

## Viscosities of Sodium Polystyrenesulphonate in Methanol-Water Mixed Solvent Media in Presence of Sodium Chloride

### Introduction

The anomalous concentration dependence of viscosity of polyelectrolyte solutions with no added salt has been known for a long period.<sup>1</sup> Early investigations appeared to suggest an unbound rise in the reduced viscosity ( $\eta_{sp}/c_p$ ;  $\eta_{sp}$  = specific viscosity and  $c_p$  = polymer concentration) of salt-free polyelectrolyte solutions as one lowers the polyion concentration.<sup>2,3</sup> In these studies, which are summarized in the pioneering work of Fuoss,<sup>2,3</sup> a straight line is obtained when the reciprocal of reduced viscosity is plotted against the square root of the concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the inverse of the intrinsic viscosity. However, careful investigations on the dilute solution behaviour revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum,<sup>4</sup> and normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. Thus the method of Fuoss could not be used to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. It has been argued that the observed behaviour is a consequence of the screening of long-range intermolecular interactions by the residual electrolytes in the solution.<sup>4</sup> Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentration and, therefore, was close to the limit of accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations beneath the viscosity maximum are in the very low concentration region difficult to reach experimentally. On the other hand, provided there is an excess of low-molar-mass electrolyte, at a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity ( $\eta_{sp}/c_p$ ) varies linearly with the polymer concentration ( $c_p$ ) similar to that for a neutral macromolecular solution, thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation:<sup>5,6</sup>

$$\eta_{sp}/c_p = [\eta] + k_H [\eta]^2 c_p \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity describing the solvodynamic behaviour of the polymer molecules in solution,  $c_p$  is the polyelectrolyte concentration and  $k_H$  is the Huggins constant which is a characteristic for a given polymer-solvent system.

This chapter describes the viscometric behaviour of NaPSS in absence and also in presence of an electrolyte (NaCl) in methanol-water mixed solvent media. Our objective is to focus on the role of electrostatic interactions on the viscosity of NaPSS in methanol-water mixed solvent media. The intrinsic viscosities of NaPSS in these mixtures will also be determined under favourable conditions. Use of a series of mixed solvents corresponds to a systematic variation in the relative permittivity of the media which would result in changed electro-repulsive forces working between ionic sites in the polymer chain and in changed interactions between the polyions and counterions surrounding the polyion chains. Thus both the expansibility of the polymer chains as well as the counterion binding could be conveniently monitored in a mixed solvent medium using viscometric technique.

## 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  $0.7772 \text{ g.cm}^{-3}$  and a co-efficient of viscosity of  $0.4742 \text{ mPa.s}$  at  $308.15 \text{ K}$ ; these values are in good agreement with the literature values.<sup>7</sup> Triply distilled water with a specific conductance less than  $10^{-6} \text{ S.cm}^{-1}$  at  $308.15 \text{ K}$  was used for the preparation of the mixed solvents. The sodium salt of polystyrenesulfonic acid (NaPSS) employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was 70,000.

The viscometric measurements were performed at  $308.15 \text{ K}$  using a Schultz-Immergut-type viscometer<sup>8</sup> with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The measurements were made in a thermostat maintained within  $\pm 0.01 \text{ K}$  of the desired temperature by means of a mercury-in-glass thermoregulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.<sup>9,10</sup> Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated; measurements with capillaries of different sizes were performed. This did not lead to different values of the reduced viscosity.

To avoid moisture pick up, all of the 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**

We have measured the variation of reduced viscosity of NaPSS with polymer concentration in pure water as well as in methanol-water mixtures containing 8, 16, and 25 mass percent of methanol at 308.15 K. In each of these cases, the effect of varying added salt concentration ( $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $1 \times 10^{-1}$ , and  $5 \times 10^{-1}$  mol.L<sup>-1</sup> NaCl) was also investigated.

### ***Variation of Reduced Viscosity with Polyelectrolyte Concentration***

Figures 1-4 show the typical dependence of the reduced viscosity with polyelectrolyte concentration for the investigated systems. In absence of an added electrolyte, the reduced viscosity is found to increase as polymer concentration decreases bending up at low concentration. No maximum was, however, detected in the  $\eta_{sp}/c_p$  vs.  $c_p$  profile within the concentration range studied here under salt-free conditions (Figures 1-4). In polymer solutions containing  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , and  $1 \times 10^{-2}$  mol.L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behaviour, in which  $\eta_{sp}/c_p$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c_p$  greatly, and the maximum is shifted towards higher polymer concentration. This is a characteristic behaviour of the viscosity of polyelectrolyte solutions. This large decrease in the reduced viscosity can be explained by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. The maximum results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum of the reduced viscosity vs. polyelectrolyte concentration profiles, the pair potential has its maximum; it decreases upon dilution because of an increase in the intermolecular distances and also decreases with increasing concentration due to the screening of electrostatic interactions. Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentration and, therefore, was close to the limit of accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations beneath the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

It was previously demonstrated<sup>11</sup> that the maximum in the viscosity curve can be described using the Hess and Klein approach.<sup>12</sup> On the basis of weak coupling approximation (WCA), they derived relaxation equations for solutions of charged hard spheres in the presence of salt. This approach gives the excess of viscosity due to electrostatic interaction which can be represented by the following equation:

$$\eta_{sp} / c_p \sim c_p / \kappa^3 \quad (2)$$

where  $c_p$ , the polyelectrolyte concentration is expressed in Eqv.L<sup>-1</sup> and  $\kappa$  is the inverse Debye screening length.

Now, since  $\kappa^2 = 4\pi l_B (c_p + c_s)$  or  $\kappa^2 = 4\pi l_B (c_p / \xi + 2c_s)$  when the charge parameter ( $\xi$ ) is  $>1$  or  $\leq 1$ , respectively, we can write

$$\begin{aligned} \eta_{sp} / c_p &\sim c_p / (c_p / \xi + 2c_s)^{3/2} \\ \text{or } c_p &/ (c_p + 2c_s)^{3/2} \end{aligned} \quad (3)$$

when  $\xi$  is  $>1$  or  $\leq 1$ , respectively.

Recently, Antonietti *et al.*<sup>13</sup> expressed the reduced viscosity for charged latex particles as:

$$\frac{\eta_{sp}}{c_p} = [\eta] \left[ 1 + k' [\eta] c_p + \left( \frac{\eta_{sp}}{c_p} \right)_{HK} \right] \quad (4)$$

in which  $(\eta_{sp} / c_p)_{HK}$  represents the electrostatic contribution expressed in Eq. (2). In salt free solutions, the concentrations of the residual ions in the solvent media were estimated to be of the order of  $\sim 2 \times 10^{-6}$  mol. L<sup>-1</sup> NaCl from the analysis of the viscosity data using Eq. (4) and which is in close agreement with that reported by Cohen and Priel.<sup>14</sup> The dashed lines in Figures 1- 4 display the fits of the experimental data using Eq. (4) and the agreement between them is excellent. A quantitative fit according to Eq. (4) can describe this behaviour, as seen by the lines along the data points in Figures 1-4. Due to the large number of parameters, however, it is impossible for the present data set to extract quantitative information, since each parameter value is rather unstable. The instability of the parameters was also observed by Antonietti *et al.*<sup>13</sup> It is thus not possible to determine the intrinsic viscosities of polyelectrolytes in solutions using Eq. (4).

### ***Influence of Large Amount of Added Salt: Determination of Intrinsic Viscosity***

When the added salt concentration is sufficiently high (0.10 and 0.50 mol.L<sup>-1</sup> NaCl), the polyelectrolyte effect was suppressed and a linear variation of  $\eta_{sp}/c_p$  vs.  $c_p$  similar to that of neutral polymer solutions is observed. This is due to the screening of electrostatic interactions within and among the polyion chains. We were thus able to determine the intrinsic viscosity of NaPSS in methanol-water mixed solvent media using the Huggins equation, Eq. (1).

From the present experimental  $\eta_{sp}/c$  vs.  $c_p$  data, the intrinsic viscosities and the Huggins constants were determined by the method of least squares using Eq. (1) and the results are given in Table 1.

### ***Influence of Medium on the Intrinsic Viscosity and the Huggins Constant***

It can be seen from Table 1 that the intrinsic viscosities of NaPSS decrease as the solvent medium becomes richer in methanol whereas a reverse trend is observed with the Huggins constants. This observation demonstrates that the solvent interacts with the polymer gradually poorly (*i.e.*, with less thermodynamic affinity) as the medium gets richer in methanol and hence the polymer-polymer contacts are becoming more probable than the polymer-solvent contacts and, therefore, the solvodynamic dimension of the chain will be gradually reduced. This explains both the lower intrinsic viscosity and the higher values of the Huggins constants in a solvent medium richer in methanol. This is consistent with the general view that high  $k_H$  values are the characteristics of the poor solvents.<sup>15</sup>

### ***Influence of Salt Concentration on the Intrinsic Viscosity***

The intrinsic viscosity value of NaPSS in a given solvent medium decreases as the concentration of NaCl is increased from 0.10 to 0.50 mol.L<sup>-1</sup> (*cf.* Table 1). A similar decrease in the intrinsic viscosity of a cationic polyelectrolyte with increasing concentration of an added electrolyte was also noticed earlier.<sup>16</sup> The present observation indicates an increase in the compactness of the polyion structure with increasing salt concentration.

## Conclusions

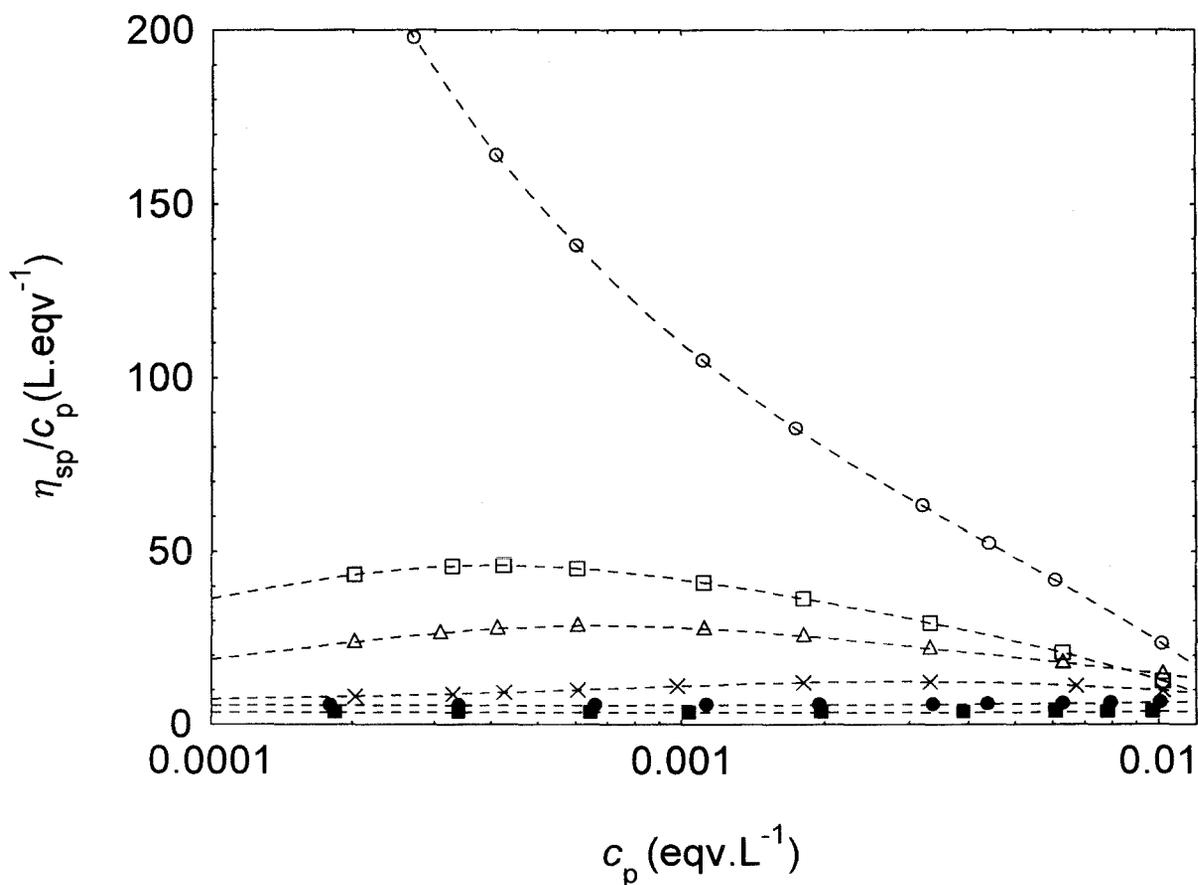
The present chapter reported precise measurements on the viscosities of the solutions of NaPSS in water and in three methanol-water mixtures containing 8, 16, and 25 mass% of methanol at 308.15 K in presence of varying concentration of added sodium chloride. The viscosity of the present system reveals the characteristic behaviour of polyelectrolyte solutions. In absence of added salt, the reduced viscosity is found to increase as polymer concentration decreases bending up at low concentration. No maximum was, however, observed in the  $\eta_{sp}/c_p$  vs.  $c_p$  profile within the concentration range studied here under salt-free conditions. In polymer solutions containing  $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ , and  $1 \times 10^{-3}$  mol.L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behaviour, in which  $\eta_{sp}/c_p$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c_p$  greatly, and the maximum is shifted towards higher polymer concentration. This large decrease in the reduced viscosity can be explained by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. When the added salt concentration is sufficiently high (0.10 and 0.50 mol.L<sup>-1</sup> NaCl), regular neutral polymer behaviour is recovered thus enabling us to determine the intrinsic viscosity of NaPSS in methanol-water mixed solvent media using the Huggins equation. The results have been discussed in terms of the variation in the coiling of the polyion chain and counterion condensation.

## References

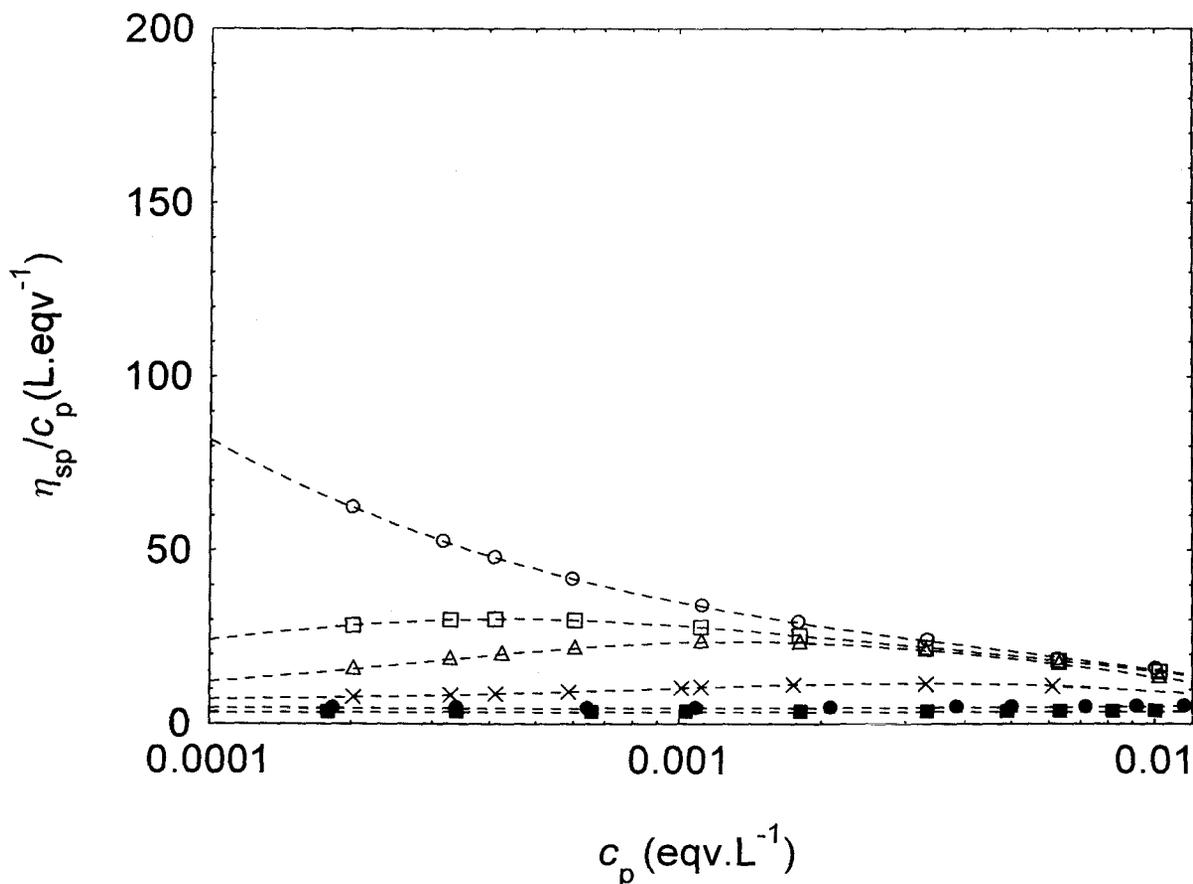
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**Table 1.** Intrinsic viscosities ( $[\eta]$ ) and Huggins constants ( $k_H$ ) of NaPSS in methanol-water mixtures containing 0, 8, 16 and 25 mass% of methanol in presence of NaCl at 308.15 K

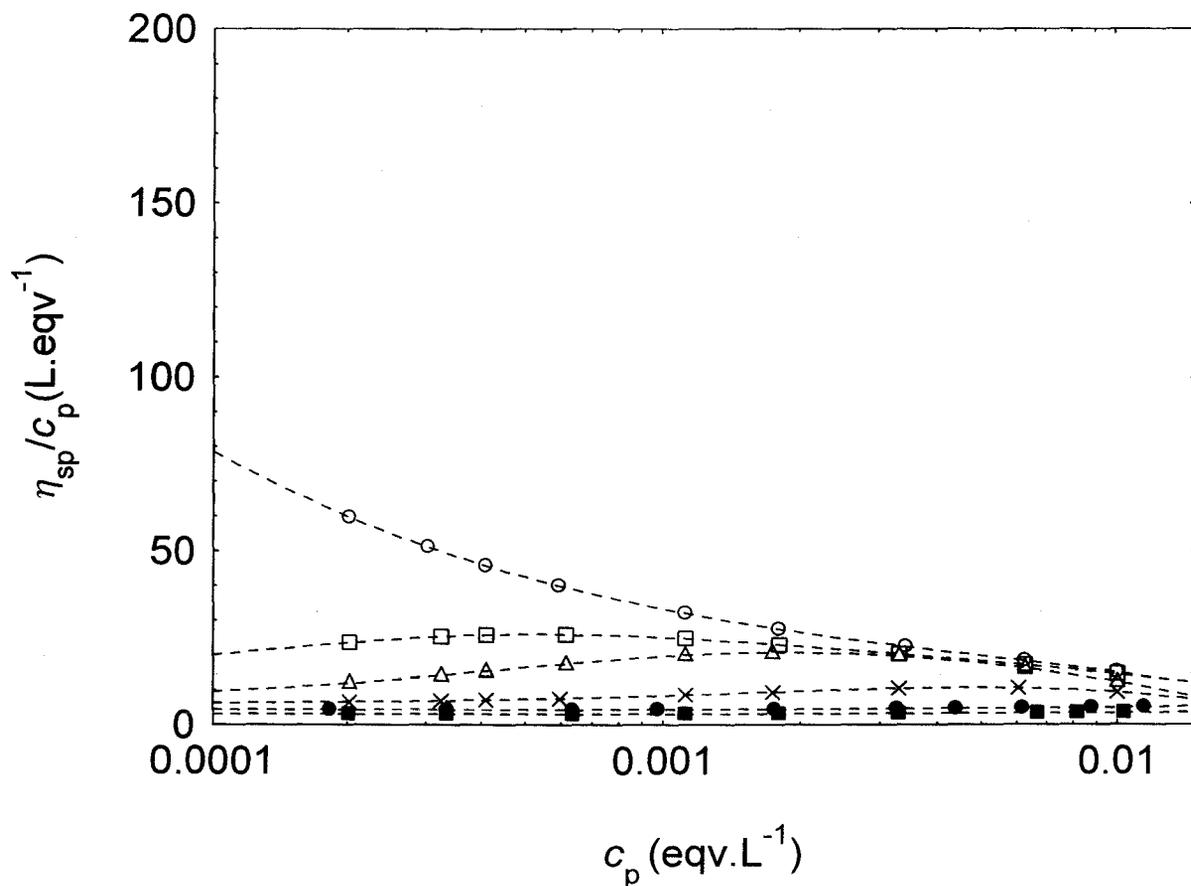
Solvent	[NaCl] / mol.L <sup>-1</sup>	$[\eta]$ / L.eqv <sup>-1</sup>	$k_H$
0% Methanol	0.10	5.51	2.76
	0.50	3.45	1.93
8% Methanol	0.10	4.50	2.82
	0.50	3.32	2.49
16% Methanol	0.10	4.41	3.15
	0.50	3.12	3.03
25% Methanol	0.10	4.18	3.33
	0.50	3.07	3.10



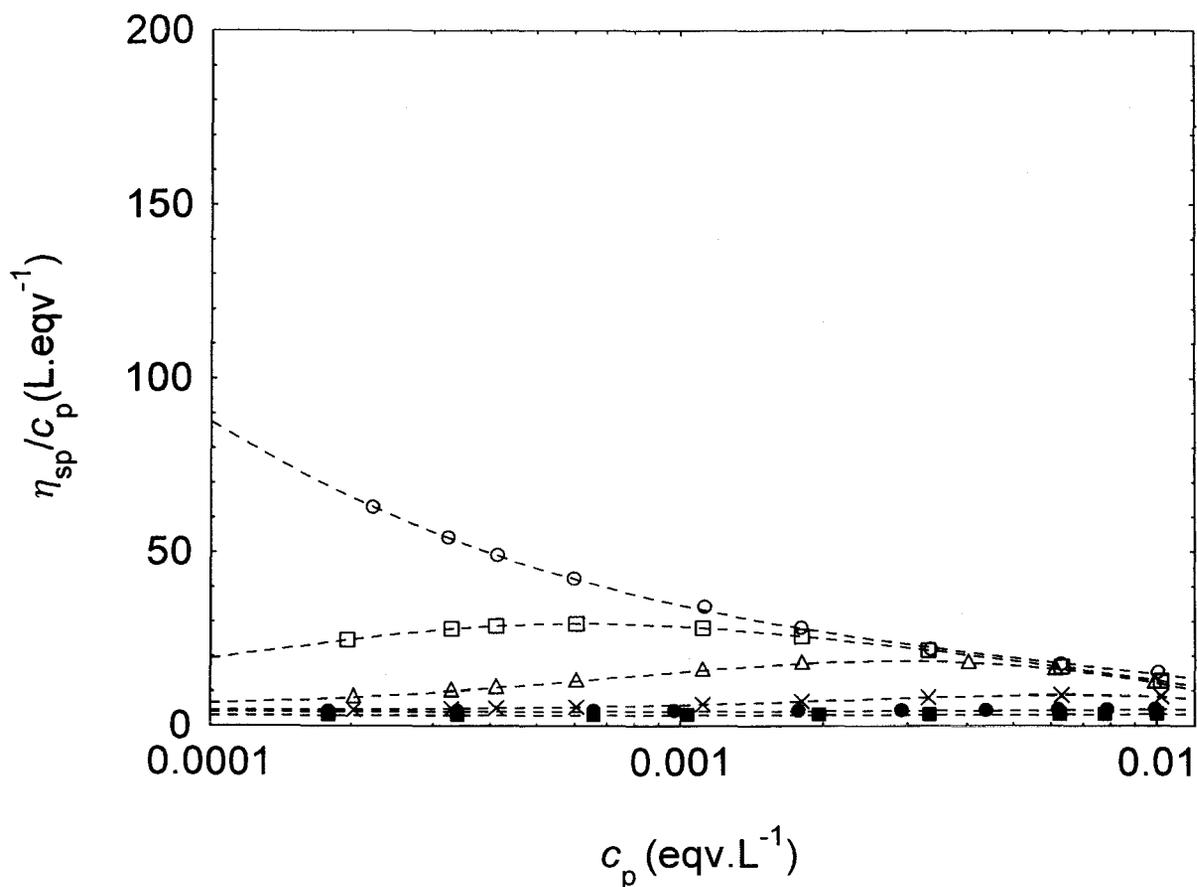
**Figure 1.** The variation of the reduced viscosity for NaPSS with the polyelectrolyte concentration in water (○), in presence of  $1 \times 10^{-4}$  mol.L<sup>-1</sup> NaCl (□), in presence of  $1 \times 10^{-3}$  mol.L<sup>-1</sup> NaCl (Δ), in presence of  $1 \times 10^{-2}$  mol.L<sup>-1</sup> NaCl (x), in presence of  $1 \times 10^{-1}$  mol.L<sup>-1</sup> NaCl (●) and in presence of  $5 \times 10^{-1}$  mol.L<sup>-1</sup> NaCl (■). The dashed lines represent the fits according to Eq. (3).



**Figure 2.** The variation of the reduced viscosity for NaPSS with the polyelectrolyte concentration in 8 mass% methanol ( $\circ$ ), in presence of  $1 \times 10^{-4} \text{ mol} \cdot L^{-1}$  NaCl ( $\square$ ), in presence of  $1 \times 10^{-3} \text{ mol} \cdot L^{-1}$  NaCl ( $\Delta$ ), in presence of  $1 \times 10^{-2} \text{ mol} \cdot L^{-1}$  NaCl ( $\times$ ), in presence of  $1 \times 10^{-1} \text{ mol} \cdot L^{-1}$  NaCl ( $\bullet$ ) and in presence of  $5 \times 10^{-1} \text{ mol} \cdot L^{-1}$  NaCl ( $\blacksquare$ ). The dashed lines represent the fits according to Eq. (3).



**Figure 3.** The variation of the reduced viscosity for NaPSS with the polyelectrolyte concentration in 16 mass% methanol ( $\circ$ ), in presence of  $1 \times 10^{-4} \text{ mol.L}^{-1}$  NaCl ( $\square$ ), in presence of  $1 \times 10^{-3} \text{ mol.L}^{-1}$  NaCl ( $\Delta$ ), in presence of  $1 \times 10^{-2} \text{ mol.L}^{-1}$  NaCl ( $\times$ ), in presence of  $1 \times 10^{-1} \text{ mol.L}^{-1}$  NaCl ( $\bullet$ ) and in presence of  $5 \times 10^{-1} \text{ mol.L}^{-1}$  NaCl ( $\blacksquare$ ). The dashed lines represent the fits according to Eq. (3).



**Figure 4.** The variation of the reduced viscosity for NaPSS with the polyelectrolyte concentration in 25 mass% methanol ( $\circ$ ), in presence of  $1 \times 10^{-4} \text{ mol.L}^{-1}$  NaCl ( $\square$ ), in presence of  $1 \times 10^{-3} \text{ mol.L}^{-1}$  NaCl ( $\Delta$ ), in presence of  $1 \times 10^{-2} \text{ mol.L}^{-1}$  NaCl ( $\times$ ), in presence of  $1 \times 10^{-1} \text{ mol.L}^{-1}$  NaCl ( $\bullet$ ) and in presence of  $5 \times 10^{-1} \text{ mol.L}^{-1}$  NaCl ( $\blacksquare$ ). The dashed lines represent the fits according to Eq. (3).