

Effect of Salt on the Conductivity of Sodium Polystyrenesulfonate in Methanol -Water Mixed Solvent Media

Introduction

In Chapter IV, the results of conductivity measurements on salt-free solutions of sodium polystyrenesulfonate (NaPSS) in methanol-water mixed solvent media¹ have been reported. The conductivity behaviour, however, might change considerably upon addition of salts and hence studies on the conductivity of polyelectrolytes in the presence of a salt might provide important insight into the polyion-counterion interactions in such cases.

Although the polyelectrolyte conductivities have been well understood in salt-free semidilute solutions² in the light of the scaling description for the configuration of a polyion chain in accordance with Dobrynin *et al.*,³ the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning⁴ were the first to make an attempt to describe the electric transport properties of polyelectrolyte solutions in presence of a simple salt using the Manning counterion condensation theory⁵ without much success.

In view of the inadequacy of the Manning theory of the electrical transport for salt-containing polyelectrolyte 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 performed.⁶⁻¹⁰ Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which provides the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_p + \kappa_s \quad (1)$$

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 polyelectrolyte.

Earlier investigations,⁶⁻¹⁰ however, revealed that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in generally agree with those predicted by simple additivity, Eq. (1).

Ander group^{6,7} modified the above additivity equation 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 through

$$\kappa = \kappa_p + \kappa_s (D_2 / D_2^0) \quad (2)$$

where D_2 and D_2^0 are the co-ion 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 measure⁵ 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 $\kappa_s (D_2 / D_2^0)$.

Although the “modified” additivity has been found to be somewhat better than the “primitive” one, departures from the experimental results are still prominent.⁶⁻¹⁰ Later, Bordi *et al.*¹¹ evaluated equivalent conductances for a hydrophilic polyion with a salt in the light of scaling theory approach³ and compared them with their experimental results. The agreement is rather good, although a quantitative description is still awaiting.

Very recently, one of us has introduced¹² a simple model to analyze the conductivity of semidilute polyelectrolyte solutions in the presence of an added electrolyte based on scaling theory for the conductivity of semidilute polyelectrolyte solutions neglecting the asymmetry field effect.² This new model has been extensively tested with data on NaPSS in the presence of sodium chloride in 2-ethoxyethanol-water mixed solvent media at different temperatures considering a number of parameters *e.g.*, temperature, relative permittivity of the medium, and concentration of the added salt. Very good quantitative agreement with only one adjustable parameter has been achieved.

In this chapter, we obtained conductivity data for NaPSS in the presence of sodium chloride in methanol-water mixed solvent media at different temperatures and analyzed the results using the recently proposed model.¹²

Theory

According to Dobrynin *et al.*³ a polyion chain in semidilute solutions 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 uncondensed counterions. Due to the strong electrostatic interactions within each correlation blob, the chain is in a fully extended state 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 .

According to Colby *et al.*,² the specific conductivity of a salt-free polyelectrolyte solution (c_p) neglecting the asymmetry field effect is given by

$$\kappa_p = fc_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f}{3\pi\eta_0} \ln\left(\frac{\xi_0}{\xi_e}\right) \right] \quad (3)$$

where λ_c^0 is the limiting equivalent conductivity of the counterions, c_p the number density of monomers, and η_0 the coefficient of the viscosity of the medium. Here, the term f , the fraction of uncondensed counterions, provides also a measure of polyion-counterion interaction in the absence of an electrolyte.

The interactions between the polyion and the counterions would, obviously, be modified in the presence of an electrolyte and this would result in a different level of counterion condensation, *i.e.*, in a different value of f and will be designated as f' . The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt $\kappa_{p(\text{eff})}$ can then be expressed as

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

The total specific conductivity of a polyelectrolyte solution with added simple electrolyte should, thus, 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 the simple salt

$$\kappa = \kappa_s + f'c_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f'}{3\pi\eta_0} \ln\left(\frac{\xi_0}{\xi_e}\right) \right] \quad (5)$$

In the above equation, f' can be treated as an adjustable parameter and this can be conveniently 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) provided κ_s is known. 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 (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.7772 g.cm^{-3} and a co-efficient of viscosity of 0.4742 mPa.s at 308.15 K ; these values are in good agreement with literature values.¹³ Triply distilled water with a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of methanol-water mixture used in this study at 308.15 , 318.15 , and 323.15 K are reported in Table 1 of Chapter III. The relative permittivity values of methanol-water mixtures at the experimental temperatures were obtained by regressing the relative permittivity data as function of solvent composition from the literature¹⁴ and are included in Table 1 of Chapter III.

NaPSS employed in these investigations was purchased from the Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was *ca.* 70,000.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01% . The cell was calibrated by the method of Lind and co-workers¹⁵ using aqueous potassium chloride solution. The measurements were made in a water bath maintained within $\pm 0.005 \text{ K}$ of the desired temperature. The details of the experimental procedure have been described earlier.^{16,17} Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

Results and Discussion

The specific conductivities of NaPSS as a function of the polymer concentration in two methanol-water mixtures with varying amounts of added NaCl at temperatures 308.15, 318.15 and 323.15 K are shown in Figures 1- 6. Figures 7-10, on the other hand, show the influence of temperature on the specific conductivity versus the polymer concentration profiles. From these figures and also from Table 1, it is apparent that for all the solutions studied the specific conductivities increase with polyelectrolyte concentration. Addition of salt increases the specific conductances of the polyelectrolyte-salt solutions as expected. The specific conductances of the polyelectrolyte-salt systems are, in general, found to decrease with increasing amount of methanol in the mixed solvent media (shown in Figures 11-13).

Since the present methanol-water mixtures are poor solvents for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule, we use a value of 5 \AA^0 as the effective monomer size (b) as suggested by Colby *et al.*²

Under poor solvent conditions, the electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) are given by²

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

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

The specific conductivity values of the polyelectrolyte-salt system as a function of polyelectrolyte concentration in a given solvent medium at a given temperature 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 their standard deviations are reported in Table 1. In Figures 1-6 we compare the calculated specific conductivities using the f' values obtained in the semidilute regime (reported in Table 1) with those obtained experimentally. It is directly evident from an inspection of these figures and from the values of the standard deviations recorded in Table 1 that the present method of analysis reproduced the experimental results quite satisfactorily. It should be noted that this test of the proposed model has been performed with 12 sets of data considering the effect of medium, temperature and the concentration of added simple salt.

Addition of salt has always resulted in a lower level of counterion condensation compared to the salt-free cases over the temperature range, although the effects are found to

be very small for the present system. The effects of temperature and the solvent composition on the fractions of uncondensed counterions in these salt-containing systems are found to be the similar as those observed for salt-free solutions (*cf.* Chapter IV).

Conclusions

The electrical conductances of solutions of NaPSS in methanol-water mixed solvent media containing 8 and 16 mass percent of methanol have been measured at three different temperatures namely, 308.15, 318.15, and 323.15 K in the presence of sodium chloride. 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 salt-free semidilute polyelectrolyte solutions proposed by Colby *et al.*² using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*³ Excellent agreement between the experimental results and those obtained according to this model has always been observed.

References

1. A. Bhattarai, P. Nandi, and B. Das, *J. Polym. Research*, **13**, 475 (2006).
2. R. H. Colby, D. C. Boris, W. E. Krause, and J. S. Tan, *J. Polym. Sc.: Part B: Polym. Phys.*, **35**, 2951 (1997).
3. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).
4. D. I. Devore and G. S. Manning, *J. Phys. Chem.*, **78**, 1242 (1974).
5. G. S. Manning, *J. Chem. Phys.*, **51**, 934(1969).
6. M. Kowblansky and P. Ander, *J. Phys. Chem.*, **81**, 2024 (1977).
7. D. E. Wingrove and P. Ander, *Macromolecules*, **12**, 135 (1979).
8. J. Nagaya, A. Minakata, and A. Tanioka, *Langmuir*, **15**, 4129 (1999).
9. A. Minakata, H. Takahashi, T. Nishio, J. Nagaya, and A. Tanioka, *Colloids Surf. A.*, **209**, 213 (2002).
10. J. Nagaya, A. Minakata, and A. Tanioka, *Colloids Surf. A.* **148**, 163 (1999).
11. F. Bordi, C. Cametti, and T. Gili, *Phys. Rev. E*, **68**, 011805 (2003).
12. R. De and B. Das, *J. Chem. Eng. Data*, **55**, 2108 (2010).
13. H. Doe, T. Kitagawa, and K. Sasabe, *J. Phys. Chem.*, **88**, 3341 (1984).
14. P. S. Albright and L. J. Gosting, *J. Am. Chem. Soc.*, **68**, 1061 (1946).
15. Jr. J. E. Lind, J. J. Zwolenik and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1957).
16. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).
17. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).

Table 1. Fraction of Uncondensed Counterions (f') and the Standard Deviations (σ) for NaPSS in the Presence of NaCl at Temperatures 308.15, 318.15 and 323.15 K in Methanol-Water Mixed Solvent Media as Obtained According to Eq. (5).

Temperature K	Mass % of methanol	NaCl (mol.L ⁻¹)	f'	$\sigma \times 10^6$
308.15	8 % methanol	1×10^{-4}	0.258	3.8
		1×10^{-3}	0.246	2.2
	16 % methanol	1×10^{-4}	0.251	2.2
		1×10^{-3}	0.239	1.3
318.15	8 % methanol	1×10^{-4}	0.237	4.3
		1×10^{-3}	0.230	6.9
	16 % methanol	1×10^{-4}	0.233	2.9
		1×10^{-3}	0.232	4.9
323.15	8 % methanol	1×10^{-4}	0.247	4.0
		1×10^{-3}	0.236	6.0
	16 % methanol	1×10^{-4}	0.231	1.1
		1×10^{-3}	0.230	5.1

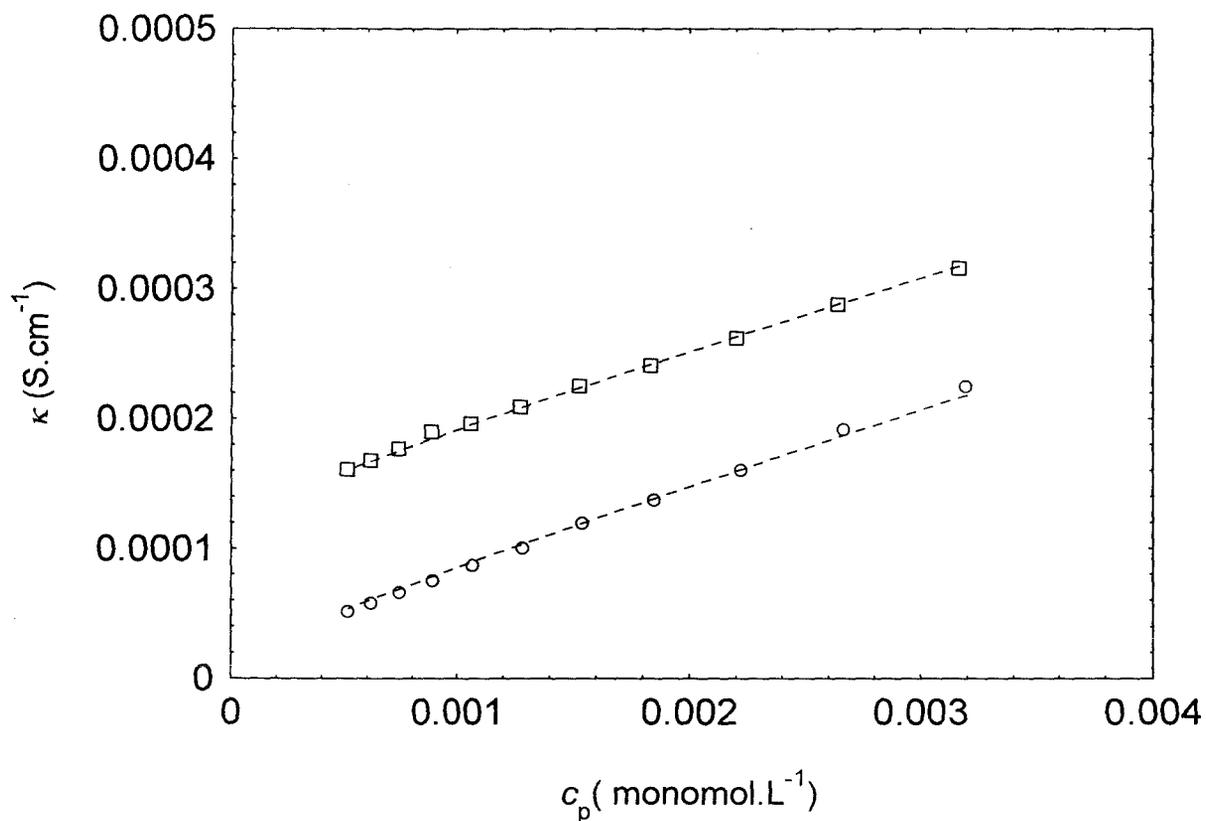


Figure 1. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 308.15 K in 8 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

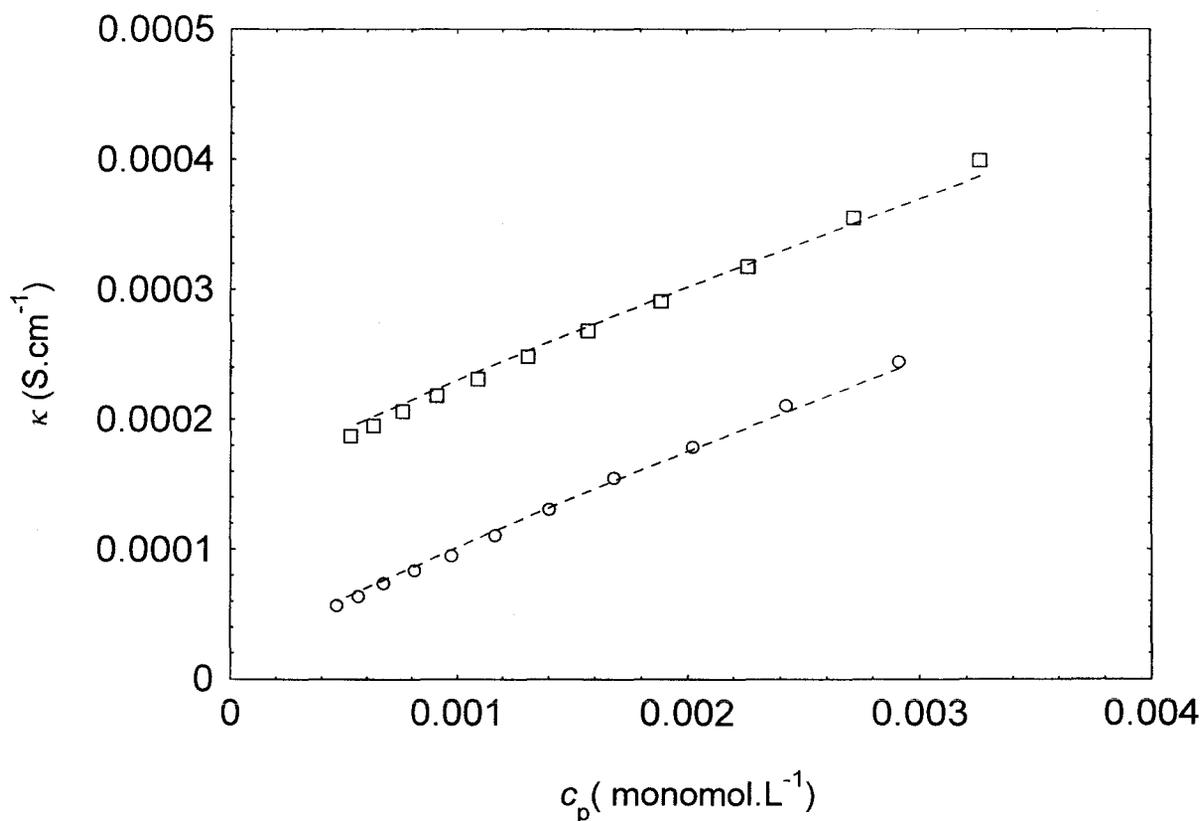


Figure 2. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 318.15 K in 8 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

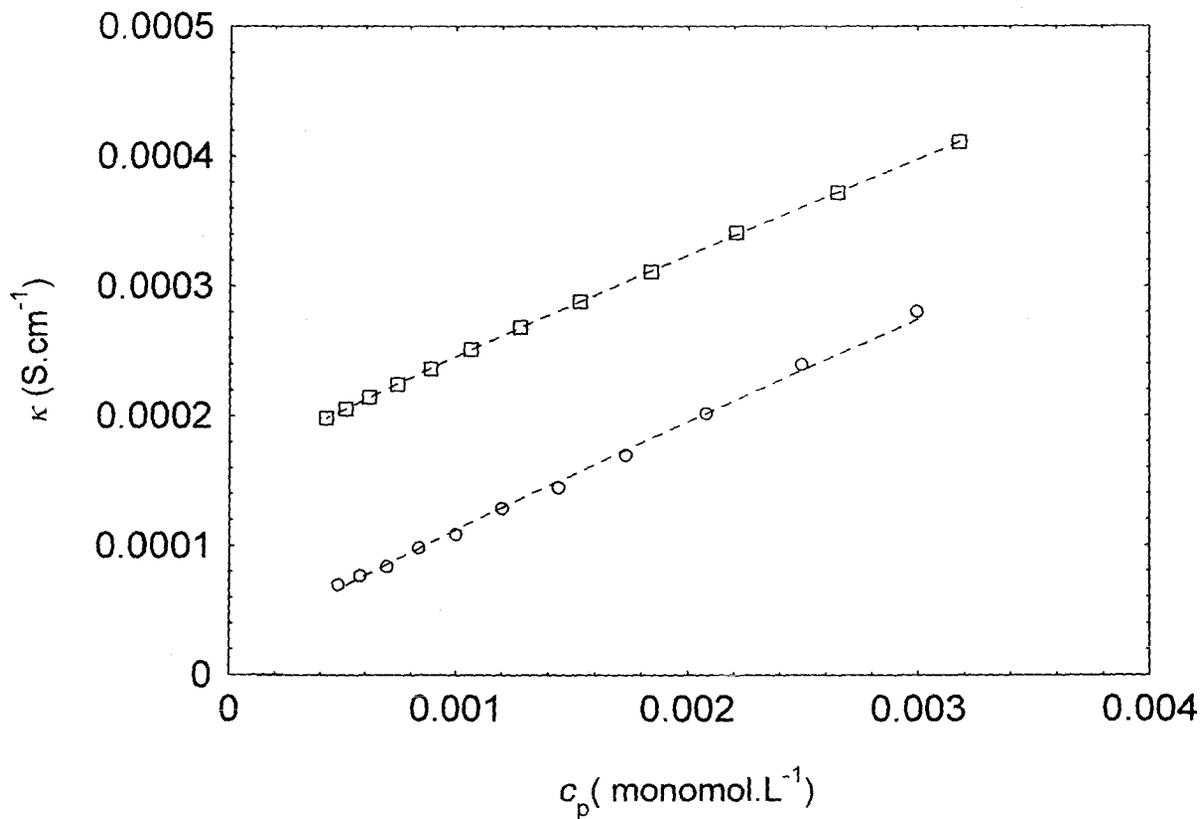


Figure 3. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 323.15 K in 8 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

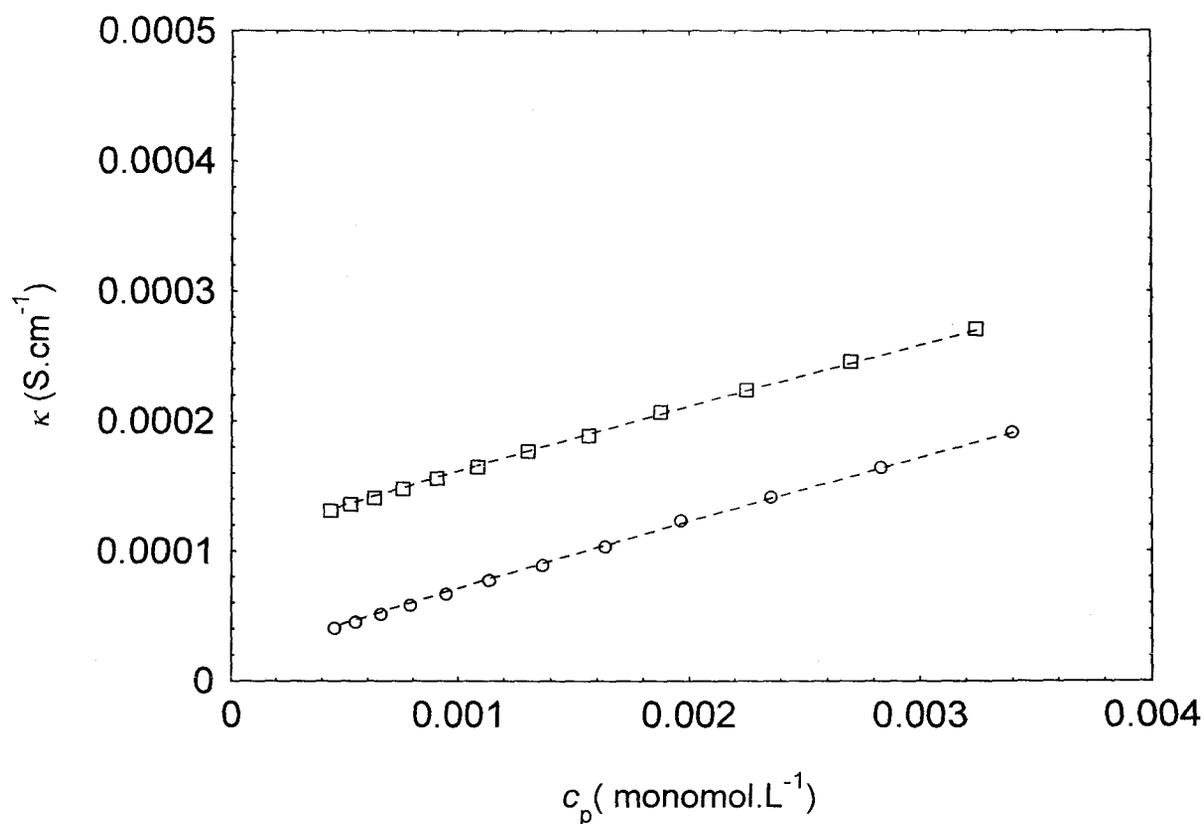


Figure 4. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 308.15 K in 16 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

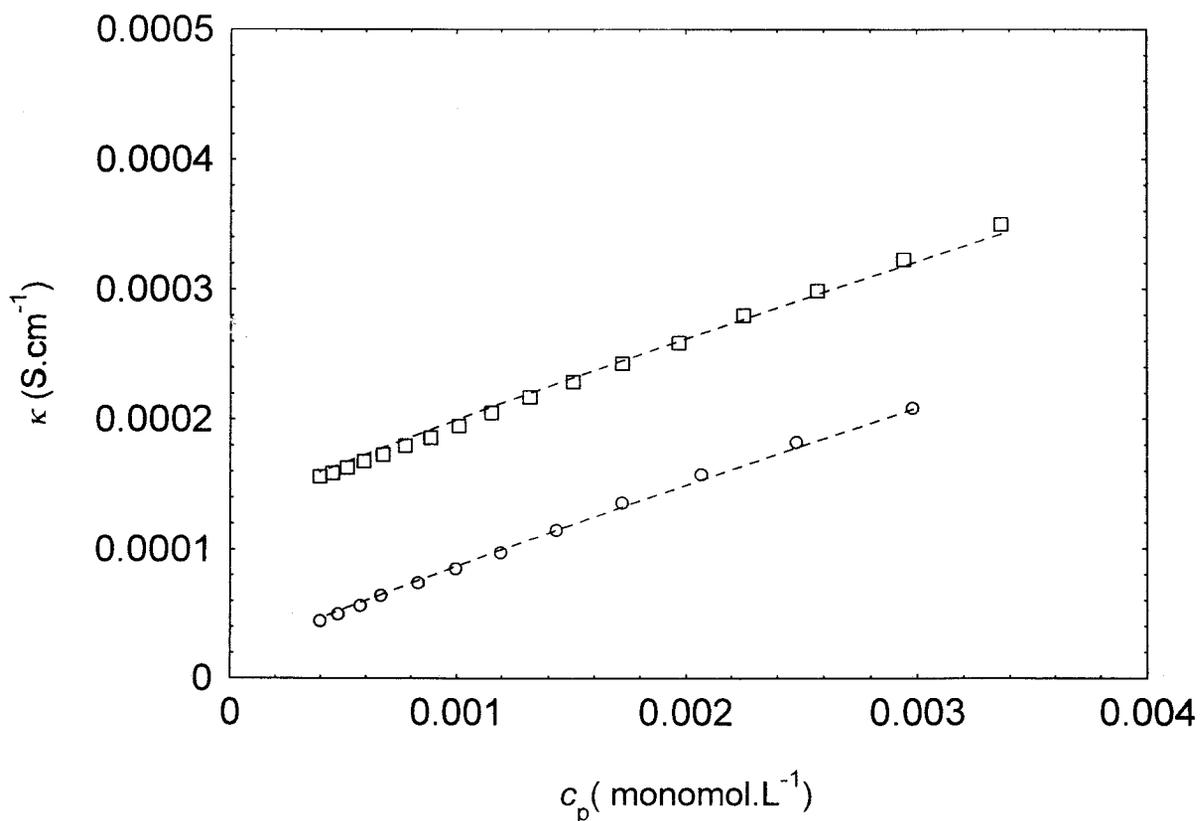


Figure 5. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 318.15 K in 16 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

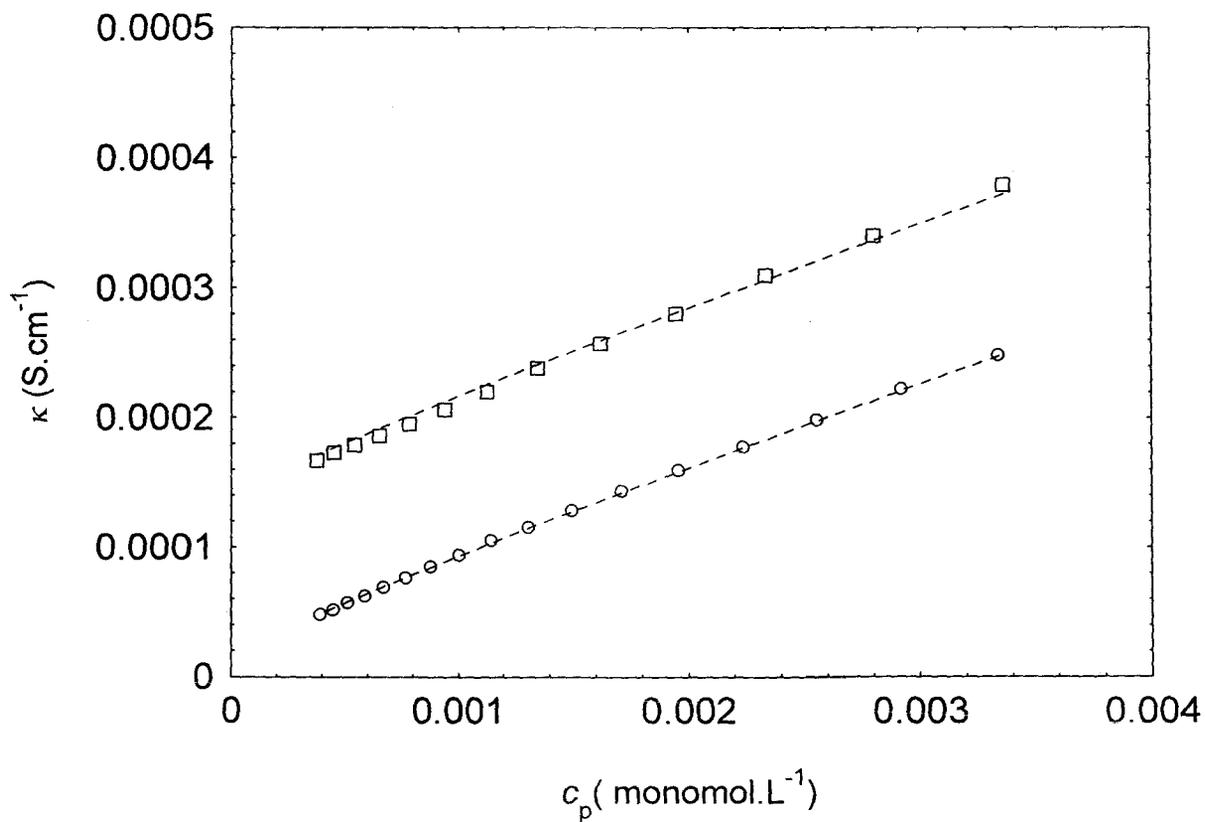


Figure 6. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 323.15 K in 16 mass% methanol. Experimental: Open symbols represent experimental values whereas the dashed lines are according to Eq. (5). Circles and squares represent the polyelectrolyte solutions in presence of (0.0001 and 0.001) mol.L⁻¹ NaCl respectively (see text).

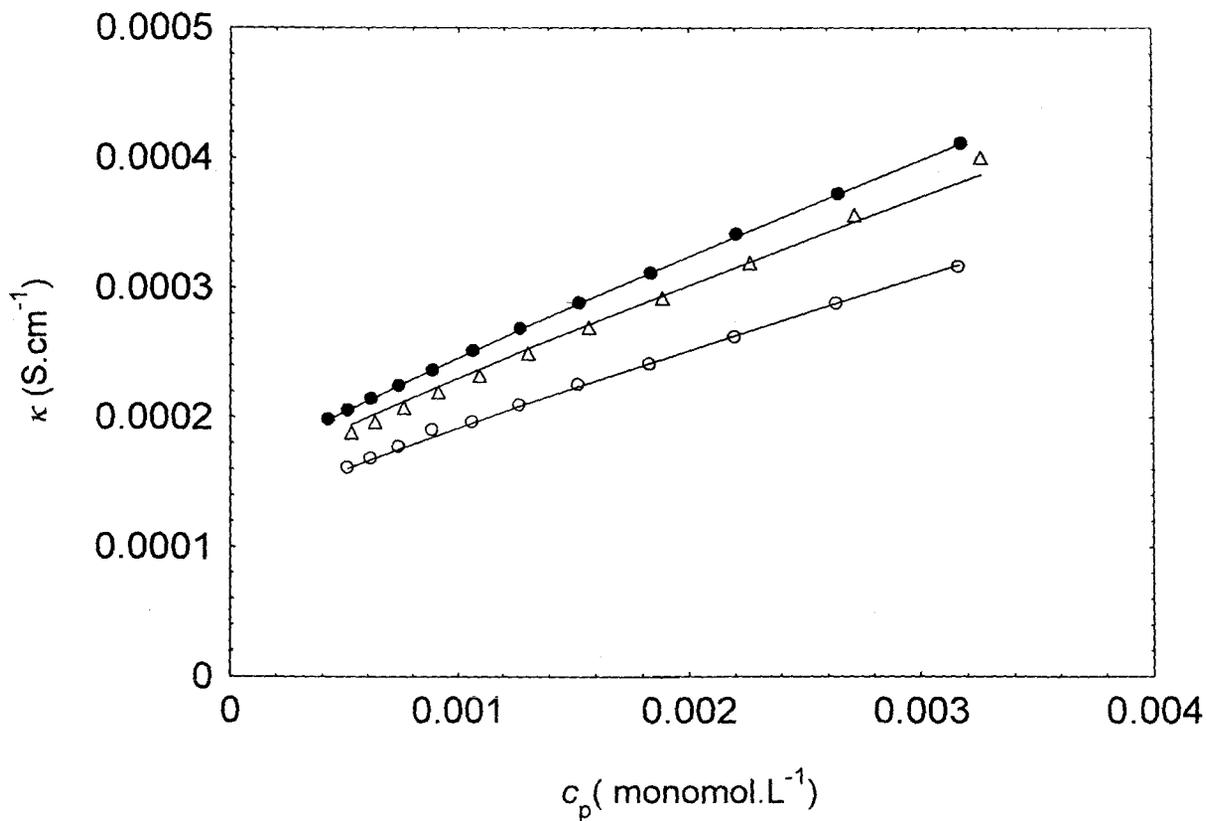


Figure 7. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 318.15 K (Δ) and 323.15 K (●) in 8 mass% methanol in the presence of 0.001 mol.L⁻¹ NaCl. Lines are used to guide the eye.

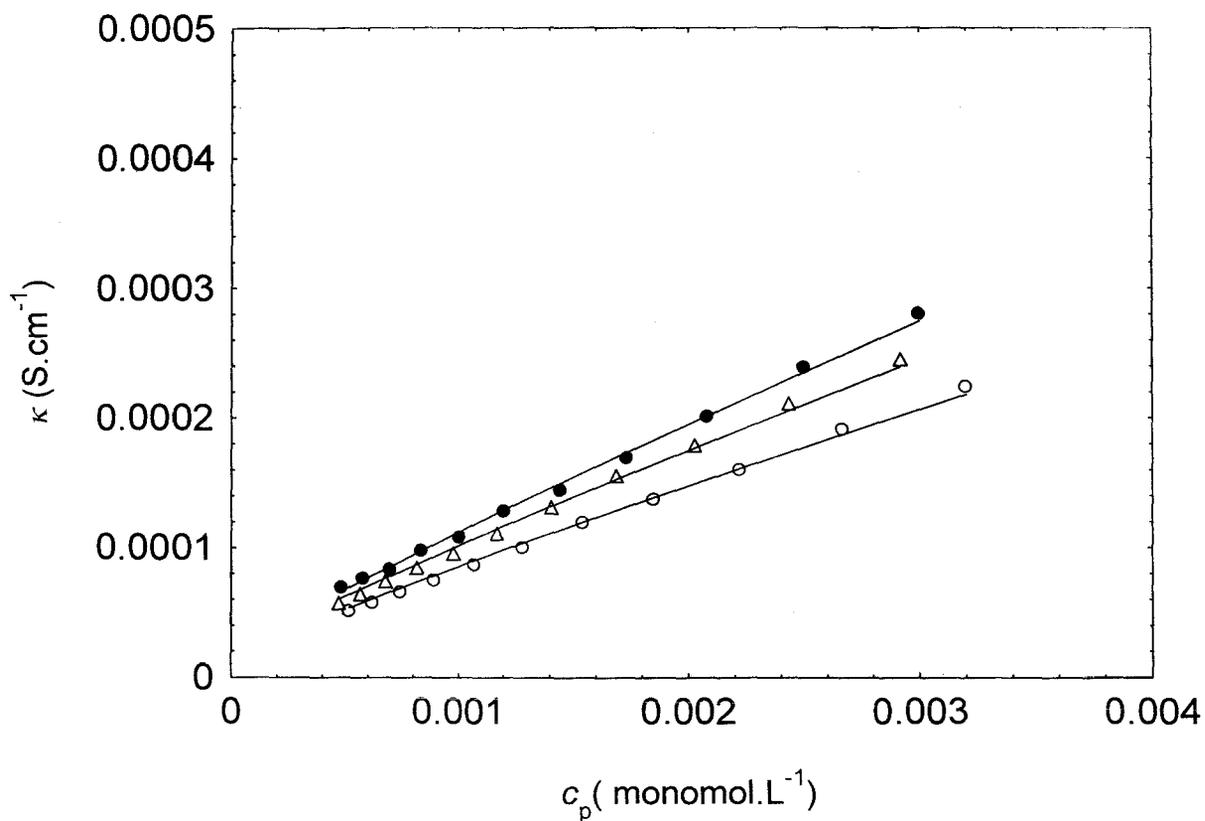


Figure 8. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 318.15 K (△) and 323.15 K (●) in 8 mass% methanol in the presence of $0.0001 \text{ mol.L}^{-1}$ NaCl. Lines are used to guide the eye.

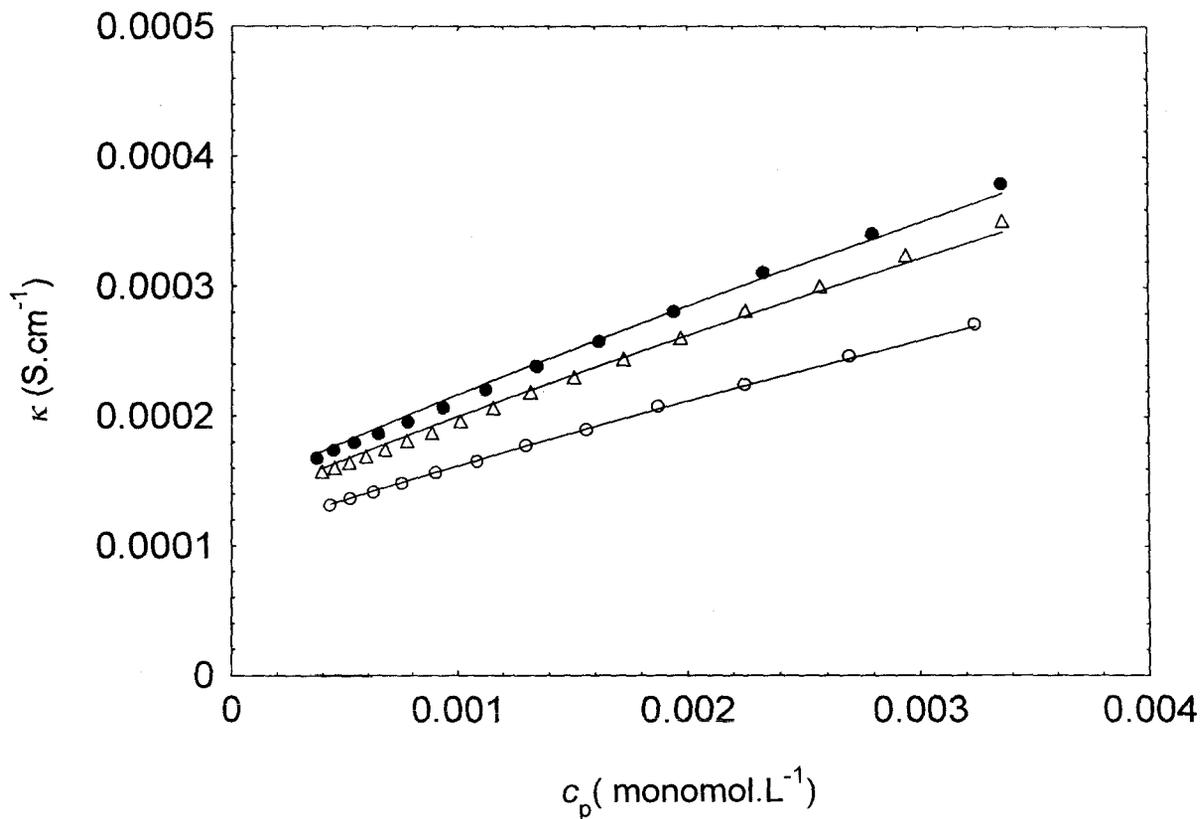


Figure 9. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 318.15 K (△) and 323.15 K (●) in 16 mass% methanol in the presence of 0.001 mol.L⁻¹ NaCl. Lines are used to guide the eye.

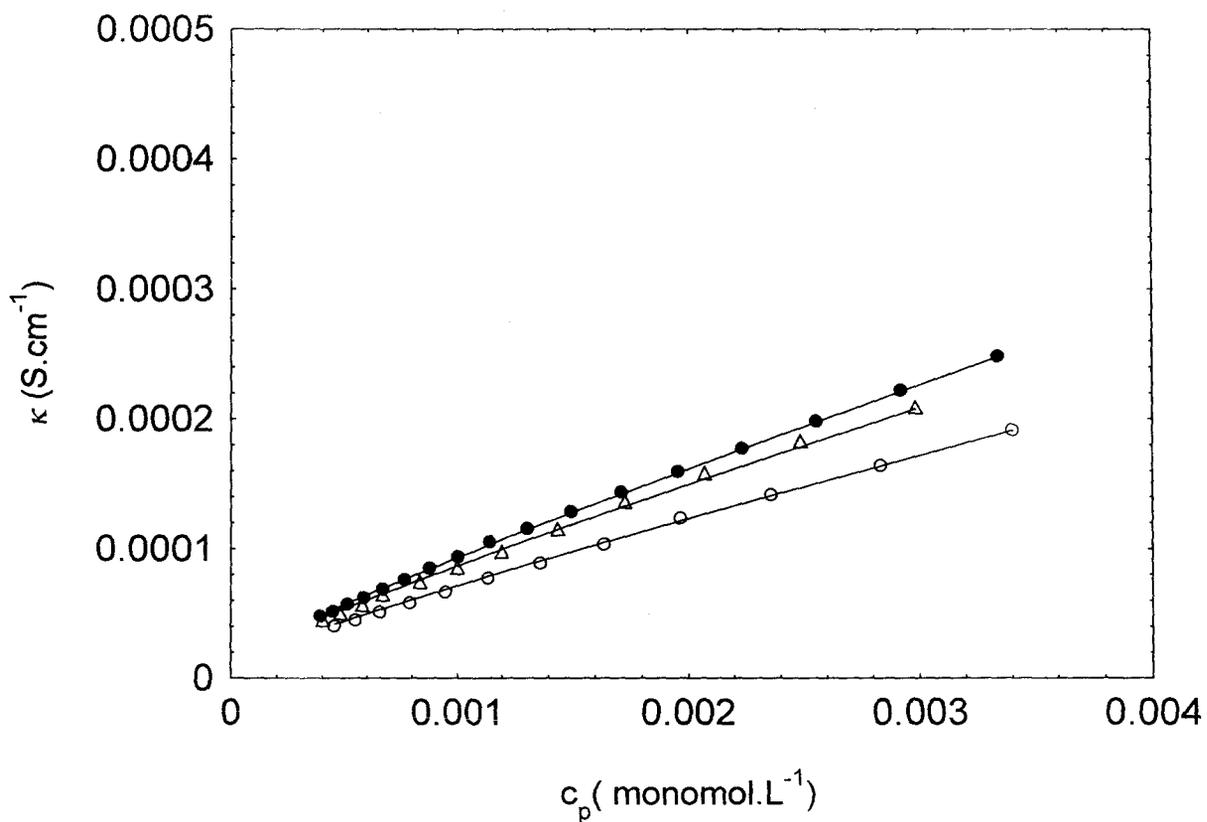


Figure 10. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures 308.15 K (○), 318.15 K (△) and 323.15 K (●) in 16 mass% methanol in the presence of $0.0001 \text{ mol.L}^{-1}$ NaCl. Lines are used to guide the eye.

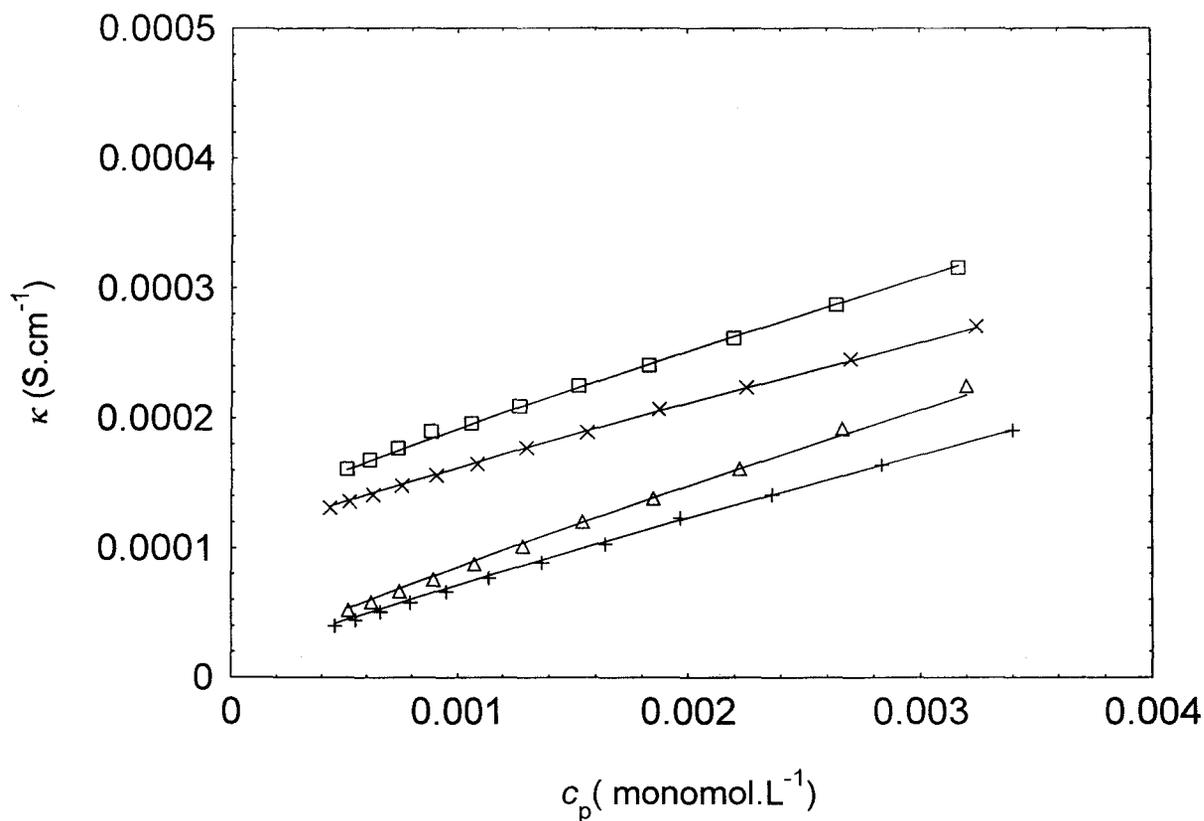


Figure 11. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at a temperature of 308.15 K in 8 mass% methanol with 0.001 mol.L⁻¹ NaCl (□) and with 0.0001 mol.L⁻¹ NaCl (Δ) and 16 mass% methanol with 0.001 mol.L⁻¹ NaCl (×) and with 0.0001 mol.L⁻¹ NaCl (+). Lines are used to guide the eye.

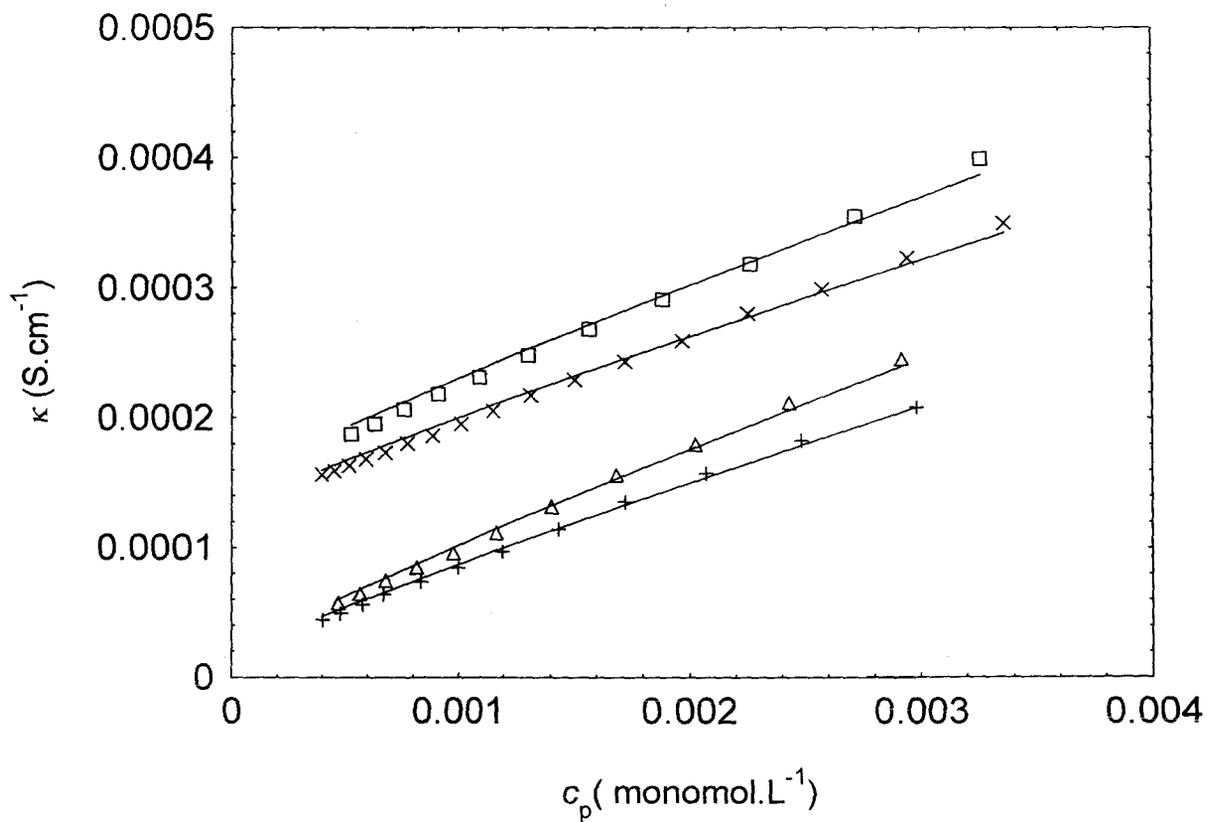


Figure 12. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at a temperature of 318.15 K in 8 mass% methanol with 0.001 mol.L^{-1} NaCl (\square) and with $0.0001 \text{ mol.L}^{-1}$ NaCl (Δ) and 16 mass% methanol with 0.001 mol.L^{-1} NaCl (\times) and with $0.0001 \text{ mol.L}^{-1}$ NaCl (+). Lines are used to guide the eye.

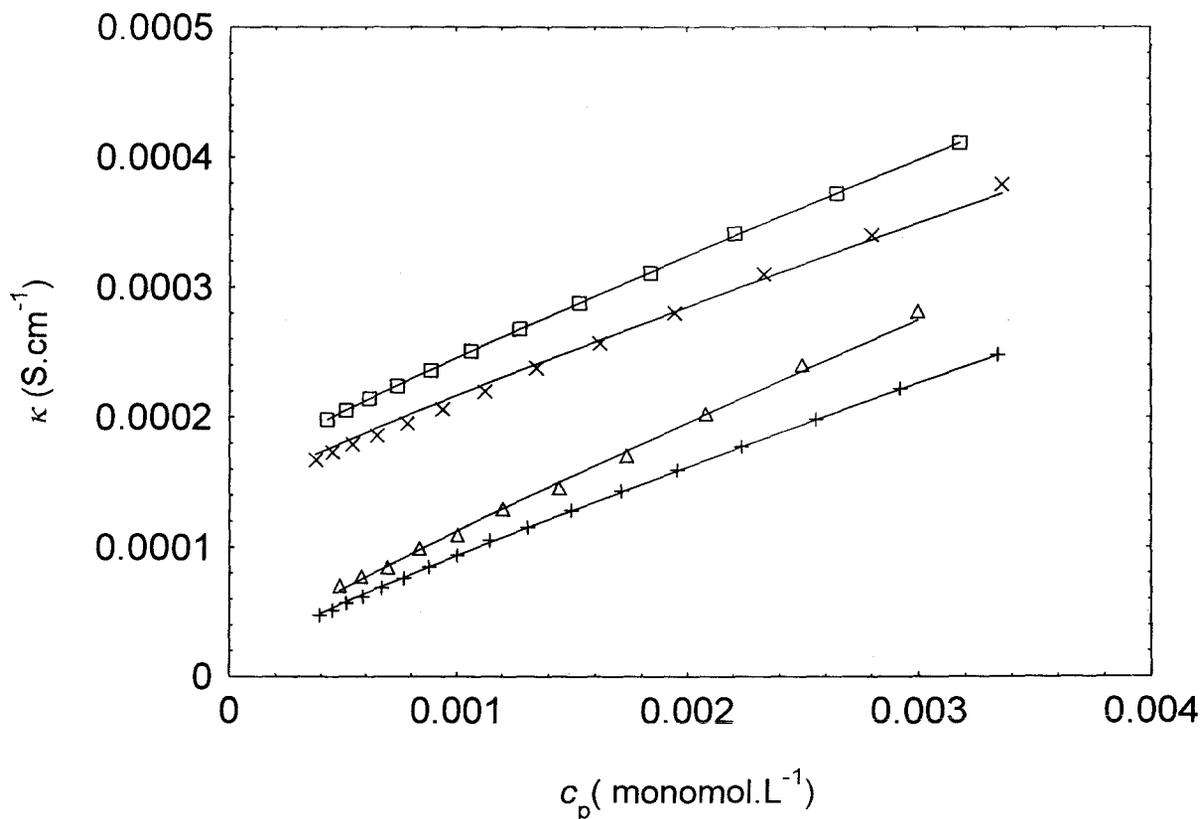


Figure 13. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at a temperature of 323.15 K in 8 mass% methanol with 0.001 mol.L⁻¹ NaCl (□) and with 0.0001 mol.L⁻¹ NaCl (Δ) and 16 mass% methanol with 0.001 mol.L⁻¹ NaCl (×) and with 0.0001 mol.L⁻¹ NaCl (+). Lines are used to guide the eye.