Chapter V

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

Introduction

In Chapter IV, we have reported the results of conductivity measurements on salt-free solutions of sodium polystyrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media. Addition of low-molar-mass salts to a polyelectrolyte solution might change its conductivity behavior dramatically and hence studies on the conductivity of polyelectrolytes in presence of a salt might help elucidate the interactions of polyelectrolytes with added salts. In this study, conductivities of NaPSS have been measured in presence of varying concentrations of sodium chloride (NaCl), in acetonitrile-water mixed solvent media as a function of temperature.

Some earlier experimental results[1] on the conductivities of aqueous polyelectrolyte-salt solutions revealed partial agreement with the predictions using the additivity of the specific conductivities of the polyelectrolyte and the salt. The additivity equations were, however, shown [2-5] not to hold for some other aqueous polyelectrolyte-salt systems. It is thus, apparent that in order to arrive at a definite conclusion on the interactions prevailing in polyelectrolyte-salt solutions from the results of conductivity measurements, more investigation is needed considering as many parameters as possible.

We, therefore, obtained accurate conductivity data for the polyelectrolyte-salt system mentioned above. The present study considers a multitude of parameters such as relative permittivity of solvent, concentration of polyelectrolyte, concentration of added salt and the temperature.

These experimental results have been analyzed to evaluate the extent of deviation from the additivity in order to assess the polyelectrolyte-salt interactions with a view to obtain information on the changes in the polyion conformation if any induced by the salt.

Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. Triply distilled water with a specific conductance of less then 10^{-6} S cm^{-1} at 308.15K was used for the preparation for the solvent mixtures. The physical properties of acetonitrile-water mixture used in this study at 308.15, 313.15, and 318.15 K are reported in Table 1 of Chapter III.

Also included in this table are the limiting equivalent conductivities of the counterion (Na^+), λ_c^0, in 10, 20, and 40 volume percent of acetonitrile-water mixtures taken from our earlier investigation[6] (*cf.* Appendix).

Sodium polystyrenesulfonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 70 kDa.

Conductance measurements were performed 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 measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier.[7] 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, the experimental solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates and the results were averaged.

Results and Discussion

Primitive Additivity

First, the experimental specific conductivity data were analyzed phenomenologically in terms of an additivity contributions of the polyelectrolyte and the simple salt to the total specific conductivity (known as "primitive" additivity). Such an approach is usually used in the literature in describing the behaviour of salt-containing polyelectrolyte solutions.[2-4] Traditionally, this approach takes the form of an assumed additivity of the specific conductances of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the following equation,

$$\kappa = \kappa_{\mathrm{p}} + \kappa_{\mathrm{S}} \tag{1}$$

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. In a polyelectrolyte-salt solution, therefore, the polyelectrolyte specific conductance is given by

$$\kappa_{\mathrm{p}} = \kappa - \kappa_{\mathrm{S}} \tag{2}$$

If a true additivity holds, the values of κ_{p} obtained for a given polyelectrolyte in salt-free (where κ_{s} = 0) and salt-containing solutions would be identical. However, this is not observed in the present study. This is clearly evident from Figures 1a, 2a, 3a, 4a, 5a, 6a, 7a, 8a, and 9a where experimental values of specific conductiviyies (κ) of sodium polystyrenesulfonate in presence of varying concentrations of sodium chloride in acetonitrile-water nixtures have been plotted as a function of the equivalent polyelectrolyte concentration (c).

The fact that the true value of the polyelectrolyte specific conductance cannot be calculated from the specific conductance data obtained in salt-containing polyelectrolyte solutions by using simple additivity of polyelectrolyte and simple salt specific conductances demonstrates clearly the existence of polyelectrolyte-salt interactions. This kind of behaviour of polyelectrolyte-salt solutions has also been reported earlier for other systems.[3-6]

Modified Additivity

Later Ander group[2,3] 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 through

$$\kappa_{\mathrm{p}} = \kappa - \kappa_{\mathrm{S}}\left(D_2 / D_2^0\right) \tag{3}$$

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 measure 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 $\kappa_s(D_2 / D_2^0)$.

Now, in absence of the experimental data for D_2 / D_2^0 for the present system, these were calculated by using the Manning's theory as[11]

$$D_2 / D_2^0 = 1-(1/3)\xi X\left[2+X(1+\pi\xi^{-1})\right]^{-1} \tag{4}$$

when $\xi<1$, but when $\xi>1$, D_2 / D_2^0 takes the following form

$$D_2 / D_2^0 = 1-(1/3)\xi^{-1}X\left[\xi^{-1}X(1+\pi)+2\right]^{-1} \tag{5}$$

Here X is the ratio of the equivalent polyelectrolyte concentration (c_p) to the equivalent salt concentration (c_s), and ξ is the charge density parameter of the polyelectrolyte.

Figures 1b, 2b, 3b, 4b, 5b, 6b, 8b, and 9b clearly show that the "modified" additivity also fails to provide the true values of the polyelectrolyte specific conductance from the specific conductance data obtained in salt-containing polyelectrolyte and simple salt solutions. Therefore, the effects of salt on the specific conductance for the system under investigation could not be quantitatively described by the additivity inspite of taking into account the interactions among all ionic species present in solution following Eq. (3).

Conclusions

The electrical conductances of solutions of sodium polystyrenesulfonate in three acetonitrile-water mixed solvent media containing 10, 20, and 40 volume percent acetonitrile have been measured at three different temperatures namely, 308.15, 313.15, and 318.15 K in presence of sodium chloride. The conductance data have been analyzed on the basis of so-called "primitive" and "modified" additivities of the specific conductances of the polyelectrolyte and salt. Although the performance of the "modified" additivity is somewhat better than the "primitive" one, both fail to provide a quantitative description of the experimental conductivity of sodium polystyrenesulfonate-sodium chloride system in acetonitrile-water mixtures.

The observations indicate that

(1) the effective specific conductance of the added simple salt may not be given by $\kappa_s(D_2 / D_2^0)$. The derivation of the salt diffusion ratio only takes into account the relaxation effect. The effect of electrophoretic countercurrent, which is neglected while deriving Eqs. (4) and (5), might play a decisive role,

(2) the polyion specific conductance is greatly affected by the addition of the salts. In the present case, the polyion mobility should decrease with the addition of salts, suggesting the decrease in the apparent charge of the polyion due to its changing conformation in salt solutions,

(3) the contribution of the polyion to the specific conductance may be influenced by the solute-solvent solvodynamic interactions. Namely, the specific conductance depends on whether the polyion is free-draining or non-draining, and

(4) the polyion mobility is sensitive to the concentration of the added salt which might induce some conformational changes in the polyion structure thus affecting its specific conductance in salt solutions. The effect is found to be more prominent as the concentration of the added salt is increased.

Finally, it can be concluded that the theory of the conductivity of polyelectrolyte-salt solutions is still not completely developed to elucidate the interactions in such systems and that it needs modifications on the lines described above.

References

1. J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).
2. M. Kowblansky and P. Ander, *J. Phys. Chem.*, **81**, 2024 (1977).
3. D. E. Wingrove and P. Ander, *Macromolecules*, **12**, 135 (1979).
4. J. Nagaya, A. Minakata, and A. Tanioka, *Langmuir*, **15**, 4129 (1999).
5. A. Minakata, H. Takahashi, T. Nishio, J. Nagaya, and A. Tanioka, *Collloids Surf.* A., **209**, 213 (2002).
6. D. Ghosh and B. Das, *J. Chem. Eng. Data,* **49**, 1771 (2004).
7. B. Das and D.K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).

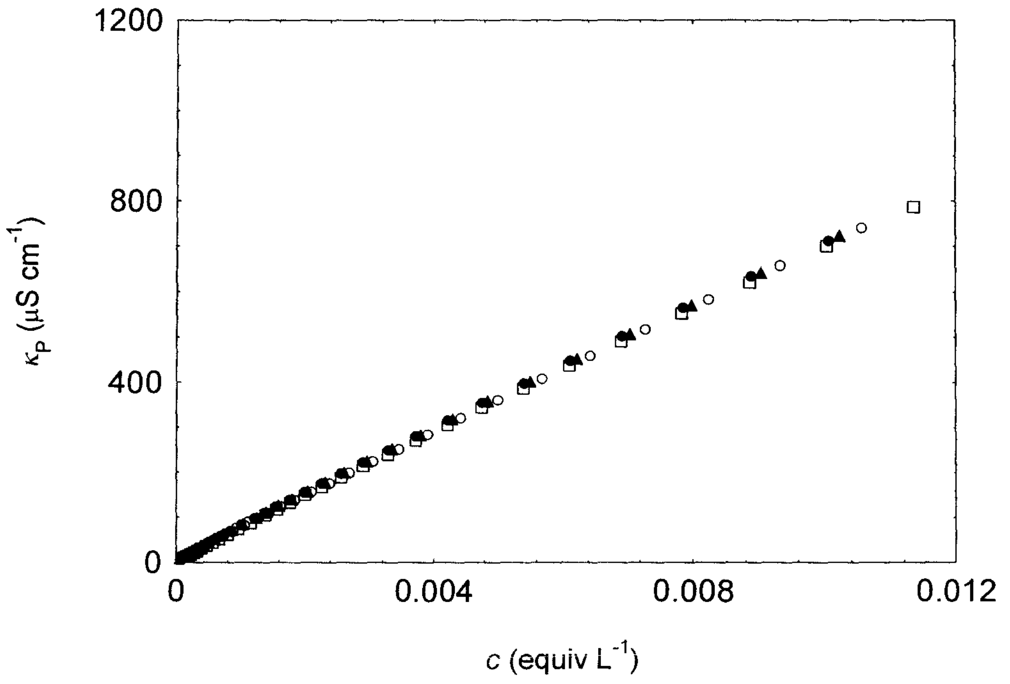

Figure 1a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

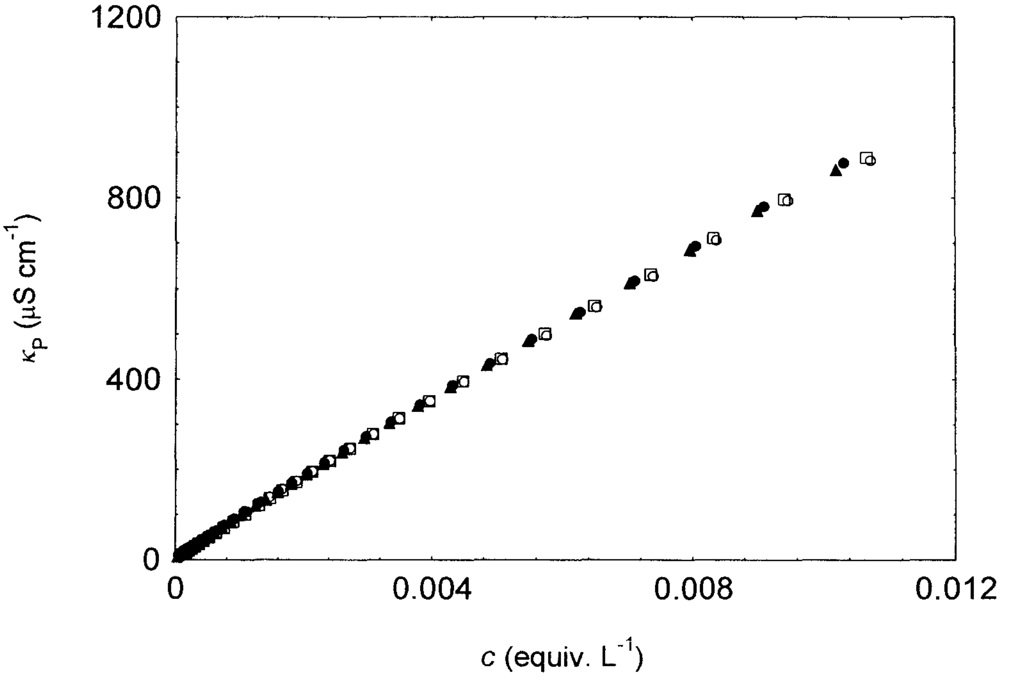

Figure 1b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

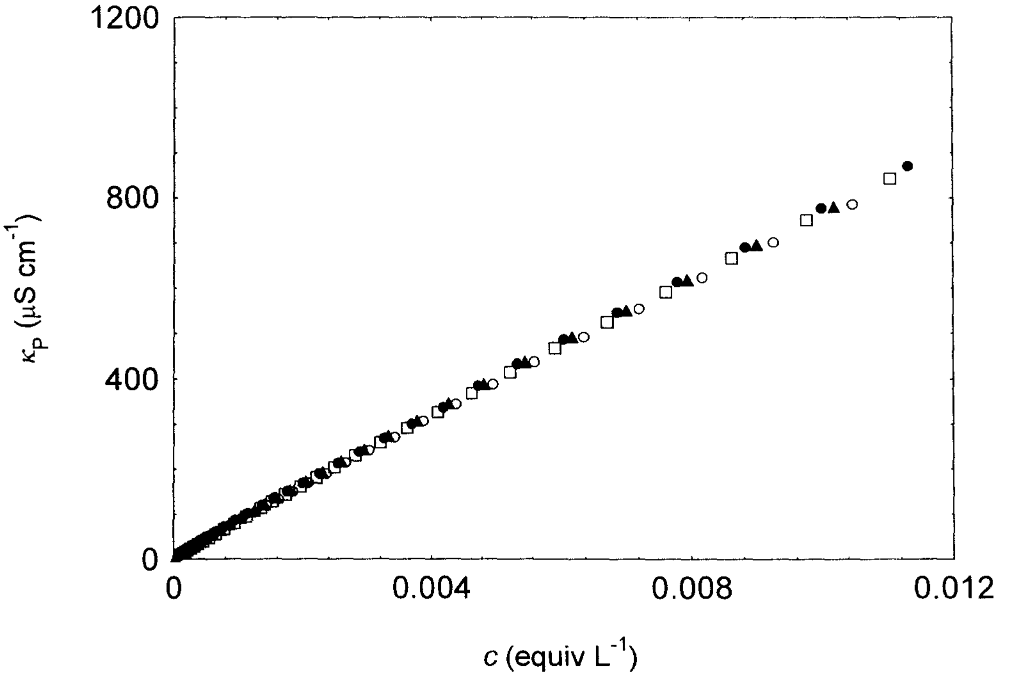

Figure 2a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

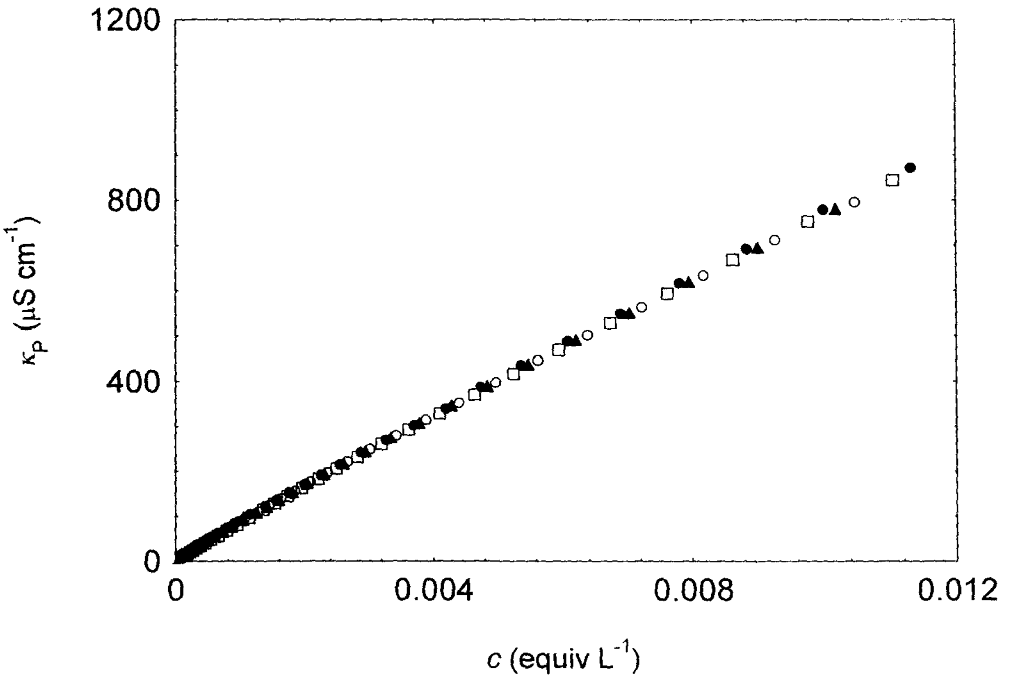

Figure 2b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

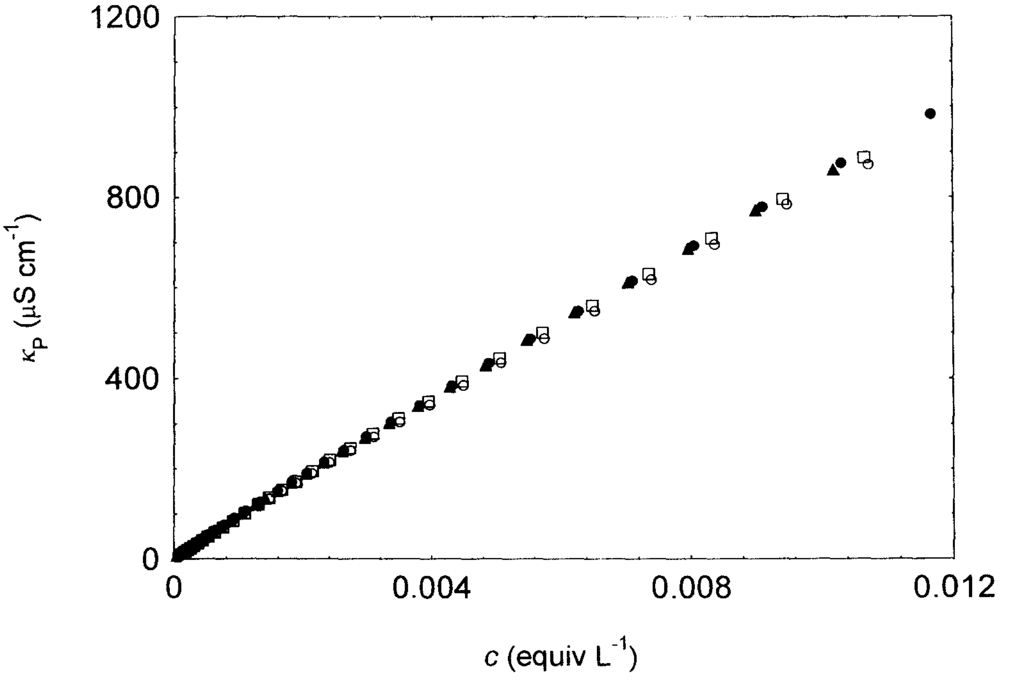

Figure 3a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

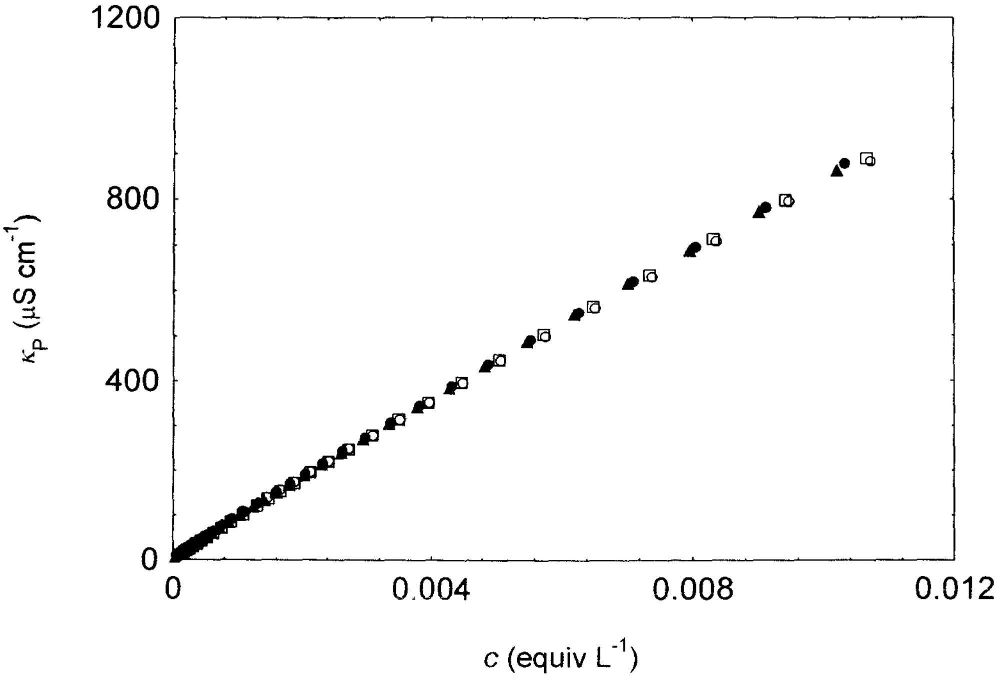

Figure 3b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 10 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Symbols represent modified additivity. (▲) 0.00001, (□) 0.0001, and (○) 0.001 mol L^{-1} NaCl respectively.

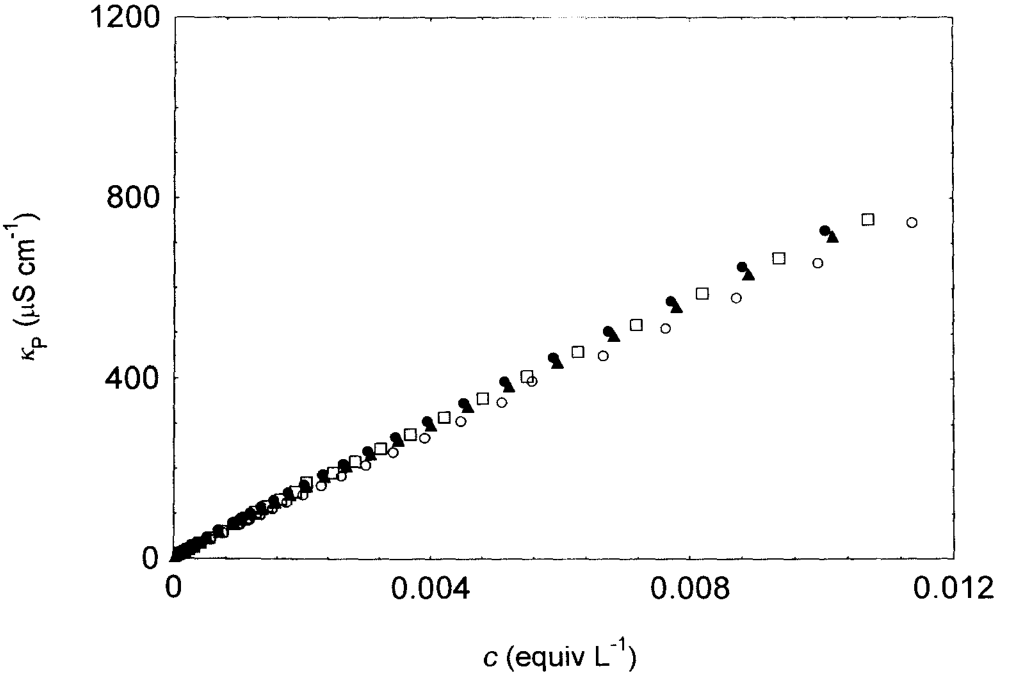

Figure 4a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

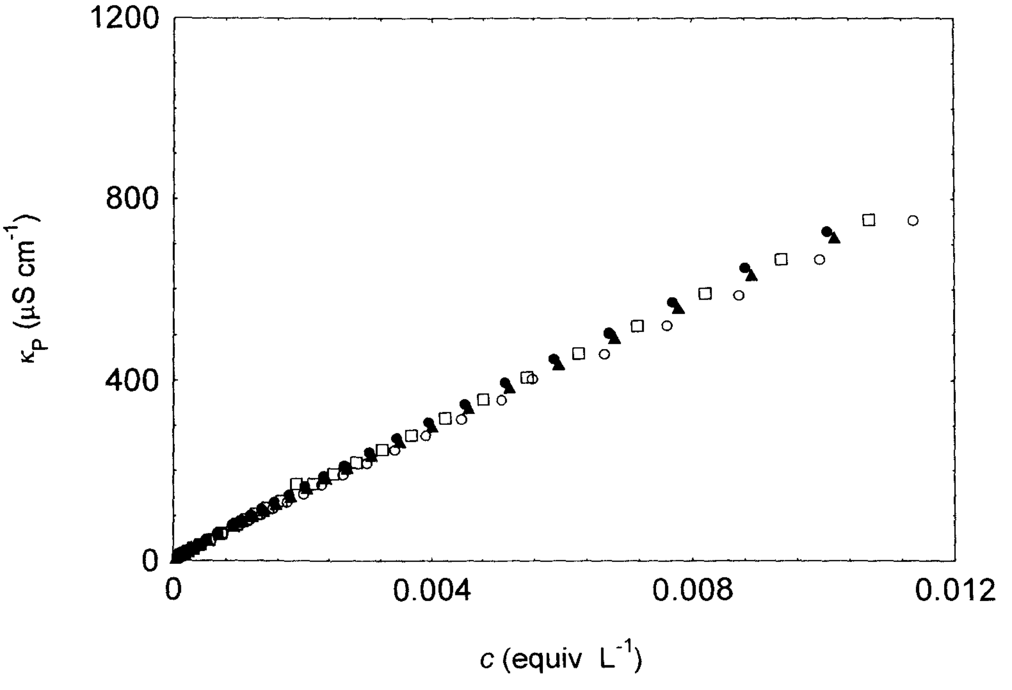

Figure 4b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

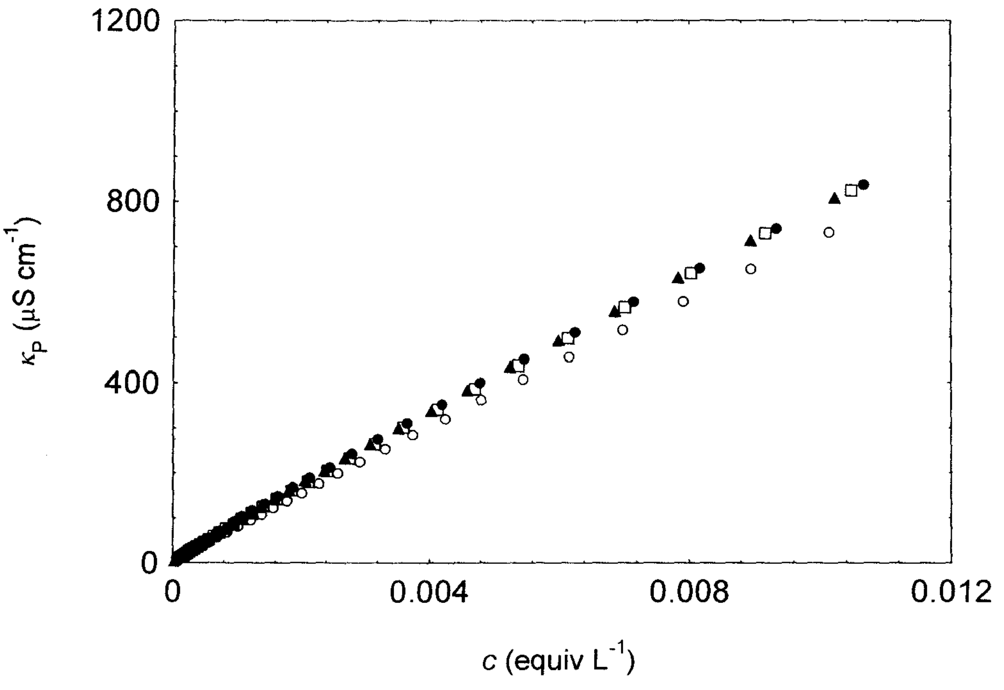

Figure 5a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

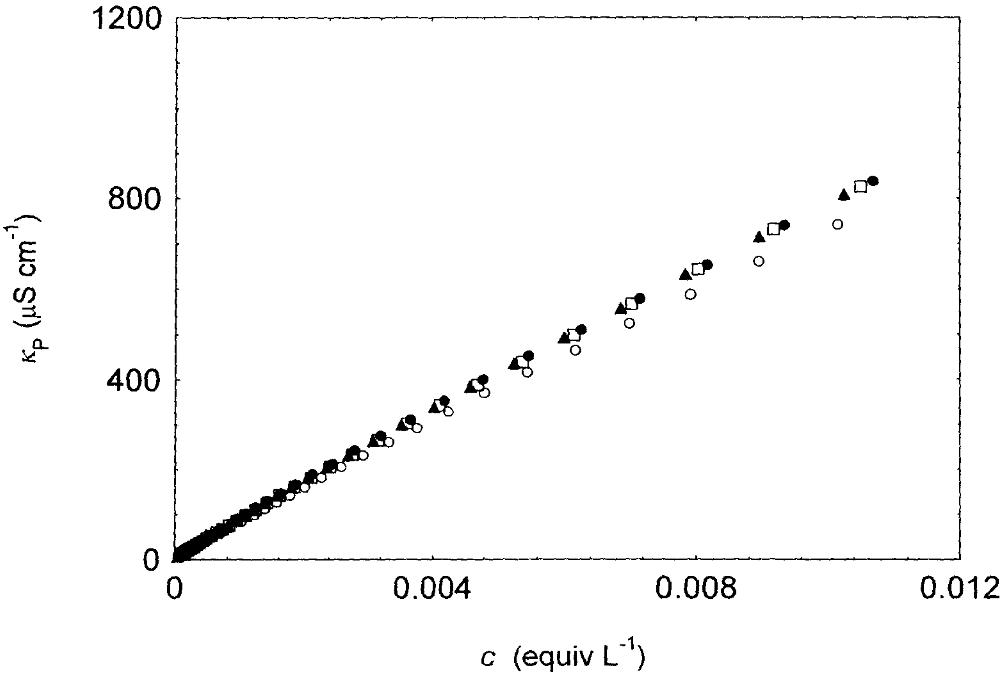

Figure 5b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (•); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

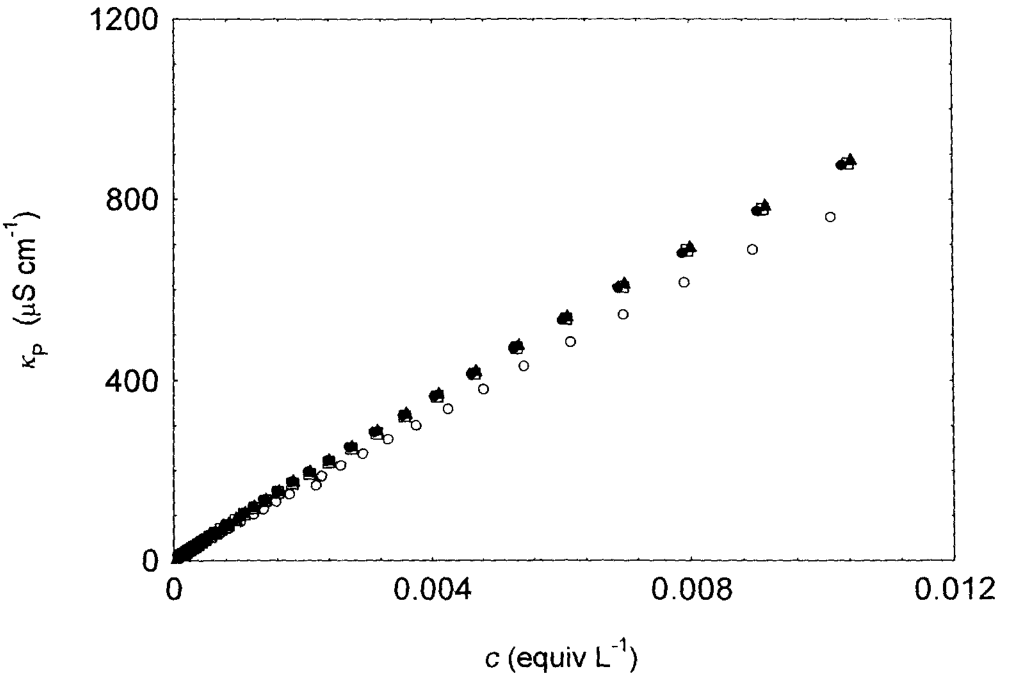

Figure 6a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

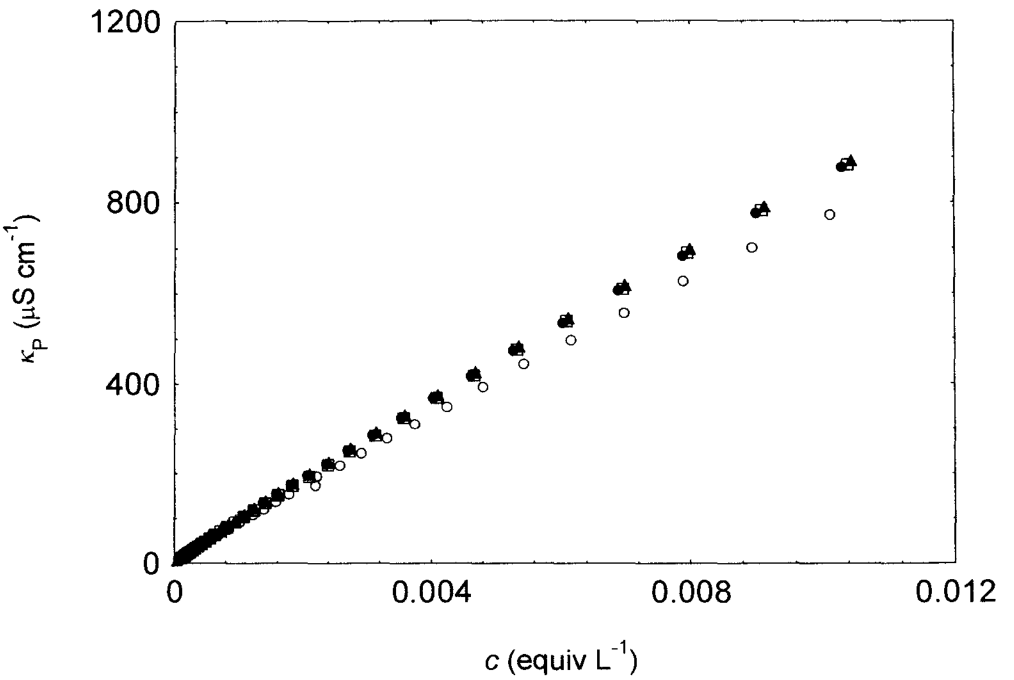

Figure 6b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 20 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

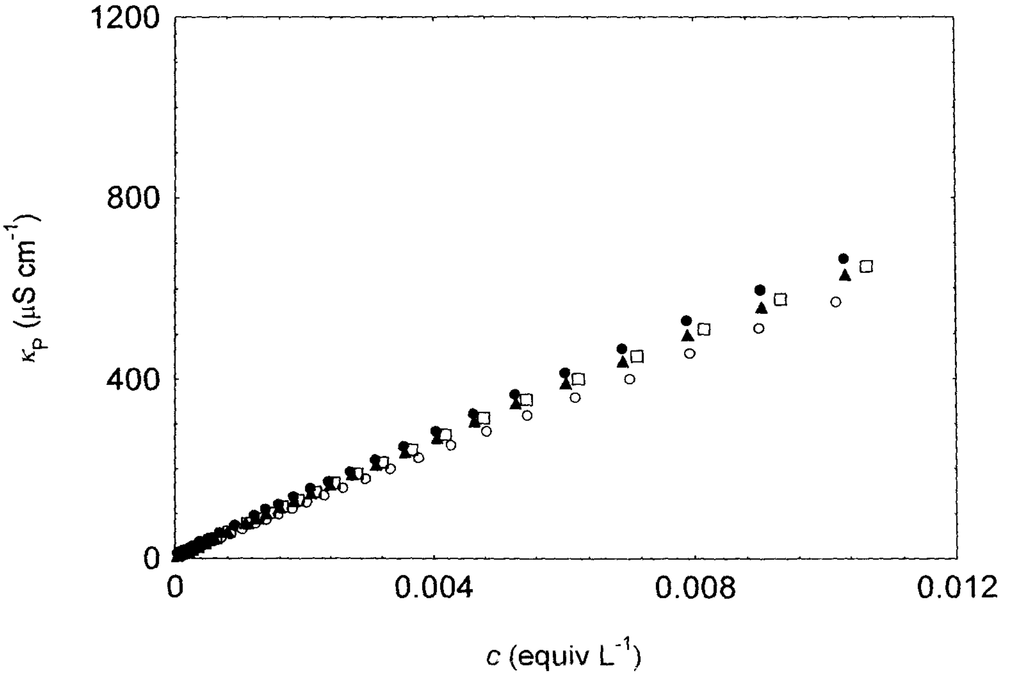

Figure 7a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

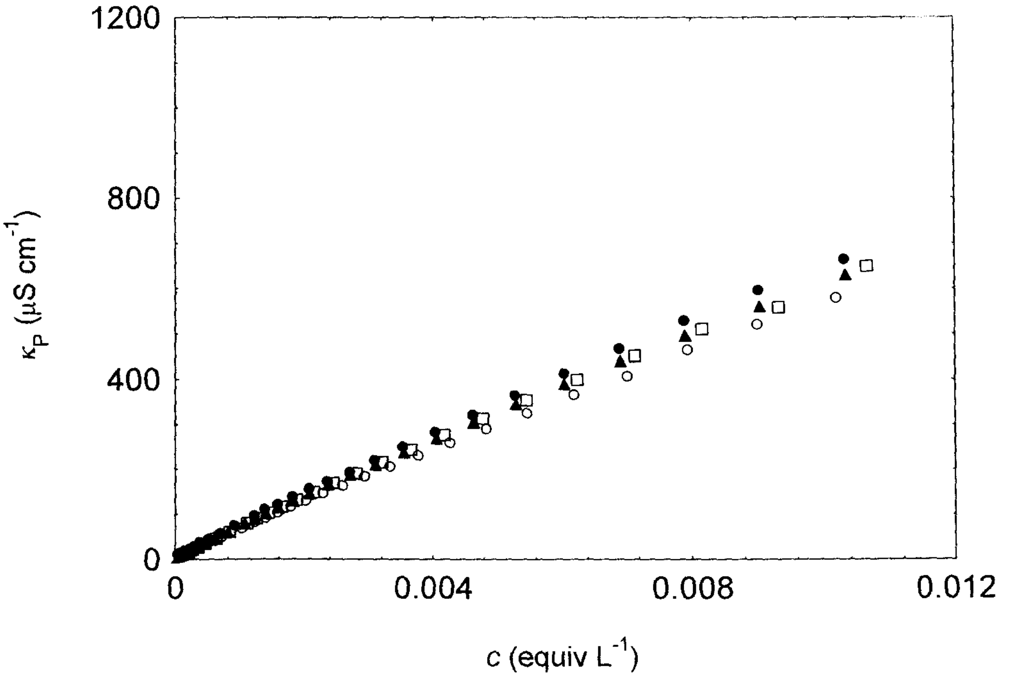

Figure 7b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 308.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

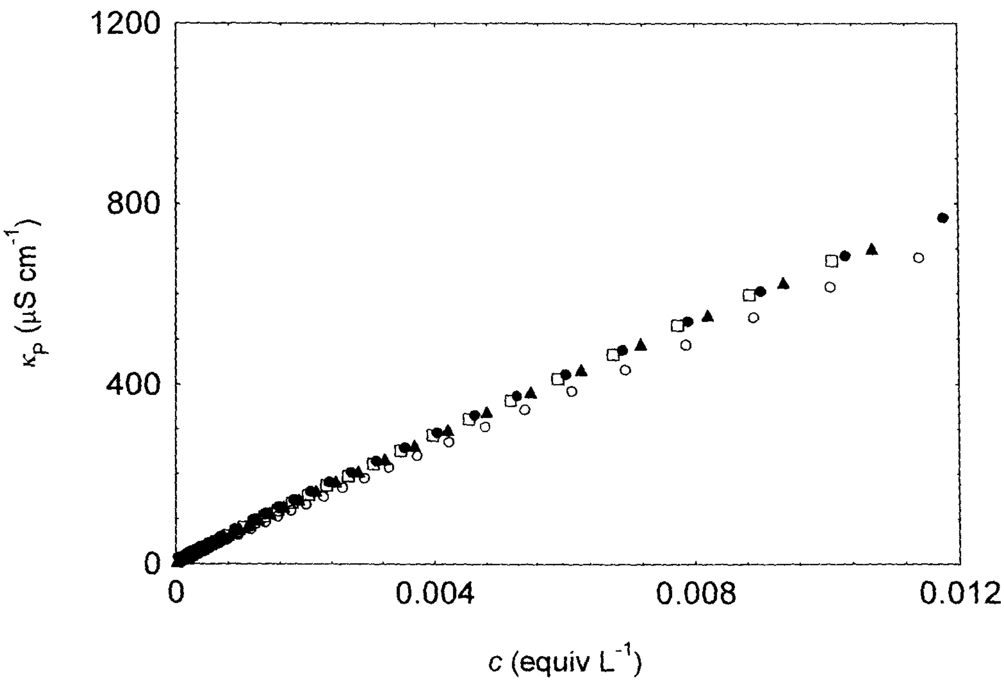

Figure 8a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

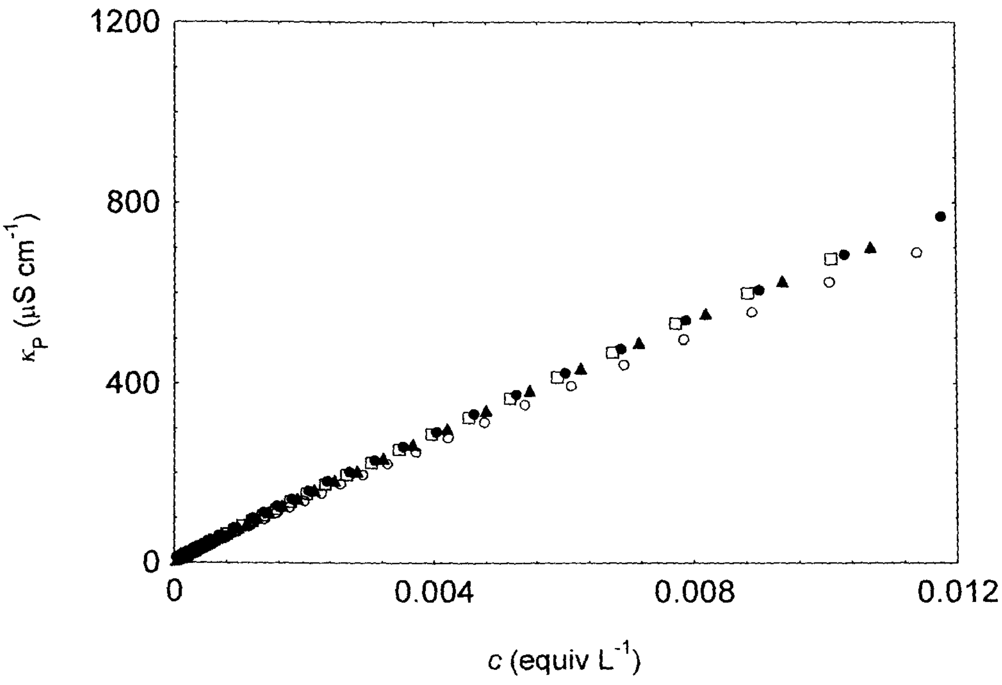

Figure 8b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 313.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

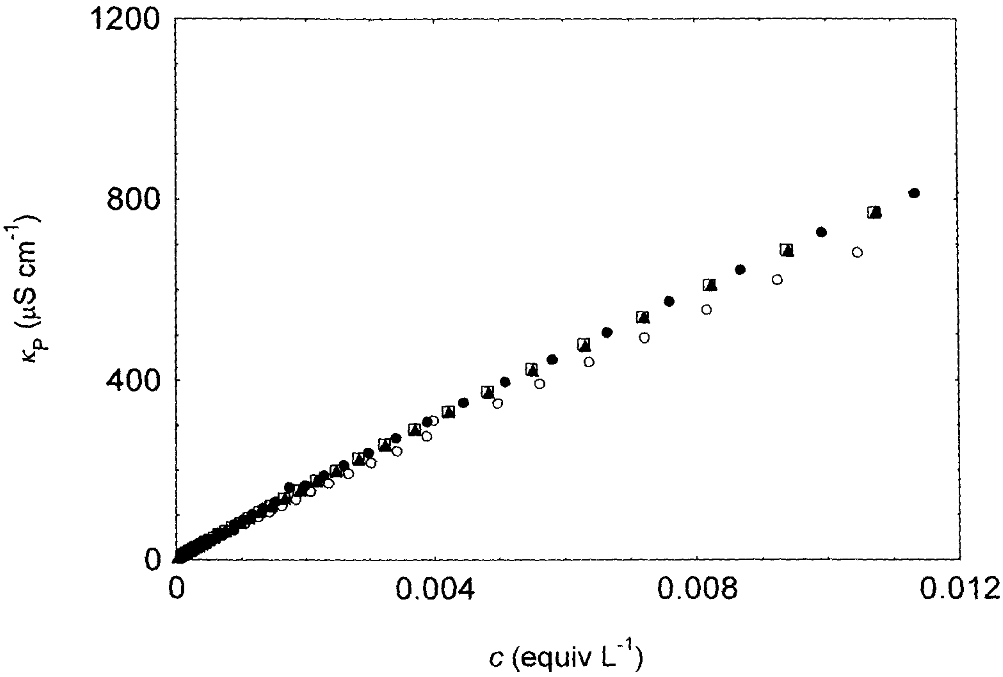

Figure 9a. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to primitive additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).

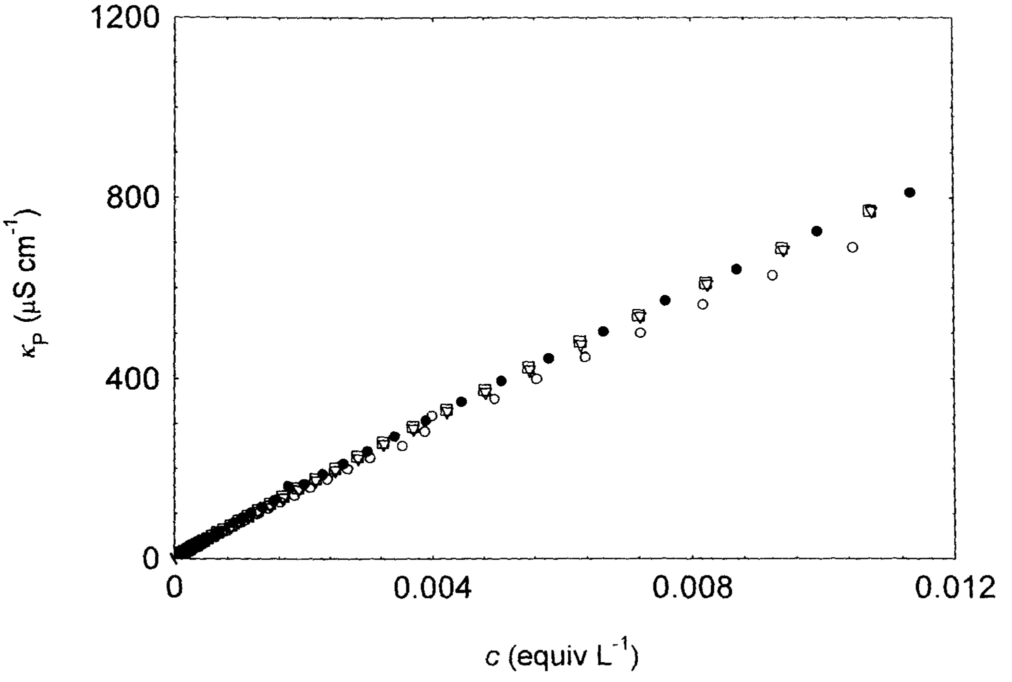

Figure 9b. Specific conductivities of NaPSS as a function of the polymer concentration (c) at 318.15 K in an acetonitrile-water mixture containing 40 vol percent of acetonitrile. Experimental (salt-free polyelectrolyte solutions): (●); Results according to modified additivity, in presence of 0.00001 mol L^{-1} NaCl (▲), 0.0001 mol L^{-1} NaCl (□), and 0.001 mol L^{-1} NaCl (○).