

## Chapter VII

# Effect of Different Low-Molar Mass Electrolytes on the Viscometric Behaviour of Sodium Polystyrenesulfonate in Methanol-Water Mixed Solvent Media

### Introduction

The previous chapter (chapter VI) describes the viscometric behaviour of NaPSS in absence and also in presence of an electrolyte (NaCl) in methanol-water mixed solvent media. We investigated the role of electrostatic interactions on the viscosity of NaPSS in methanol-water mixed solvent media. The intrinsic viscosities of NaPSS in these mixtures have also been determined under favourable conditions. The characteristic viscosity behaviour of the polyelectrolyte solutions, namely the appearance of a peak in the reduced viscosity versus polyelectrolyte concentration profiles, and a large decrease in the reduced viscosity with the addition of the salt have been explained on the basis of the intrachain and interchain electrostatic interactions and intermolecular distances. The addition of a low-molar mass electrolyte (NaCl) to the polyelectrolyte solution resulted in shielding of the ionic sites with a reduction of the coil dimensions and drastically lowers the value of the reduced viscosity. Finally a situation was reached when there was an excess of NaCl ( $[NaCl] \geq 0.10 \text{ mol.L}^{-1}$ ), the reduced viscosity varies linearly with the polymer concentration similar to that for a neutral macromolecular solution, thus enabling us to determine the intrinsic viscosity using the well-known Huggins equation<sup>1,2</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.

A number of studies dealing with the effect of different low-molar mass electrolytes on the viscosity behaviour of polyelectrolytes have been reported in aqueous solutions.<sup>3-10</sup> However, systematic investigations of the effect of medium on the viscosity of polyelectrolytes are relatively scarce.<sup>11-16</sup> The present chapter describes a comprehensive study on the influence of different salts with varying cations and anions on the intrinsic

viscosities of NaPSS in methanol-water mixtures. The viscosity data have been analyzed to obtain information as to the polyion chain conformation and binding of counterions and coions on the chain.

## 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>17</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 physical properties of methanol-water mixtures are available in Table 1 of chapter III.

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>18</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>19,20</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

A representative plot (Figure 1) shows the variation of the reduced viscosity of NaPSS as a function of polymer concentration in water and in three methanol-water mixtures containing 8, 16 and 25 mass% of methanol in presence of  $0.10$  and  $0.50 \text{ mol.L}^{-1}$  of KBr. The profiles are found to be linear with positive  $k_H$  values indicating complete screening of the charged sites on the polyion chain. Similar behaviour was also observed in presence of  $0.10$  and  $0.50 \text{ mol.L}^{-1}$  of NaCl, NaBr and KCl. The intrinsic viscosity and the Huggins constant

values obtained by the method of least squares fitting of the experimental reduced viscosity values to Eq. (1) are listed in Table 1.

From Table 1, it is apparent that the intrinsic viscosities and the Huggins constants for the present polyelectrolyte system vary with the medium, the kind and the concentration of the added low-molar mass electrolyte. This observation, thus, indicates that the polyelectrolyte NaPSS differs quite appreciably in its solvodynamic behaviour under varying conditions<sup>21,22</sup> investigated here.

### ***Influence of Anions with a Common Cation and of Cations with a Common Anion on the Intrinsic Viscosity of NaPSS***

From Table 1, it can be seen that the intrinsic viscosities of NaPSS in aqueous and aquo-methanolic salt solutions (both in presence of 0.10 and 0.50 mol.L<sup>-1</sup> of salts) decrease in the order Cl<sup>-</sup> > Br<sup>-</sup> for the pairs NaCl and NaBr, and KCl and KBr. Moreover, the intrinsic viscosities of NaPSS are also found to decrease in the order Na<sup>+</sup> > K<sup>+</sup> for the pairs NaCl and KCl, and NaBr and KBr. A similar behaviour was also observed earlier for some other aqueous polyelectrolyte solutions in presence of excess of alkali halides.<sup>4,8</sup>

The results could be interpreted on the basis of the Pearson soft and hard acid and base (SHAB) principle, which states that hard acid species prefer to bind hard base species while soft acid species prefer to bind soft base species.<sup>23</sup>

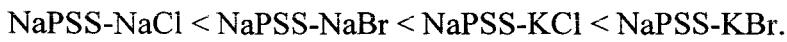
Both Na<sup>+</sup> and K<sup>+</sup> ions are hard bases although their hardness decreases in the order: Na<sup>+</sup> > K<sup>+</sup>, since K<sup>+</sup> ions possess lower surface charge density and are easily polarisable compared to the Na<sup>+</sup> ions. Again among Cl<sup>-</sup> and Br<sup>-</sup> ions, the former is harder acid compared to the latter since Br<sup>-</sup> ions with lower surface charge density are more polarisable than the Cl<sup>-</sup> ions.

Following the SHAB principle, the harder-acid species, e.g., Cl<sup>-</sup> ions, are easily bound to small hard bases such as the Na<sup>+</sup> ions. Hence the Na<sup>+</sup> ions are more easily attracted by the Cl<sup>-</sup> ions than do the K<sup>+</sup> ions. This would reduce the site binding degree of the Na<sup>+</sup> ions (compared to the K<sup>+</sup> ions) onto the negatively charged polyion. The negative charge on the polyion would, therefore, be less effectively neutralized in presence of NaCl than in presence of KCl, thus resulting in a less coiled structure of the polyion chain and hence a higher intrinsic viscosity value in presence of NaCl. Similarly, the higher intrinsic viscosity of NaPSS in presence of NaBr than that in presence of KBr could be ascribed to the preference

of the  $\text{Br}^-$  ions to bind  $\text{Na}^+$  ions thus resulting in a reduced degree of site binding of the  $\text{Na}^+$  ions on to the polystyrenesulfonate chain.

As pointed out earlier, the  $\text{Na}^+$  ions are more easily attracted by the  $\text{Cl}^-$  ions since both are hard species. The  $\text{Br}^-$  ions, on the other hand, are softer than the  $\text{Cl}^-$  ions and hence would experience less attraction by the  $\text{Na}^+$  ions. Thus, the availability of the  $\text{Na}^+$  ions for binding onto the polyion chain increases from NaPSS-NaCl system to NaPSS-NaBr system. This produces a more coiled structure of the polyion and hence a lower intrinsic viscosity of the polyelectrolyte in presence of NaBr than in presence of NaCl. The lower intrinsic viscosity of NaPSS in presence of KBr than in presence of KCl could similarly be interpreted by the greater degree of binding of the  $\text{K}^+$  ions on to the negatively charged polyion chain in the former system due to the weaker binding of the  $\text{Br}^-$  ions by the  $\text{K}^+$  ions.

An inspection of the intrinsic viscosity values reported in Table 1 reveals that the coiling of the polyion chains increases in the order:



This indicates that the preference for the binding of the acid-base pairs decreases in the order:



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

For a given concentration (0.10 or 0.50 mol. $\text{L}^{-1}$ ) of any of the four electrolytes investigated, the intrinsic viscosities of NaPSS are found to decrease as the solvent medium becomes richer in methanol (Table 1 and Figures 2 and 4). This could be ascribed to the decreasing relative permittivity of the medium with increasing methanol content in the mixed solvent medium which results in a stronger electrostatic interaction between the polyion and the cations present in solution. More and more number of cations would, thus, be associated with the polyion chain and this would reduce the effective charge on the polyion chain leading to a reduction of the solvodynamic dimension of the coil as the amount of methanol in the mixed solvent media increases. This observation also indicates that the solvent interacts with the polymer gradually poorly (*i.e.*, with less thermodynamic affinity) as the medium gets richer in methanol and hence polymer-polymer contacts are becoming more probable than the polymer-solvent contacts, and therefore the solvodynamic dimension of the chain will be gradually reduced. Furthermore, the Huggins constants are found to increase with increasing methanol in the methanol-water mixtures (Table 1 and Figures 3 and 5). This is consistent

with the general view that high  $k_H$  values are the characteristics of poor solvents<sup>24</sup> and with what inferred from the variation of the intrinsic viscosity values with the solvent composition.

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

The intrinsic viscosity value of NaPSS in a given solvent medium decreases as the concentration of the added electrolyte 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>4</sup> The present observation indicates that the polyion structures become more compact with increasing salt concentration due to occupation of a major proportion of the solution volume by the excess salt ions thus causing a contraction of the polyion solvodynamic dimension in the later case.

### **Conclusions**

An investigation on the viscosities of NaPSS in water as well as in methanol-water mixed media have been performed in presence of four low molar-mass electrolytes namely NaCl, KCl, NaBr and KBr having concentrations of 0.10 and 0.50 mol.L<sup>-1</sup>. The reduced viscosities of the polyelectrolyte solutions are found to vary linearly with polymer concentration for all the systems investigated which enabled us to determine the intrinsic viscosities of sodium polystyrenesulfonate in methanol-water mixtures following the Huggins equation. An inspection of the intrinsic viscosity values reveals that the coiling of the polyion chains increases in the order: NaPSS-NaCl < NaPSS-NaBr < NaPSS-KCl < NaPSS-KBr. The solvodynamic dimensions of the polyion coil are found to be reduced as the relative permittivity of the medium decreases with the increasing amount of methanol in the mixed solvent media. The present study also indicates that the polyion structures become more compact with increasing salt concentration in the medium.

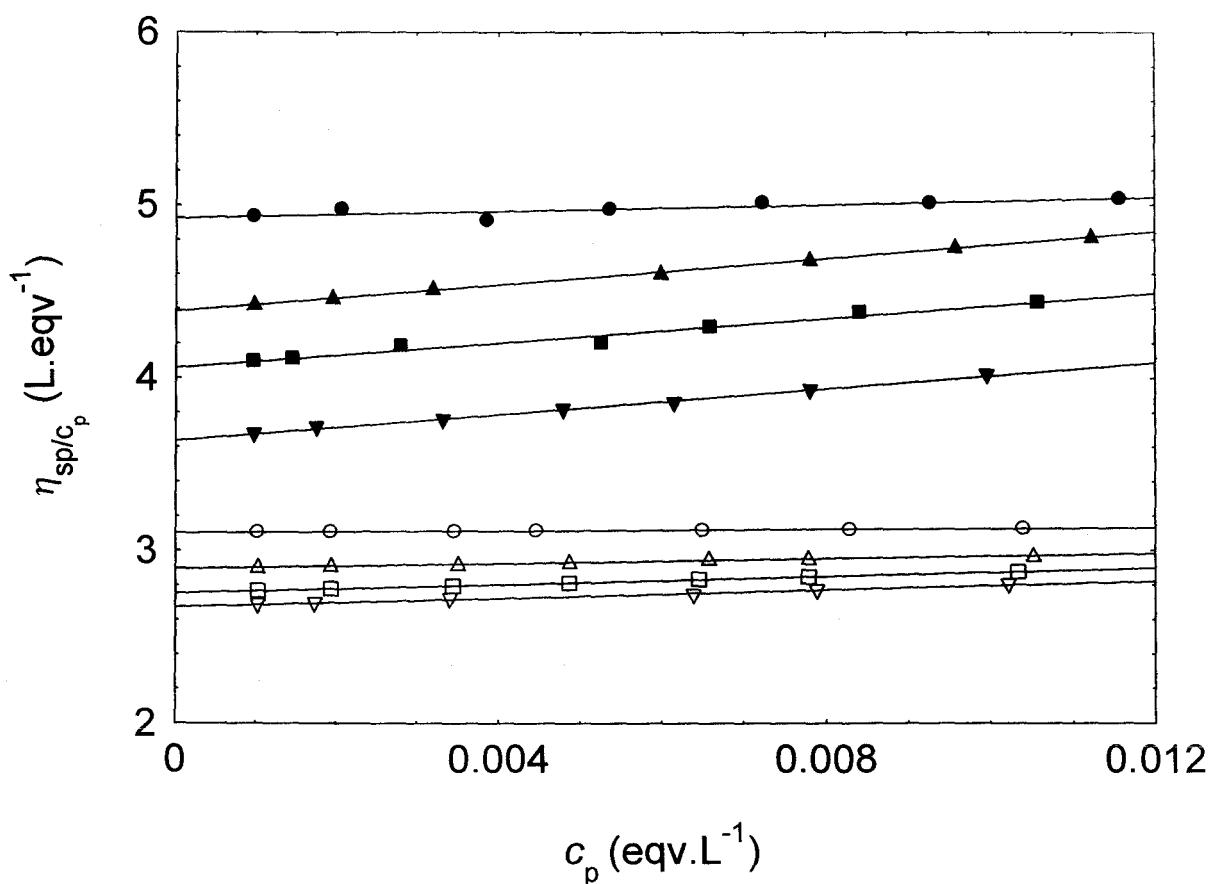
## References

1. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel, and D. Stscherbina, in *Polyelectrolytes: Formation, Characterization and Application*, Hanser Publishers: Munich, Ch. 5 (1994).
2. H. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938).
3. J. Cohen and Z. Priel, *Macromolecules*, **22**, 2356 (1989).
4. W. -F. Lee and G. -Y. Huang, *J. Appl. Polym. Sci.*, **60**, 187 (1996).
5. W. -F. Lee and G. -Y. Huang, *Polymer*, **37**, 4389 (1996).
6. W. -F. Lee and C. -H. Lee, *Polymer*, **38**, 971 (1997).
7. L. Ghimici, S. Dragan and F. Popescu, *J. Polym. Sci., Polym. Phys. Edn.*, **35**, 2571 (1997).
8. W. -F. Lee and Y. -M. Chen, *J. Appl. Polym. Sci.*, **80**, 1619 (2001).
9. L. Ghimici and S. Dragan, *Coll. Polym. Sci.*, **280**, 130 (2002).
10. X. H. Yang and W. L. Zhu, *Cellulose*, **14**, 409 (2007).
11. V. O. Aseyev, S. I. Klenin and H. Tenhu, *J. Polym. Sci. Part B: Polym Phys.*, **36**, 1107 (1998).
12. S. Dragan and L. Ghimici, *Polymer*, **42**, 2887 (2001).
13. T. Kamiyama, M. Morita and T. Kimura, *J. Chem. Eng. Data*, **49**, 1350 (2004).
14. P. Nandi, A. Bhattacharai, and B. Das, *J. Polym. Sci., Polym. Phys. Ed.*, **45**, 1765 (2007).
15. L. Ghimici, M. Nichifor and B. Wolf, *J. Phys. Chem. B*, **113**, 8020 (2009).
16. R. Sharma, B. Das, P. Nandi and C. Das, *J. Polym. Sci., Polym. Phys. Ed.*, **48**, 1196 (2010).
17. H. Doe, T. Kitagawa, and K. Sasabe, *J. Phys. Chem.*, **88**, 3341 (1984).
18. J. Schulz and E. H. Immergut, *J. Polym. Sci.*, **9**, 279 (1952).
19. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).
20. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).
21. T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942).
22. T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.*, **65**, 2319 (1943).
23. J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York (1972).
24. A. Tager, *Physical Chemistry of Polymers*, Mir Publishers, Moscow, Ch. 15 (1978).

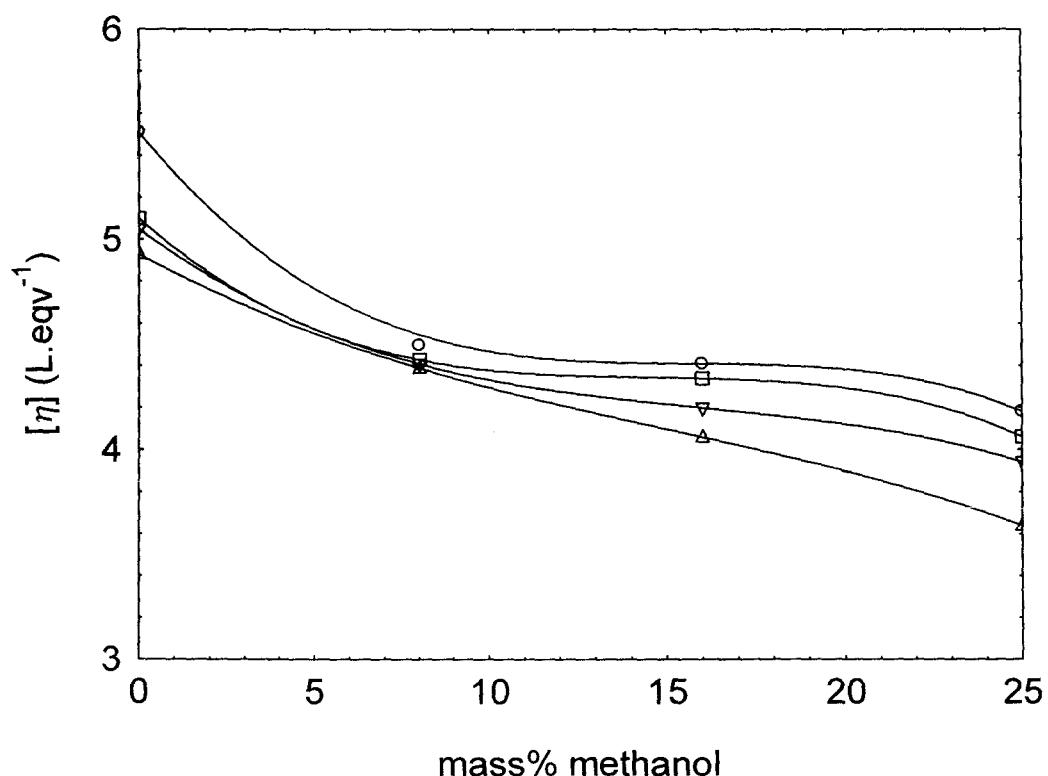
**Table 1.** Intrinsic viscosities ( $[\eta]$ ) and Huggins constants ( $k_H$ ) of NaPSS in methanol-water mixtures containing 0, 8, 16 and 25 mass% of methanol in presence of NaCl, NaBr, KCl and KBr at 308.15 K

Solvent	[salt] / mol.L <sup>-1</sup>	$[\eta]$ / L.eqv <sup>-1</sup>	$k_H$
In presence of NaCl			
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
In presence of KCl			
0% Methanol	0.10	5.10	0.63
	0.50	3.24	0.59
8% Methanol	0.10	4.43	2.48
	0.50	3.10	2.04
16% Methanol	0.10	4.34	2.79
	0.50	2.88	2.52
25% Methanol	0.10	4.06	3.23
	0.50	2.83	2.63
In presence of NaBr			
0% Methanol	0.10	5.05	0.57
	0.50	3.12	0.48
8% Methanol	0.10	4.41	2.03
	0.50	2.97	1.04
16% Methanol	0.10	4.20	2.36
	0.50	2.84	1.71
25% Methanol	0.10	3.94	2.92
	0.50	2.70	1.74

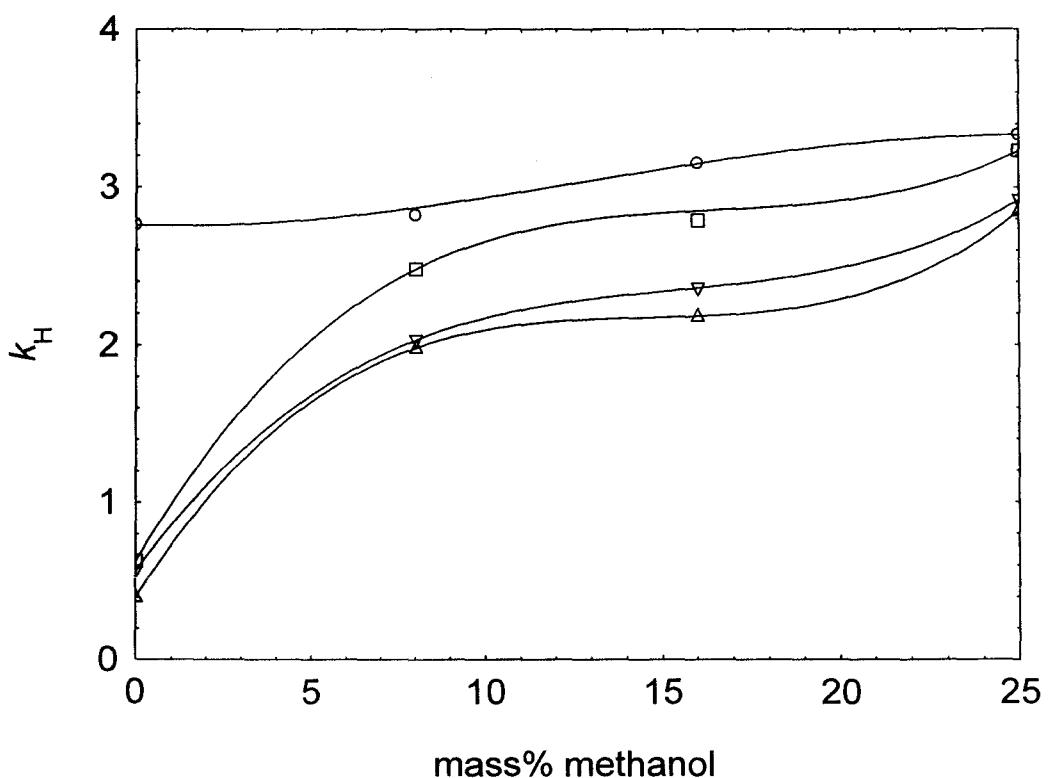
In presence of KBr			
<b>0% Methanol</b>	0.10	4.93	0.40
	0.50	3.10	0.25
<b>8% Methanol</b>	0.10	4.39	1.98
	0.50	2.90	0.86
<b>16% Methanol</b>	0.10	4.06	2.18
	0.50	2.75	1.57
<b>25% Methanol</b>	0.10	3.64	2.85
	0.50	2.67	1.72



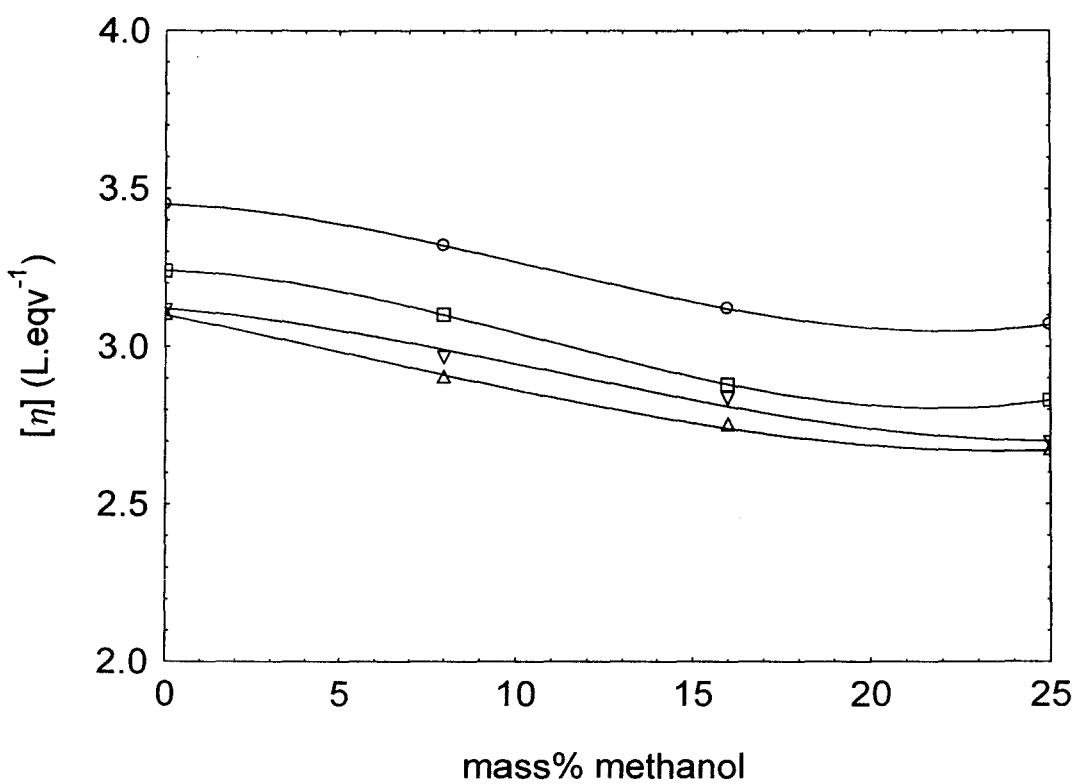
**Figure 1.** Variation of reduced viscosity of NaPSS in methanol-water mixed solvent media at 308.15 K in presence of KBr. Closed symbols refer to  $0.1 \text{ mol.L}^{-1}$  KBr whereas the open symbols to  $0.5 \text{ mol.L}^{-1}$ . Circles: 0 mass% methanol, Up triangles: 8 mass% methanol, Squares: 16 mass% methanol, and Down triangles: 25 mass% methanol. The lines are the least-squares fitted profiles.



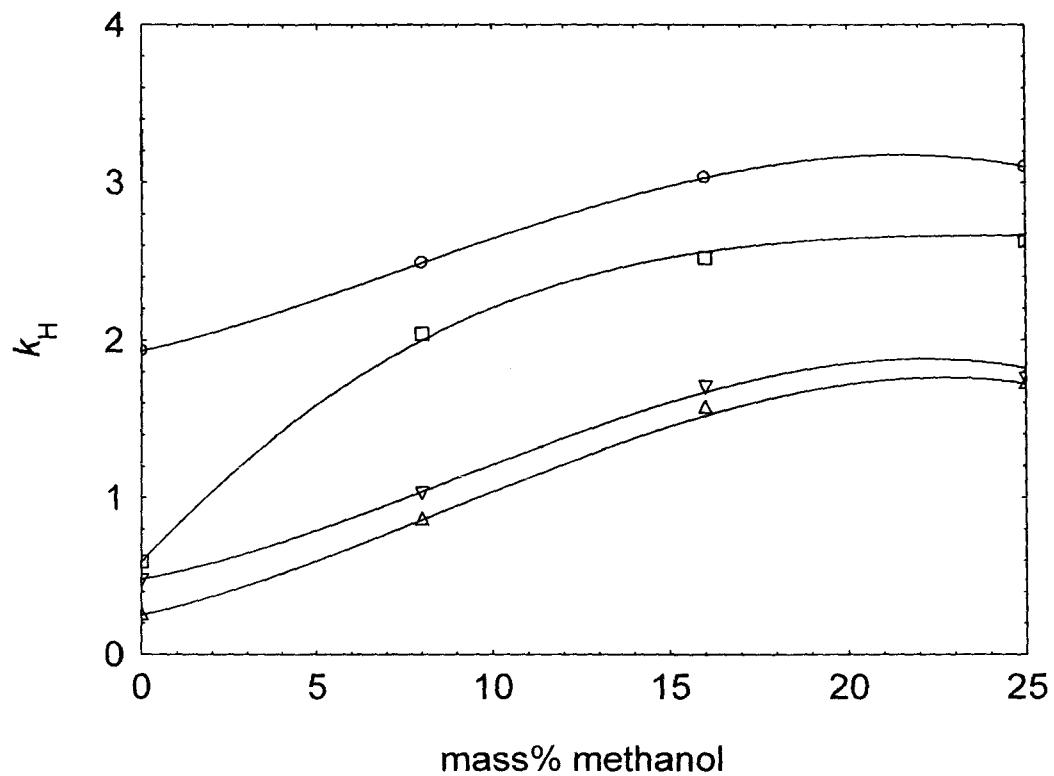
**Figure 2.** Variation of the intrinsic viscosity of NaPSS in methanol-water mixed solvent media at 308.15 K in presence of 0.10 mol.L<sup>-1</sup> NaCl (circles), 0.10 mol.L<sup>-1</sup> KCl (squares), 0.10 mol.L<sup>-1</sup> NaBr (down triangles) and 0.10 mol.L<sup>-1</sup> KBr (up triangles).



**Figure 3.** Variation of the Huggins constant of NaPSS in methanol-water mixed solvent media at 308.15 K in presence of 0.10 mol.L<sup>-1</sup> NaCl (circles), 0.10 mol.L<sup>-1</sup> KCl (squares), 0.10 mol.L<sup>-1</sup> NaBr (down triangles) and 0.10 mol.L<sup>-1</sup> KBr (up triangles).



**Figure 4.** Variation of the intrinsic viscosity of NaPSS in methanol-water mixed solvent media at 308.15 K in presence of 0.50 mol.L<sup>-1</sup> NaCl (circles), 0.50 mol.L<sup>-1</sup> KCl (squares), 0.50 mol.L<sup>-1</sup> NaBr (down triangles) and 0.50 mol.L<sup>-1</sup> KBr (up triangles).



**Figure 5.** Variation of the Huggins constant of NaPSS in methanol-water mixed solvent media at 308.15 K in presence of 0.50 mol.L<sup>-1</sup> NaCl (circles), 0.50 mol.L<sup>-1</sup> KCl (squares), 0.50 mol.L<sup>-1</sup> NaBr (down triangles) and 0.50 mol.L<sup>-1</sup> KBr (up triangles).