

## Viscosity of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media in Presence of NaCl

### Introduction

One of the most salient features of polyelectrolytes is the intense increment in viscosity that they produce when, even in minute amounts; they are dissolved in ordinary solvents in absence or in presence of a very small amount of an electrolyte, as described in the previous chapter. Early investigations of the anomalous viscosity of polyelectrolyte solutions without added appeared to suggest that the reduced viscosity would increase without limit as one lowers the polyelectrolyte concentration. In fact, the reduced viscosity versus concentration profile of a polyelectrolyte solution generally passes through a maximum whose position and height depend on the concentration of the added electrolyte. It is thus virtually impossible to obtain the intrinsic viscosity of a polyelectrolyte in salt-free solutions or in solutions containing a very small amount of an external salt by the method of extrapolation the Huggins equation<sup>1,2</sup>

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

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

In the previous chapter, we have used the method of isoionic dilution for the determination of the intrinsic viscosities of NaPSS in acetonitrile-water mixtures. Moreover, since the ionic environment around the polyions remains unaffected as a result of isoionic dilution, the original conformation of the polyion under salt-free situation is assumed to be preserved.

On the other hand, in presence excess of low-molar-mass electrolyte, at a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity ( $\eta_{sp} / c$ ) varies linearly with the polymer concentration ( $c$ ) similar to that for a neutral polymer solution, thus enabling one to determine the intrinsic viscosity using the well-known Huggins equation.<sup>1,2</sup>

This chapter describes the viscometric behaviour of NaPSS in absence and also in presence of an electrolyte (NaCl) in acetonitrile-water mixed solvent media. Our point of view is to focus on the role of electrostatic interactions on the viscosity of NaPSS in acetonitrile-water mixed solvent media. The intrinsic viscosities of NaPSS in these mixtures have also been determined.

## Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 g.cm<sup>-3</sup> and a coefficient of viscosity of 0.3126 mPa.s at 308.15 K; these values are in good agreement with the literature values.<sup>3</sup> Triply distilled water with a specific conductance less than 10<sup>-6</sup> S.cm<sup>-1</sup> at 308.15 K was used for the preparation of the mixed solvents.

NaPSS employed in these investigations was purchased from Aldrich Chemical Company, Inc. The average molecular weight ( $M_w$ ) of the sample was 70,000 with a degree of substitution (DS) of 1, and these values agree well with those obtained from physiochemical characterization in the present study.

The viscometric measurements were performed at 308.15, using a Schultz-Immergut-type viscometer<sup>4</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  $\pm 0.005$  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>5,6</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 acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 308.15 K. In each of these cases the effect of varying added salt concentration ( $1 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1 \times 10^{-2}$ ,  $5 \times 10^{-2}$ , and  $5 \times 10^{-1}$  mol L<sup>-1</sup> NaCl) was also investigated.

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

The typical dependence of the reduced viscosity with polyelectrolyte concentration for the investigated systems are shown in Figures 1-3. In absence of an added electrolyte, the reduced viscosity is found to increase as polymer concentration decreases bending up at low polyelectrolyte concentration. From Figures 1-3 no maximum was, however, detected in the  $\eta_{sp}/c$  vs.  $c$  profile within the concentration range studied here in salt-free solutions as well as in solutions containing  $1 \times 10^{-4}$  mol L<sup>-1</sup> NaCl. In polymer solutions containing  $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  mol L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behavior, in which  $\eta_{sp}/c$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c$  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.

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

Figures 1-3 show the variation of  $\eta_{sp}/c$  as a function of  $c$  for five different salt concentration in each solvent composition at given experimental temperature. When the added salt concentration is sufficiently high (0.05 to 0.50 mol L<sup>-1</sup>), the polyelectrolyte effect was suppressed and a linear variation 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 acetonitrile-water mixed solvent media using the Huggins equation, Eq. (1).

From the present experimental  $\eta_{sp}/c$  vs.  $c$  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 along with their standard errors and the correlation coefficients of fits (as  $r^2$ ).

The intrinsic viscosities of NaPSS in acetonitrile-water mixtures in presence of 0.5 mol L<sup>-1</sup> NaCl are always found to be significantly lower than the corresponding values obtained by the method of isoionic dilution maintaining total ionic strength at a very low level *e.g.*,  $6.50 \times 10^{-3}$  and  $1.25 \times 10^{-2}$  mol L<sup>-1</sup> (*cf.* Chapter VII). This indicates significant coiling of the polyion chains due to the relief of intrachain electrostatic repulsion (and hence decreasing  $k_H$ ) in presence of an excess of an added electrolyte. Moreover, the in each of the three solvent mixtures investigated, the intrinsic viscosity value obtained with a salt concentration of 0.50 mol L<sup>-1</sup> is always found to be lower than that obtained with a salt concentration of 0.05 mol L<sup>-1</sup> indicating a more compact polyion structure in presence of higher amount of salt.

### ***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 acetonitrile 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 acetonitrile 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 richer in acetonitrile. This is consistent with the general view that high  $k_H$  values are the characteristics of the poor solvents.<sup>7</sup>

## Conclusions

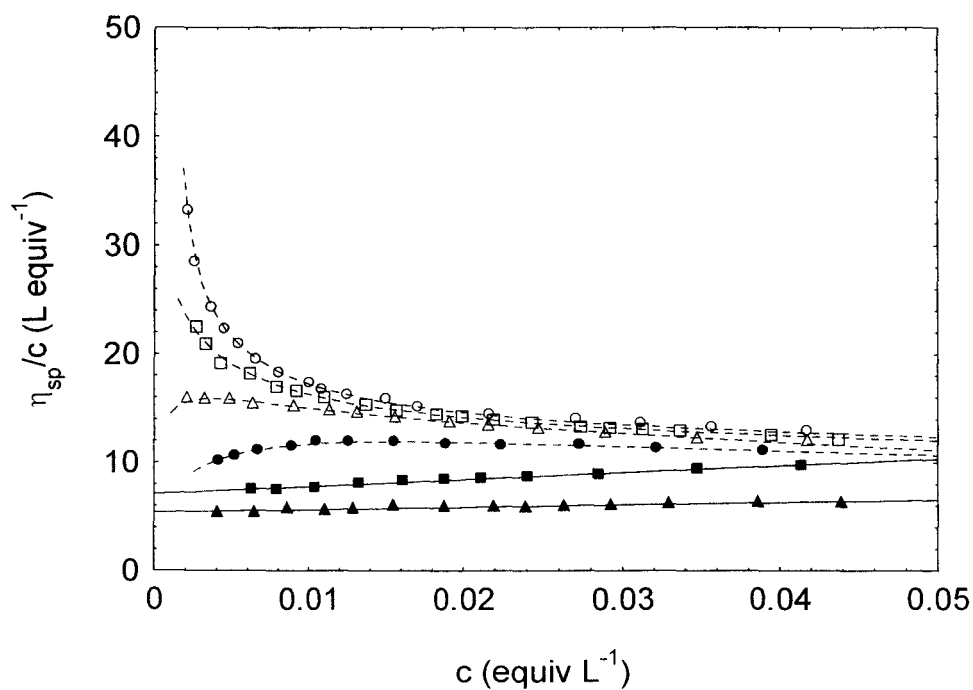
The present chapter reported precise measurements on the viscosities of the solutions of NaPSS in three acetonitrile-water mixtures containing 10, 20, and 40 volume percent of acetonitrile at 308.15 K in presence of varying concentration of added sodium chloride. The viscosity of the present system reveals 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, detected in the  $\eta_{sp}/c$  vs.  $c$  profile within the concentration range studied here under salt-free conditions as well as in solutions containing  $1 \times 10^{-4}$  mol L<sup>-1</sup> NaCl. In polymer solutions containing  $1 \times 10^{-3}$  and  $1 \times 10^{-2}$  mol L<sup>-1</sup> NaCl, on the other hand, the familiar polyelectrolyte behaviour, in which  $\eta_{sp}/c$  goes through a maximum, is observed. Increasing the ionic strength decreases the absolute value of  $\eta_{sp}/c$  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 (0.5 mol L<sup>-1</sup>), regular neutral polymer behaviour is recovered thus enabling us to determine the intrinsic viscosity of NaPSS in acetonitrile-water mixed solvent media using the Huggins equation. The variations of the intrinsic viscosity and the Huggins constant with temperature and solvent medium have been used to interpret the variation in the coiling of the polyion chain and counterion condensation.

## References

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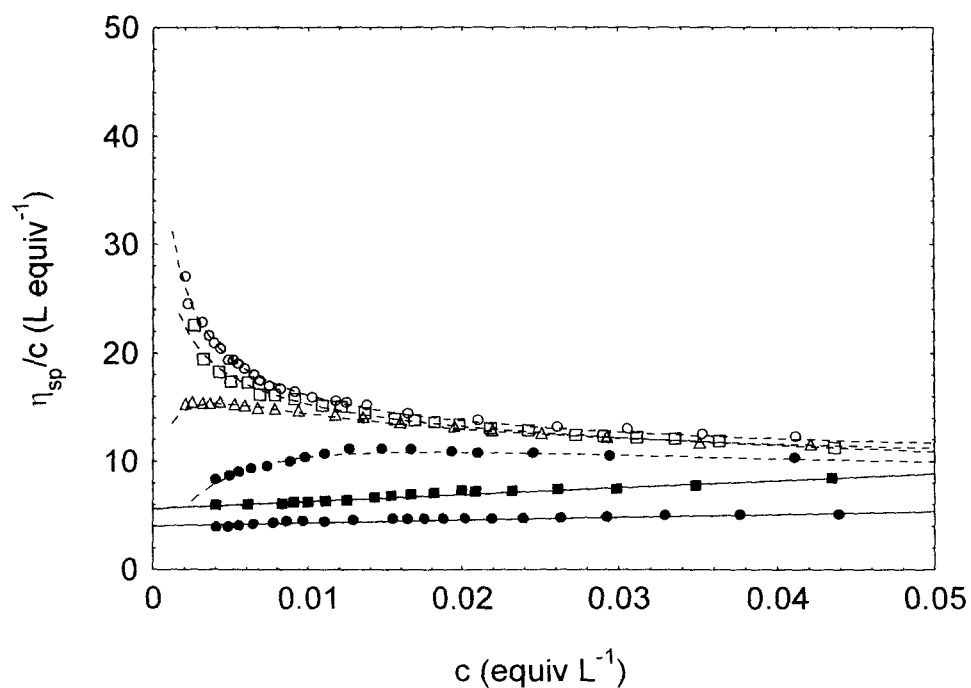
**Table 1.** Intrinsic Viscosities  $[\eta]$  (L.equiv<sup>-1</sup>), Huggins Constants  $k_H$ , and the Correlation Coefficients of Fits (as  $r^2$ ) of NaPSS in 10, 20, and 40 Volume Percent Acetonitrile-Water Mixtures in Presence of 0.05 M and 0.50 mol L<sup>-1</sup> NaCl at 308.15 K

Conc of NaCl (mol L <sup>-1</sup> )		10 Vol Percent Acetonitrile	20 Vol Percent Acetonitrile	40 Vol Percent Acetonitrile
0.05	$[\eta]$ (L.equiv <sup>-1</sup> )	7.12 ± 0.07	5.64 ± 0.07	4.06 ± 0.07
	$k_H$	1.27 ± 0.06	2.03 ± 0.11	3.46 ± 0.17
	$r^2$	0.981	0.956	0.973
0.50	$[\eta]$ (L.equiv <sup>-1</sup> )	5.40 ± 0.07	4.06 ± 0.07	2.97 ± 0.05
	$k_H$	0.78 ± 0.10	1.57 ± 0.14	2.87 ± 0.21
	$r^2$	0.838	0.864	0.943

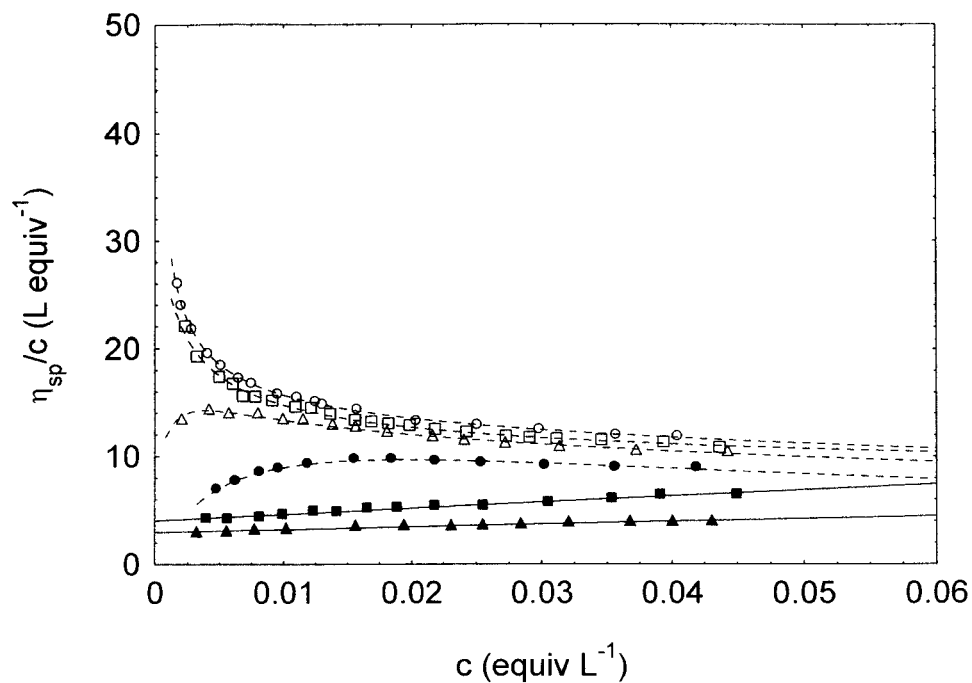


**Figure 1.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 10 volume percent acetonitrile at 308.15 K in presence of (○) 0 mol L<sup>-1</sup> NaCl, (□) 10<sup>-4</sup> mol L<sup>-1</sup> NaCl, (Δ) 10<sup>-3</sup> mol L<sup>-1</sup> NaCl, (●) 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, (■) 5 x 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, and (▲) 5 x 10<sup>-1</sup> mol L<sup>-1</sup> NaCl.





**Figure 2.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 20 volume percent acetonitrile at 308.15 K in presence of (○) 0 mol L<sup>-1</sup> NaCl, (□) 10<sup>-4</sup> mol L<sup>-1</sup> NaCl, (Δ) 10<sup>-3</sup> mol L<sup>-1</sup> NaCl, (●) 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, (■) 5 x 10<sup>-2</sup> mol L<sup>-1</sup> NaCl, and (▲) 5 x 10<sup>-1</sup> mol L<sup>-1</sup> NaCl.



**Figure 3.** Variation of reduced viscosity of NaPSS with concentration in acetonitrile-water mixture containing 40 volume percent acetonitrile at 308.15 K in presence of (○)  $0 \text{ mol L}^{-1}$  NaCl, (□)  $10^{-4} \text{ mol L}^{-1}$  NaCl, (△)  $10^{-3} \text{ mol L}^{-1}$  NaCl, (●)  $10^{-2} \text{ mol L}^{-1}$  NaCl, (■)  $5 \times 10^{-2} \text{ mol L}^{-1}$  NaCl, and (▲)  $5 \times 10^{-1} \text{ mol L}^{-1}$  NaCl.