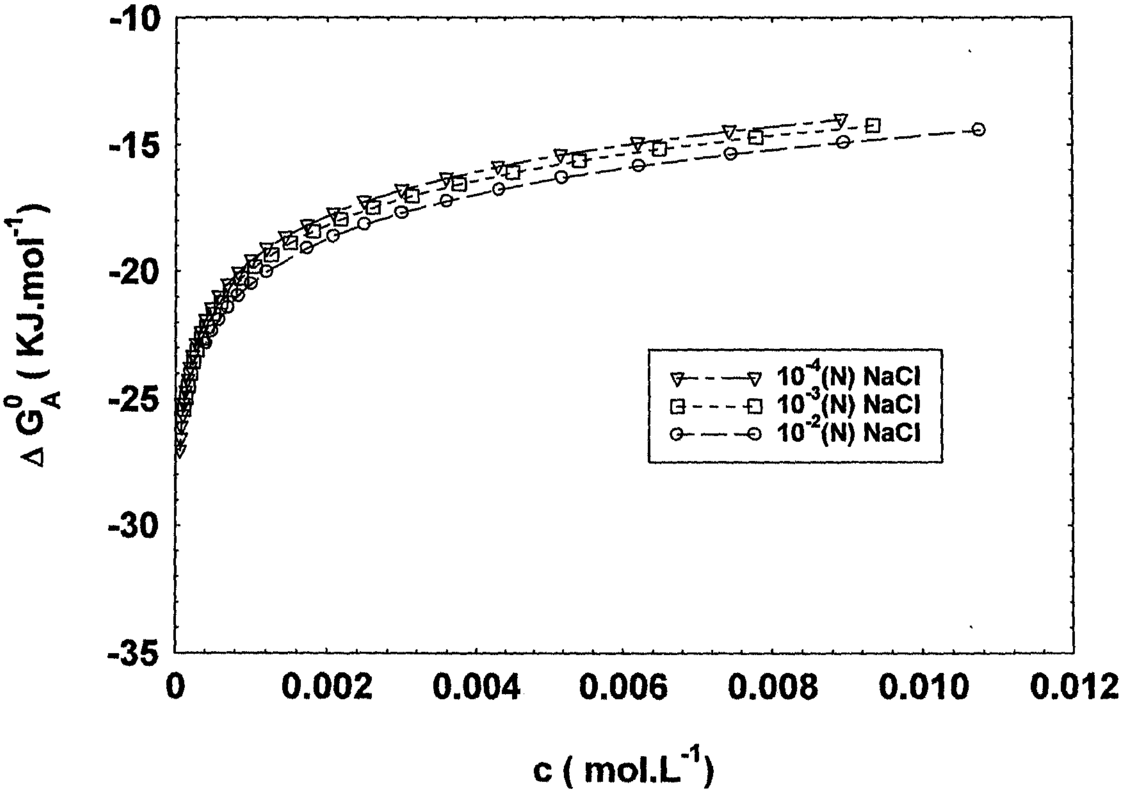

Fig. 9. Variation of standard free energy change of counterion condensation (ΔG_A^0) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added different strength of NaCl salt concentration in 30 vol. % methanol-water mixture.

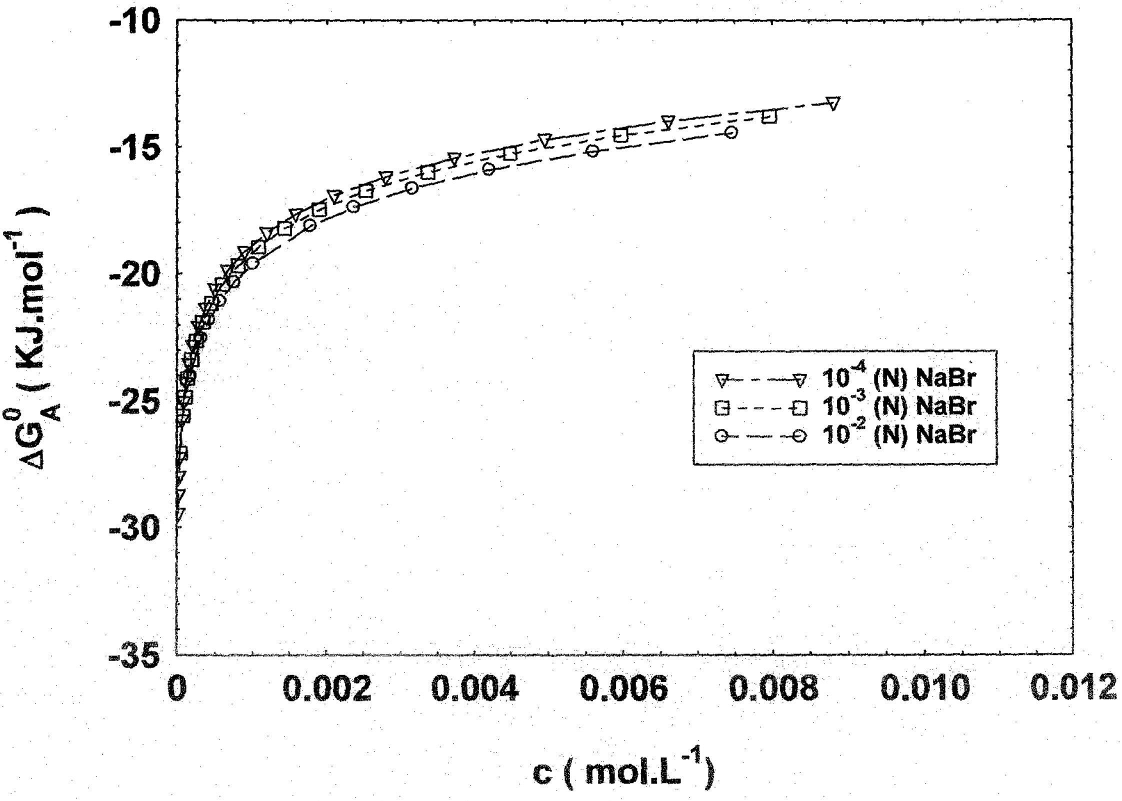

Fig. 10. Variation of standard free energy change of counterion condensation (ΔG_A^0) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added different strength of NaBr salt concentration in 20 vol. % methanol-water mixture.

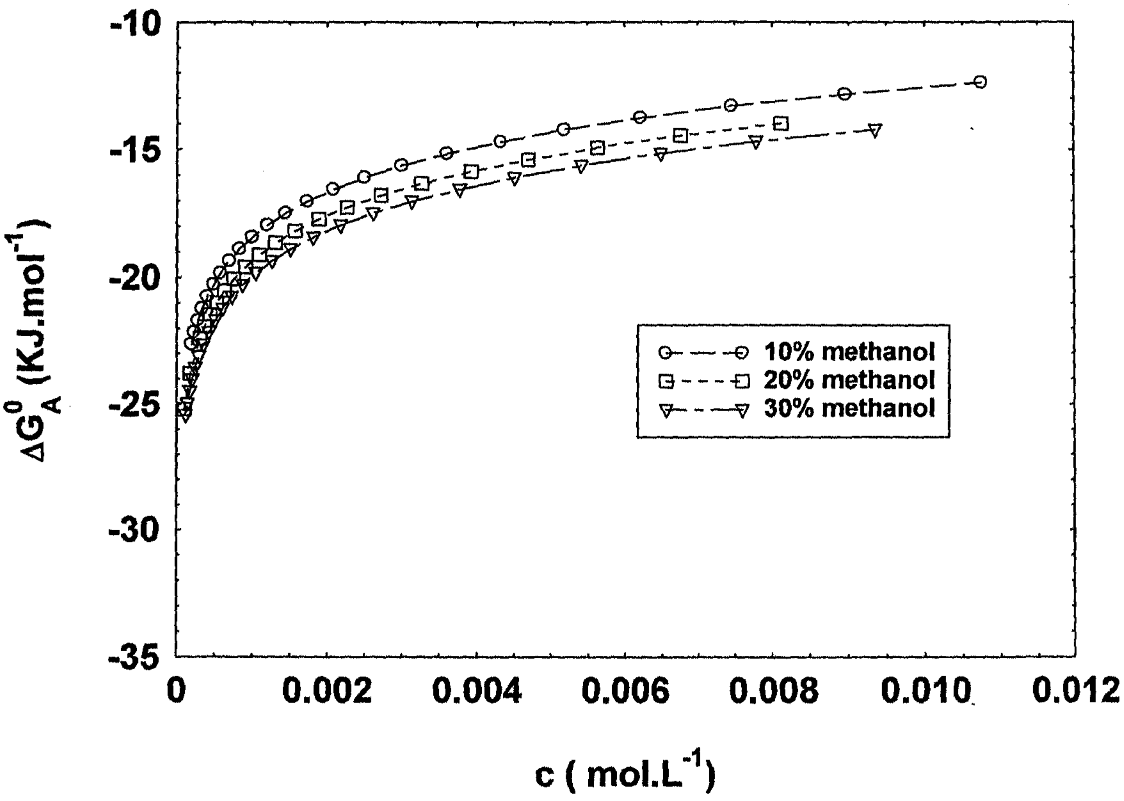

Fig. 11. Variation of standard free energy change of counterion condensation (ΔG^0_A) of sodium carboxymethylcellulose as a function of polyelectrolyte concentration in presence of added strength of 10^{-3}(N) NaCl salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.

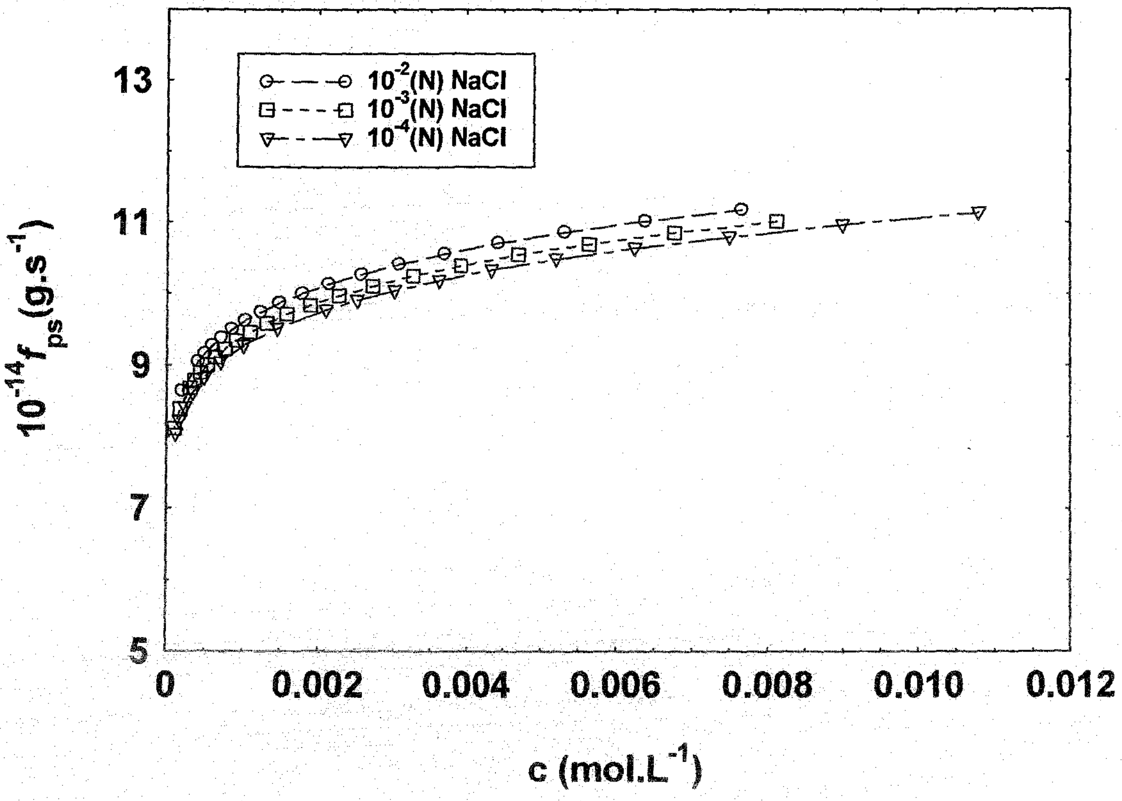

Fig. 12. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaCl salt concentration in 20 vol. % methanol-water mixture.

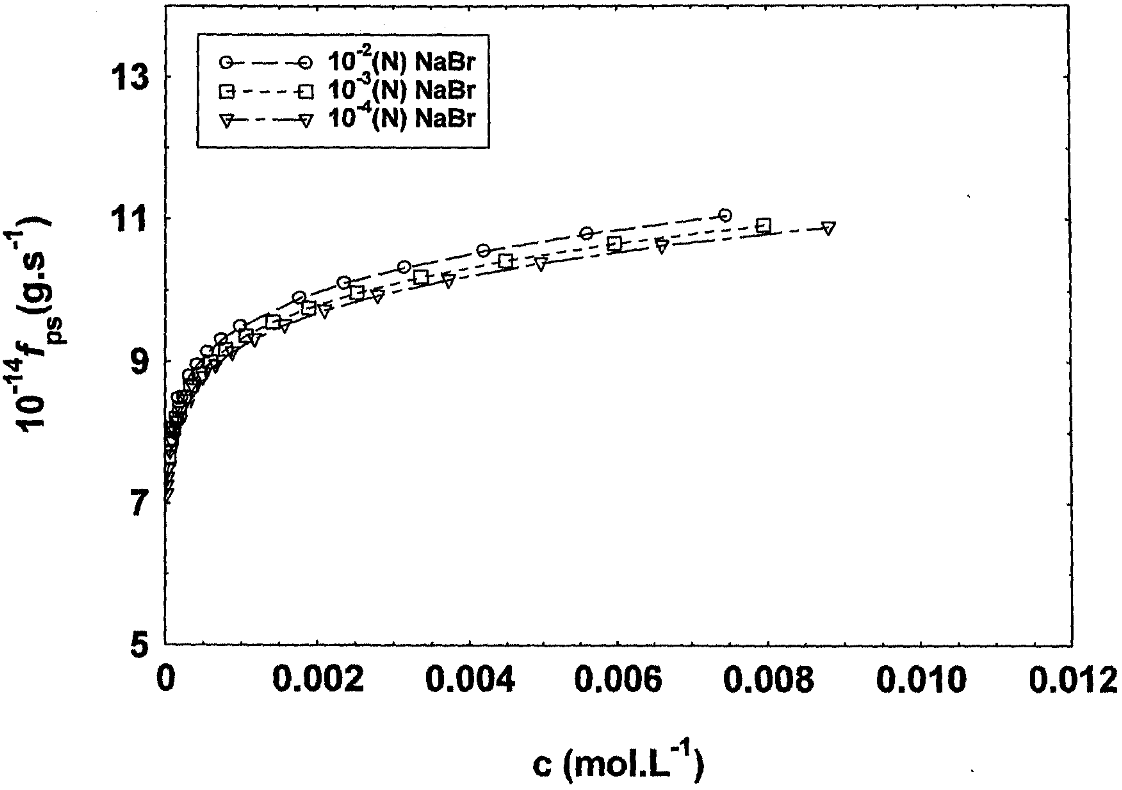

Fig. 13. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of different added NaBr salt concentration in 20 vol. % methanol-water mixture.

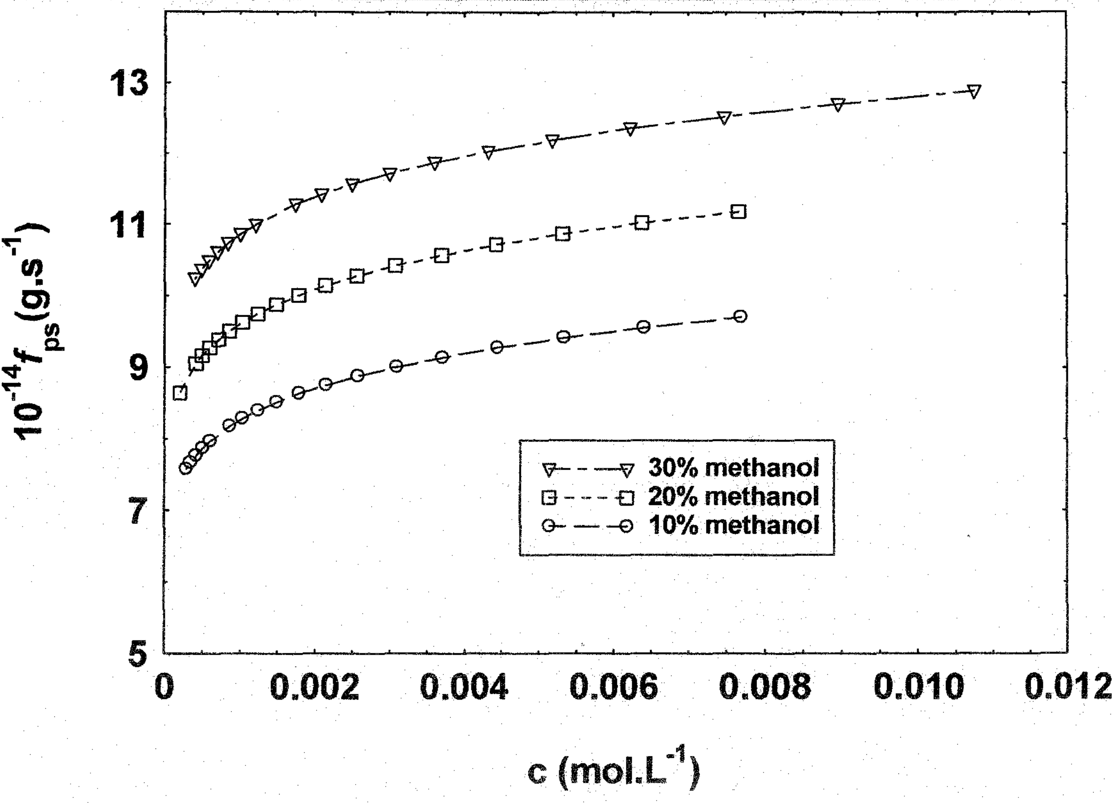

Fig. 14. Variation of the coefficient of friction between the polyion and the solvent (f_{ps}) of sodium carboxymethylcellulose solutions as a function of polyelectrolyte concentration in presence of 10^{-2}(N) added NaCl salt concentration in different (10, 20, and 30 vol. %) methanol-water mixture.