

Chapter 8

Viscosities of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media in Presence of an Electrolyte

8.1 Introduction

As described in the previous chapter, 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. 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^{1,2}

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

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.

In the previous chapter, we have used the method of isoionic dilution for the determination of the intrinsic viscosities of sodium polystyrenesulphonate in water as well as in 2-ethoxyethanol–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, provided there is an excess of low-molar-mass electrolyte, at a constant temperature, for a given polyelectrolyte-solvent pair, the reduced viscosity (η_{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.^{1,2}

This chapter describes the viscometric behaviour of sodium polystyrenesulphonate in absence and also in presence of an electrolyte (NaCl) in 2-ethoxyethanol–water mixed solvent media. Our objective is to focus on the role of electrostatic interactions on the viscosity of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media. The intrinsic viscosities of sodium polystyrenesulphonate in these mixtures have also been determined.

8.2 Experimental

2-Ethoxyethanol (G.R.E. Merck) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of $0.92497 \text{ g.cm}^{-3}$ and a co-efficient of viscosity of 1.8277 mPa.s at 298.15 K ; these values are in good agreement with the literature values.³ Triply distilled water with a specific conductance less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The sodium salt of polystyrenesulphonic acid employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was 70000 with a degree of substitution (DS) of 1.0, and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

The viscometric measurements were performed at 308.15 , 313.15 , 318.15 and 323.15 K using a Schultz-Immergut-type viscometer⁴ 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 thermo regulator, and the absolute temperature was determined by a calibrated platinum resistance thermometer and Muller bridge.^{5,6} 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 thus confirming the shear rate independence of the reduced viscosity values in the present study.

To avoid moisture pick up, the solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed in three replicates.

8.3 Results and Discussion

We have measured the variation of reduced viscosity of sodium polystyrenesulphonate with polymer concentration in pure water as well as in

2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at four different temperatures namely 308.15, 313.15, 318.15 and 323.15 K.

In each of these cases the effect of varying concentration of an added salt (1×10^{-4} , 1×10^{-3} , 1×10^{-2} and 1×10^{-1} mol·L⁻¹ of NaCl) was also investigated.

8.3.1 Variation of Reduced Viscosity with Polyelectrolyte Concentration

Figures 8.1 to 8.10 show the typical dependence of the reduced viscosity with polyelectrolyte concentration for the investigated systems. In absence of added NaCl, the reduced viscosity is found to increase as polyelectrolyte concentration decreases bending up at low concentration. No maximum was, however, detected in the η_{sp}/c_p vs. c_p profiles within the concentration range studied here under salt-free conditions. Similar non-linear increase in the reduced viscosity values as the polyelectrolyte concentration is reduced was also observed in polyelectrolyte solutions containing 1.5×10^{-3} , 2.5×10^{-3} and 4.0×10^{-3} mol·L⁻¹ of NaCl (Figures 8.1 to 8.10). An increase in the added salt concentration resulted in the reduction in the absolute values of η_{sp}/c_p greatly. This is a characteristic behaviour of the viscosity of polyelectrolyte solutions. This large decrease in the reduced viscosity can be accounted for by the increase in the screening of intrachain and interchain electrostatic interactions by the added electrolyte ions in solution. Therefore, it is virtually impossible to obtain the intrinsic viscosity of the present polyelectrolyte solutions without added salt and also in the presence of a small amount of the added salt by the usual procedure of the extrapolation of the reduced viscosity versus concentration profiles to zero polyelectrolyte concentration.

8.3.2 Influence of Large Amount of Added Salt: Determination of Intrinsic Viscosity

When the added salt concentration is sufficiently high (1×10^{-1} mol·L⁻¹), 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 sodium polystyrenesulfonate in 2-ethoxyethanol–water mixed solvent media using the Huggins equation, Eq. (1).

From the present experimental η_{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 8.1 along with their standard errors and the correlation coefficients of fits (as r^2).

The intrinsic viscosities of sodium polystyrenesulphonate in water and in 2-ethoxyethanol–water mixtures in presence of $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ 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.*, at polyelectrolyte concentrations of 1.5×10^{-3} , 2.5×10^{-3} , and $4.0 \times 10^{-3} \text{ Eqv} \cdot \text{L}^{-1}$ (*cf.* Chapter 7). 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.

8.3.3 Influence of Medium on the Intrinsic Viscosity

The intrinsic viscosity values of sodium polystyrenesulphonate are found to decrease significantly as the solvent medium becomes richer in 2-ethoxyethanol at any given temperature. The relative permittivity of the medium decreases as more and more 2-ethoxyethanol is added to water (*cf.* Table 3.1, Chapter 3) and hence more counterion condensation takes place due to an improvement of polyion-counterion interactions. The polyion chain will thus have less effective charge as the medium gets richer in 2-ethoxyethanol, and this would facilitate coiling of the polyion chain and result in a reduction in the intrinsic viscosity values.

8.3.4 Influence of Temperature on the Intrinsic Viscosity

An increase in temperature leads to a decrease in the intrinsic viscosity values in water as well as in 2-ethoxyethanol–water mixtures. Increasing temperature causes desolvation of the counterions and this would result in more counterion condensation onto the polyion chains. Increasing temperature also causes a decrease in the relative permittivity of the medium thus favouring counterion condensation. These obviously result in the contraction of the polyions as a result of coiling. It might be noted that the effect of temperature on the intrinsic viscosities and the Huggins constants are less pronounced as compared to the effect of solvent composition.

8.4 Conclusions

The present chapter reported precise measurements on the viscosities of the solutions of sodium polystyrenesulphonate in water and in four 2-ethoxyethanol–water mixtures containing 10, 25, 40 and 50 mass percent of 2-ethoxyethanol at 308.15, 313.15, 318.15 and

323.15 K in presence of varying concentration of added sodium chloride. The viscosity of the present system reveals the characteristic behaviour of polyelectrolyte solutions. Both in the absence and in the presence of small amount of an added salt (1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol·L⁻¹ NaCl), the reduced viscosity is found to increase as polymer concentration decreases bending up at low concentration. No maximum was, however, detected in the η_{sp}/c_p vs. c_p profiles within the concentration range studied in both the cases. Increasing the concentration of the added salt decreases the absolute value of η_{sp}/c_p greatly. 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 (1×10^{-1} M), regular neutral polymer behaviour is recovered thus enabling us to determine the intrinsic viscosity of sodium polystyrenesulphonate in water and in 2-ethoxyethanol–water mixed solvent media using the Huggins equation. The variations of the intrinsic viscosity with temperature and solvent medium have been interpreted in terms of the variation in the coiling of the polyion chain and counterion condensation.

8.5 References

1. H. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938).
2. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, C. Seidel and D. Stscherbina, *Polyelectrolytes: Formation, Characterization and Application*, Chapter 5, Hanser Publishers, Munich (1994).
3. G. Douheret and A. Pal, *J. Chem. Eng. Data*, **33**, 40 (1988).
4. J. Schulz and E. H. Immergut, *J. Polym. Sci.*, **9**, 279 (1952).
5. B. Das and D. K. Hazra, *Bull Chem. Soc. Jpn.*, **65**, 3470, (1992).
6. B. Das and D. K. Hazra, *J. Phys. Chem.*, **99**, 269 (1995).

Table 8.1 Intrinsic Viscosities $[\eta]$, Huggins Constants k_H , and the Correlation Coefficients of Fits (as r^2) of Sodium Polystyrenesulphonate in Water, and in 2-Ethoxyethanol–Water Mixtures with 10, 25, 40 and 50 Mass Percent of 2-Ethoxyethanol in Presence of 1×10^{-1} mol·L⁻¹ of NaCl at 308.15, 313.15, 318.15 and 323.15 K

T (K)	Mass % of Cosolvent	$[\eta]$ L·Eqv ⁻¹	k_H	r^2
308.15	0	33.47	0.05	0.9282
	10	31.63	0.06	0.9677
	25	29.80	0.08	0.9236
	40	28.22	0.07	0.9832
	50	24.66	0.08	0.9783
313.15	0	32.79	0.06	0.8618
	10	30.89	0.06	0.9038
	25	29.23	0.05	0.9171
	40	27.57	0.10	0.9082
	50	23.96	0.06	0.9391
318.15	0	31.62	0.07	0.8645
	10	29.93	0.06	0.9597
	25	28.67	0.05	0.8489
	40	26.95	0.09	0.9561
	50	22.92	0.06	0.9960
323.15	0	29.92	0.08	0.8713
	10	29.21	0.06	0.9550
	25	27.89	0.06	0.9089
	40	26.03	0.10	0.9912
	50	22.72	0.06	0.9909

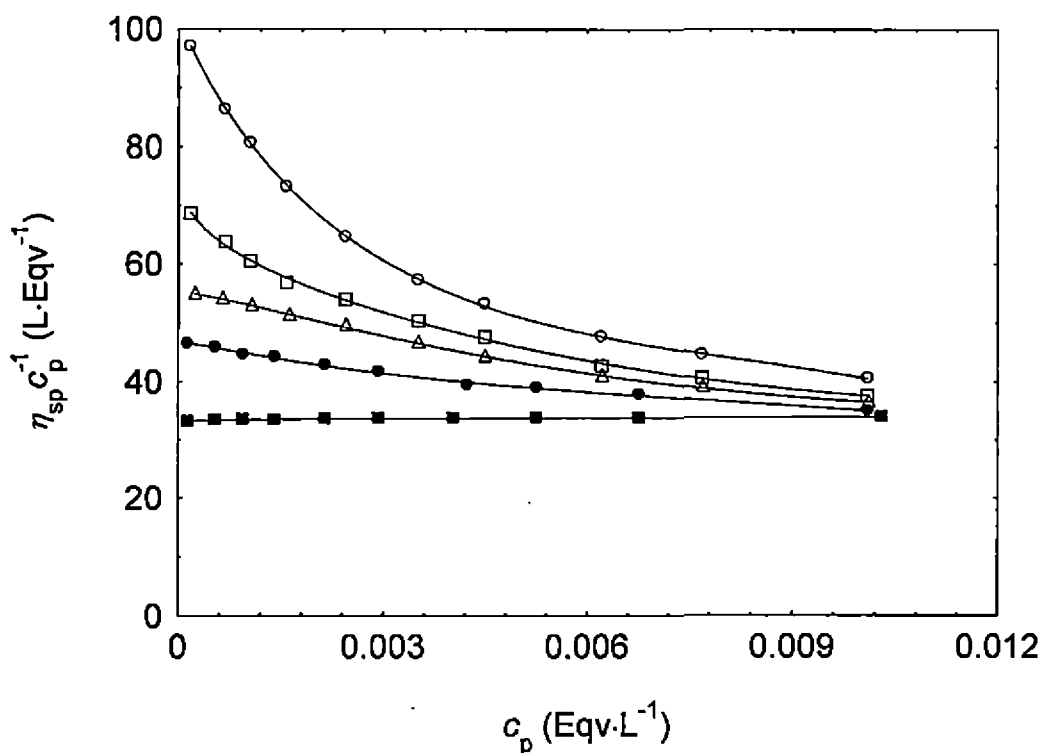


Figure 8.1 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in water at 308.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

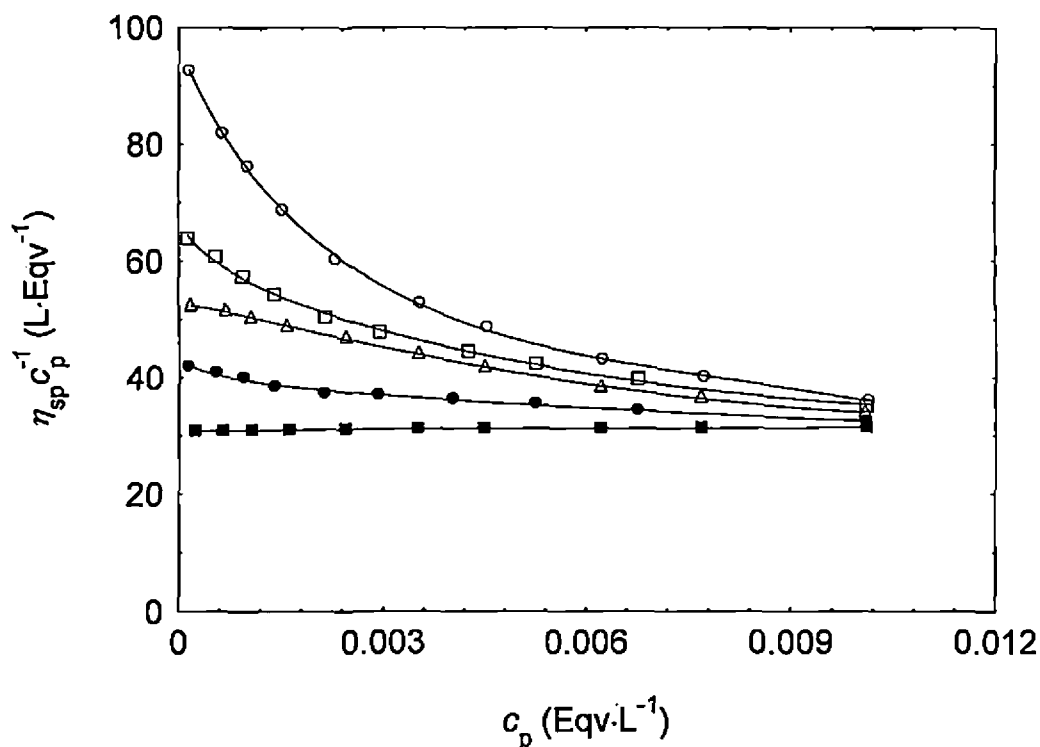


Figure 8.2 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 10 mass percent of 2-ethoxyethanol–water at 313.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

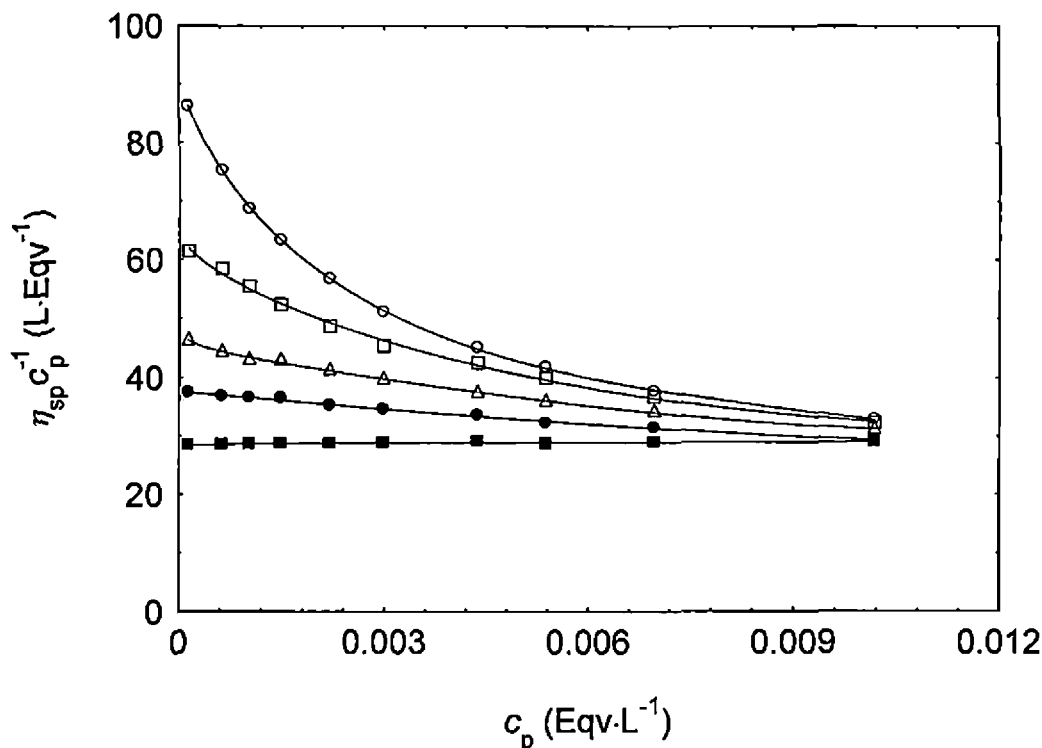


Figure 8.3 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 25 mass percent of 2-ethoxyethanol–water at 318.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

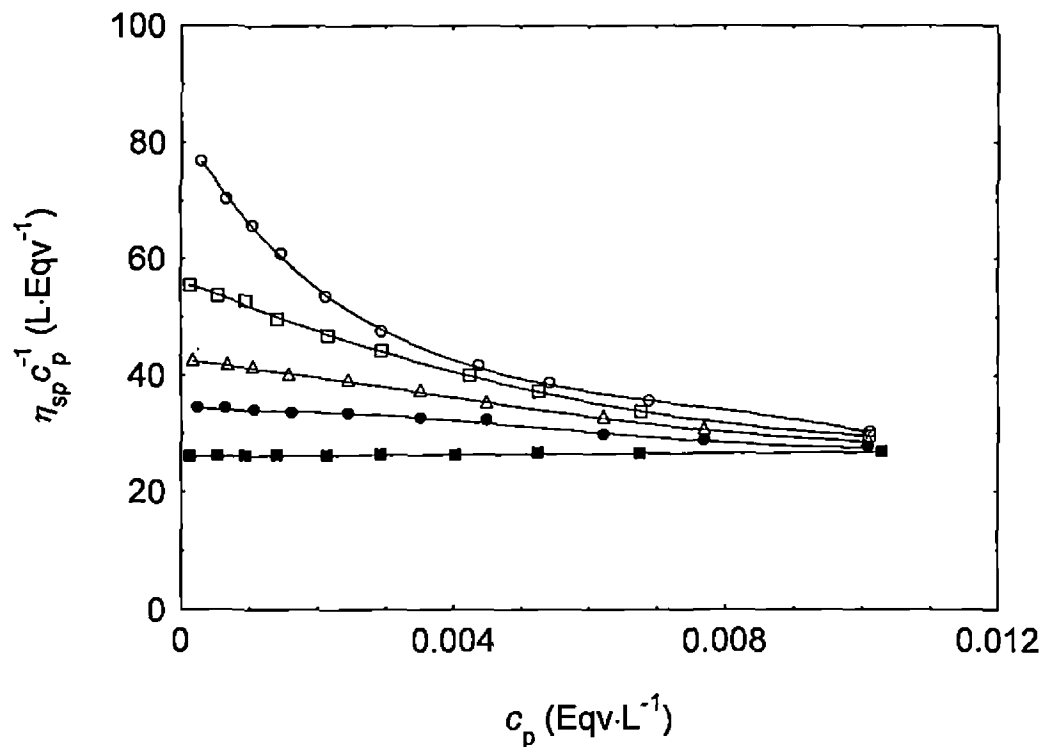


Figure 8.4 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 40 mass percent of 2-ethoxyethanol–water at 323.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

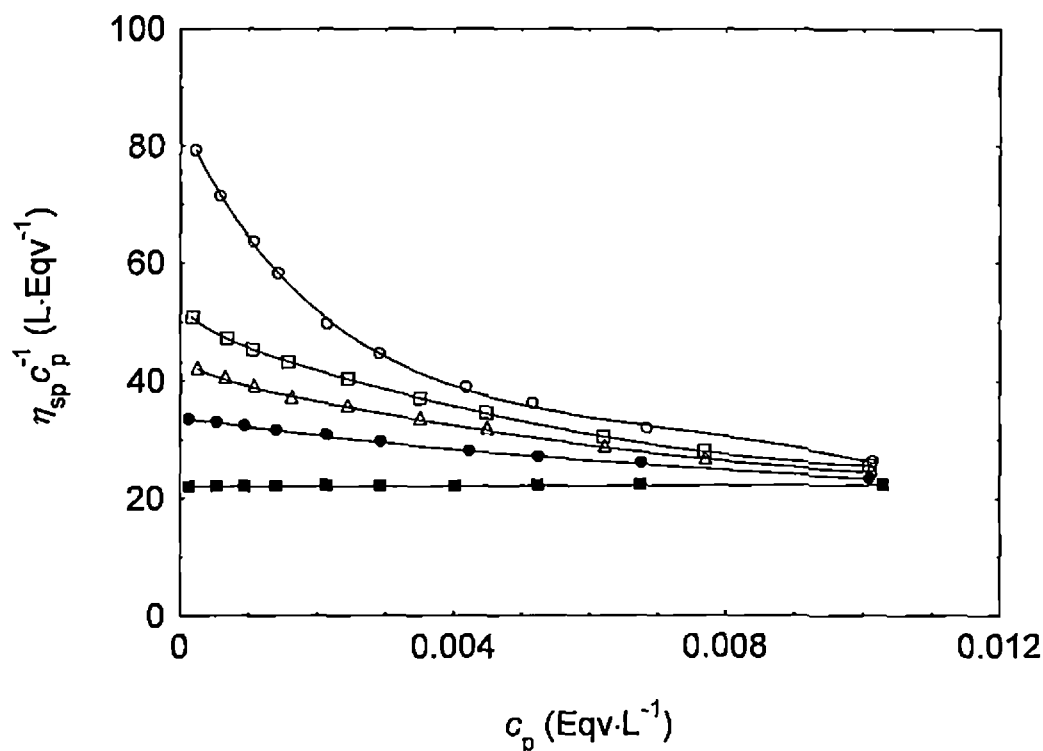


Figure 8.5 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate in 50 mass percent of 2-ethoxyethanol–water at 323.15 K in absence (open circle) and in presence (open square: 1×10^{-4} , triangle: 1×10^{-3} , closed circle: 1×10^{-2} , closed square: 1×10^{-1} mol·L⁻¹) of NaCl. Lines are used to guide the eye.

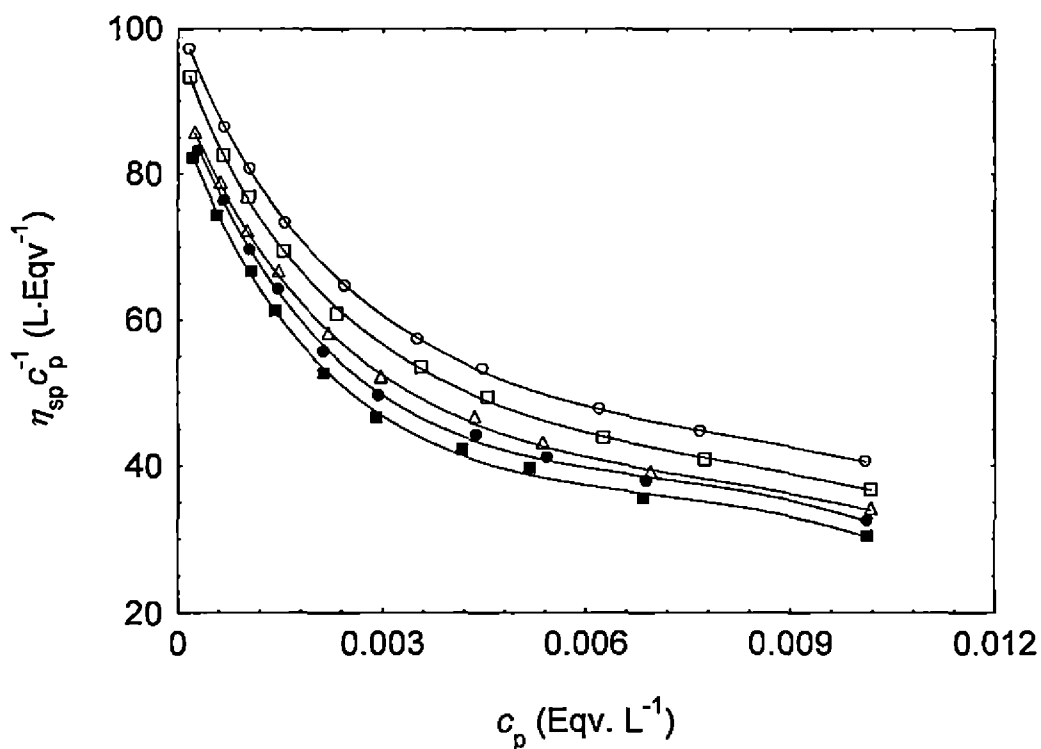


Figure 8.6 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 308.15 K in absence of added salt for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

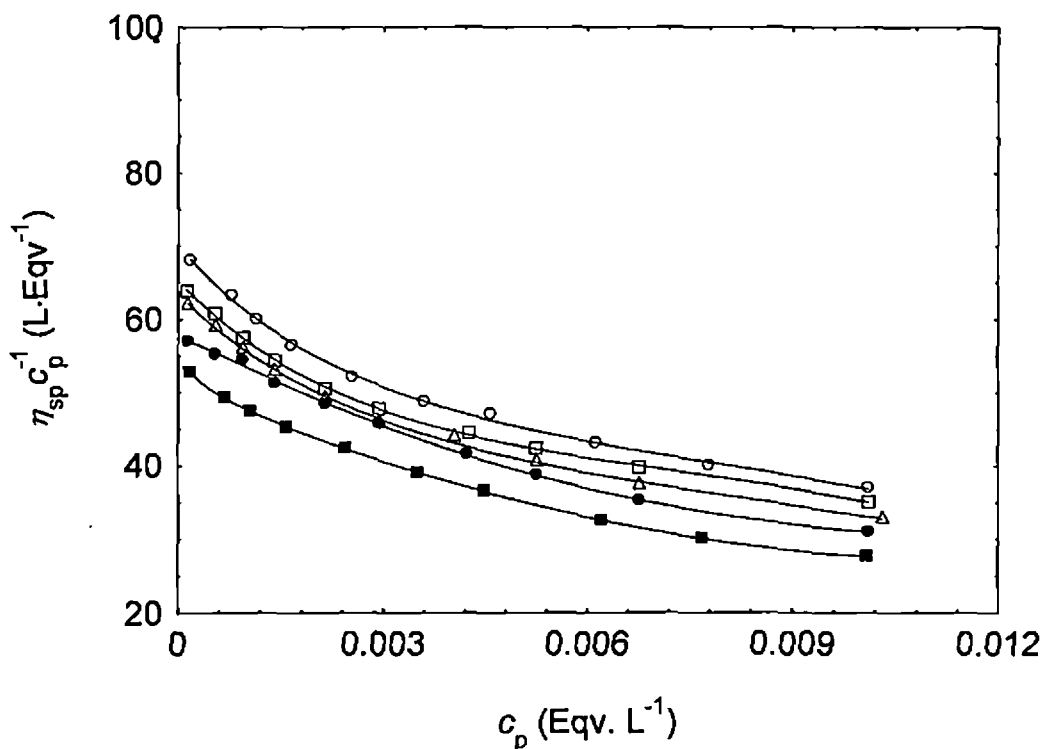


Figure 8.7 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp} / c_p) of sodium polystyrenesulphonate at 313.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

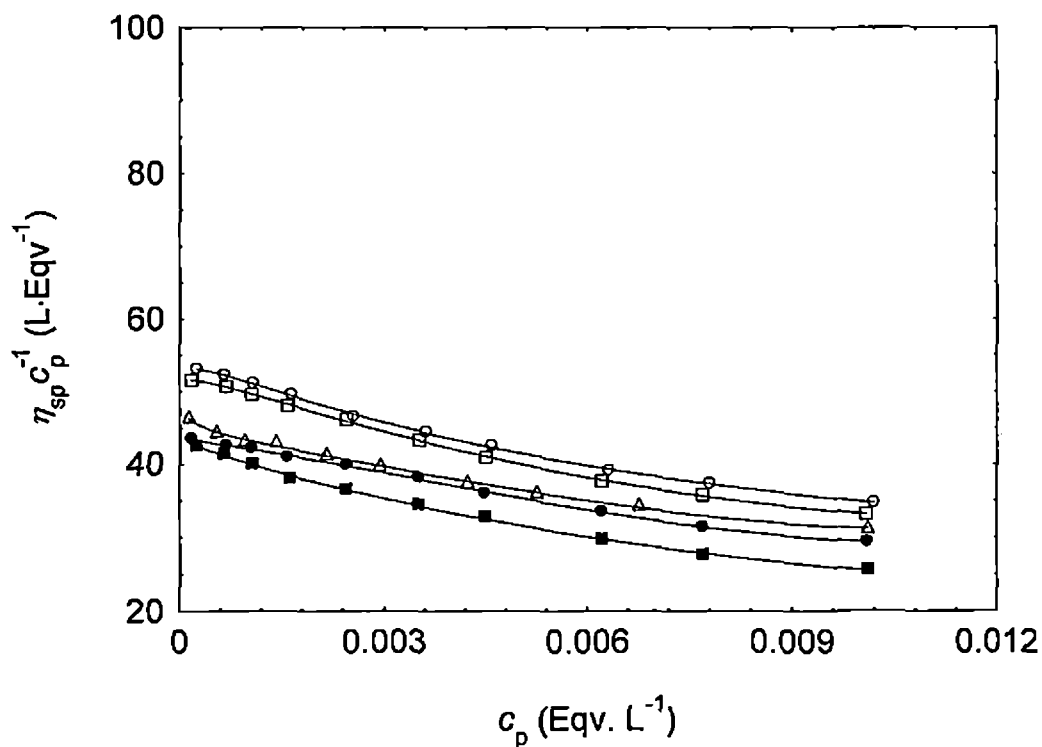


Figure 8.8 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 318.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

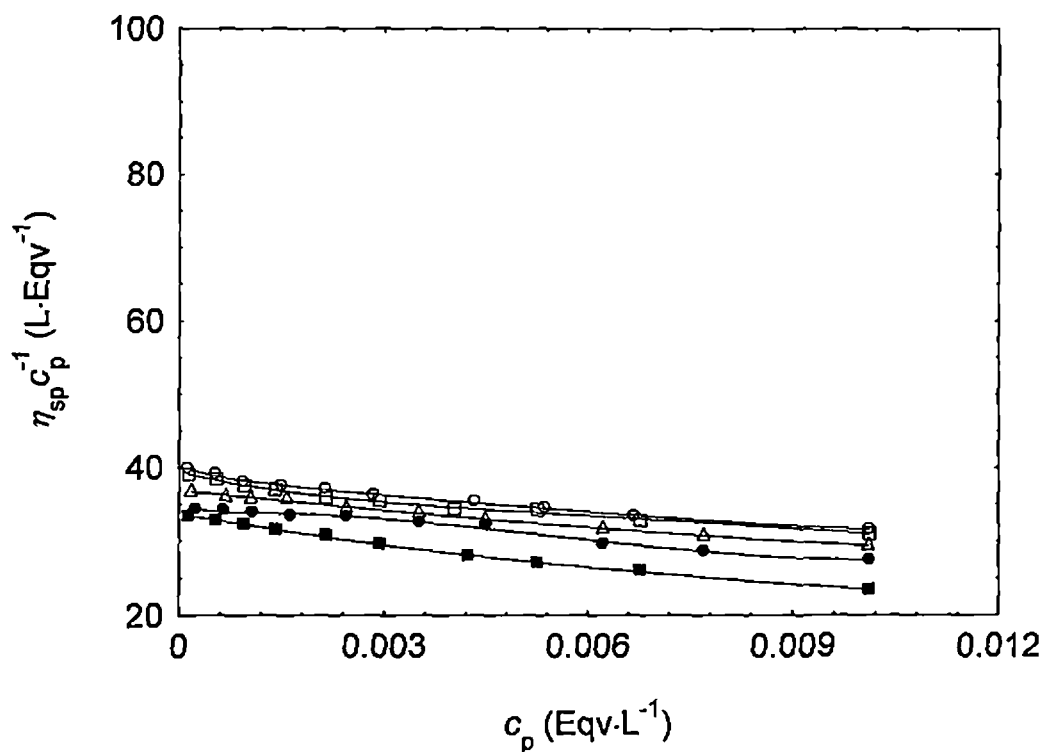


Figure 8.9 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp}/c_p) of sodium polystyrenesulphonate at 323.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass per cent; open square: 10 mass per cent; triangle: 25 mass per cent; closed circle: 40 mass per cent and closed square: 50 mass per cent). Lines are used to guide the eye.

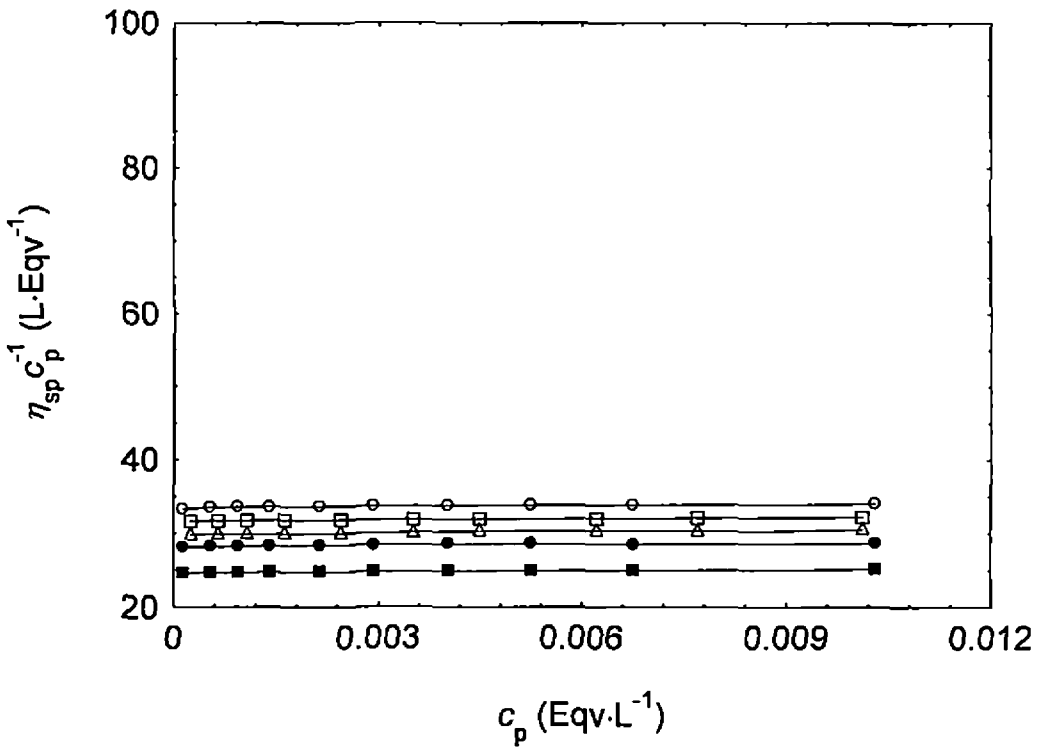


Figure 8.10 Polyelectrolyte concentration (c_p) dependence of the reduced viscosity (η_{sp} / c_p) of sodium polystyrenesulphonate at 308.15 K in presence of salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$ for different composition of 2-ethoxyethanol–water mixtures (open circle: 0 mass percent; open square: 10 mass percent; triangle: 25 mass percent; closed circle: 40 mass percent and closed square: 50 mass percent). Lines are used to guide the eye.

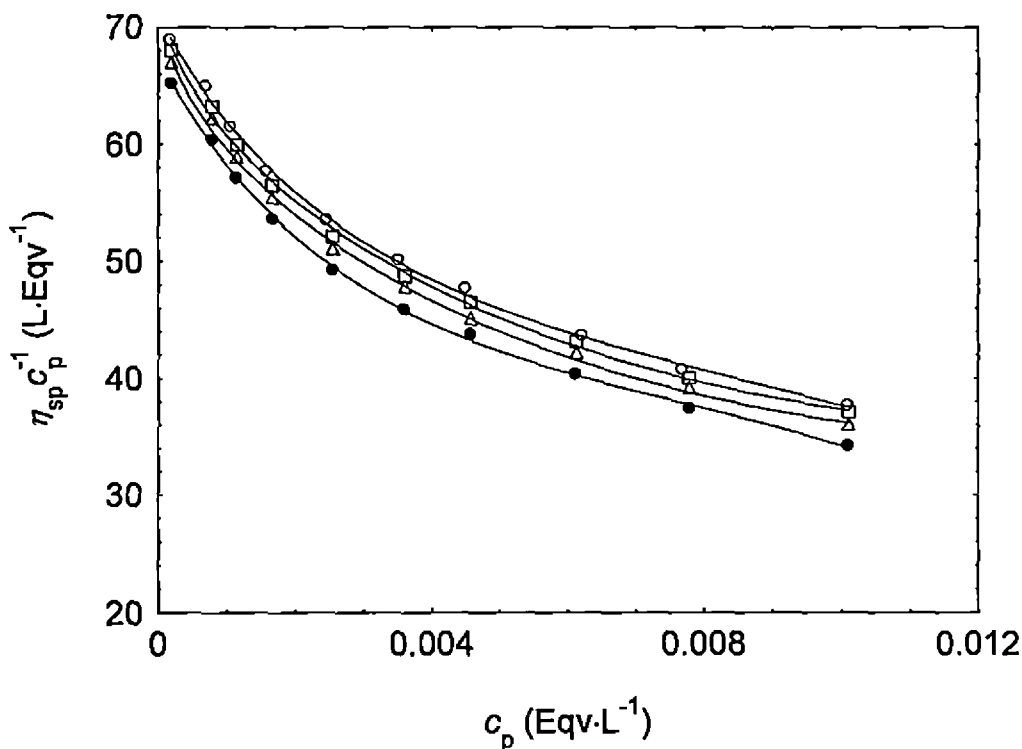


Figure 8.11 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in water in presence of the salt, NaCl, of concentration $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

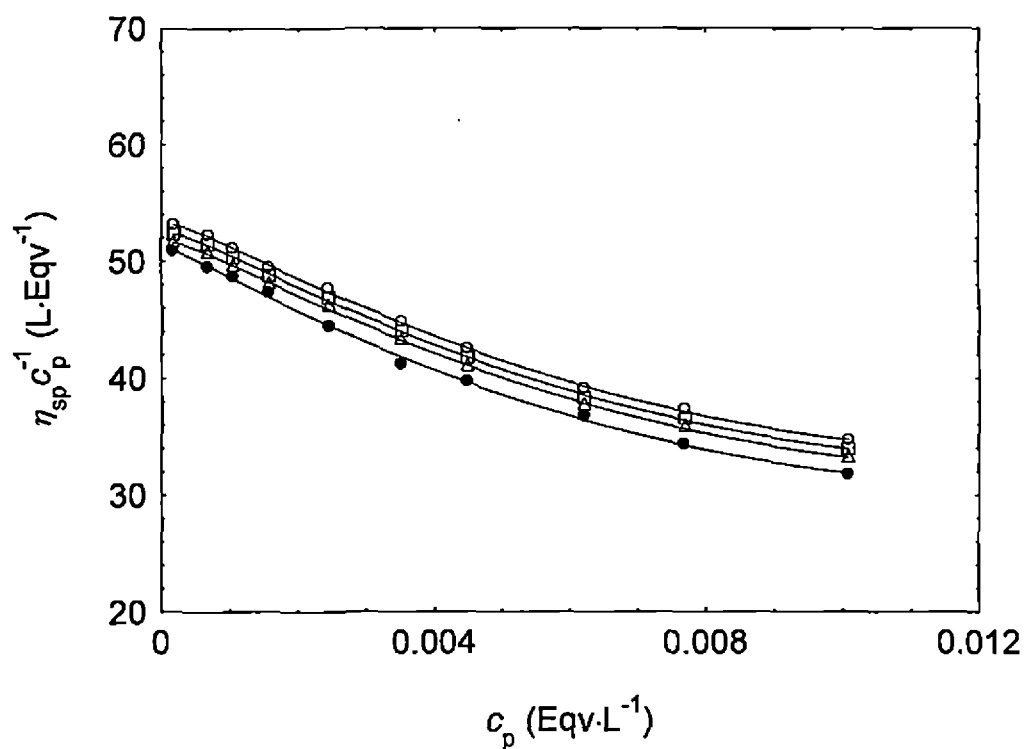


Figure 8.12 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 10 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of strength $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

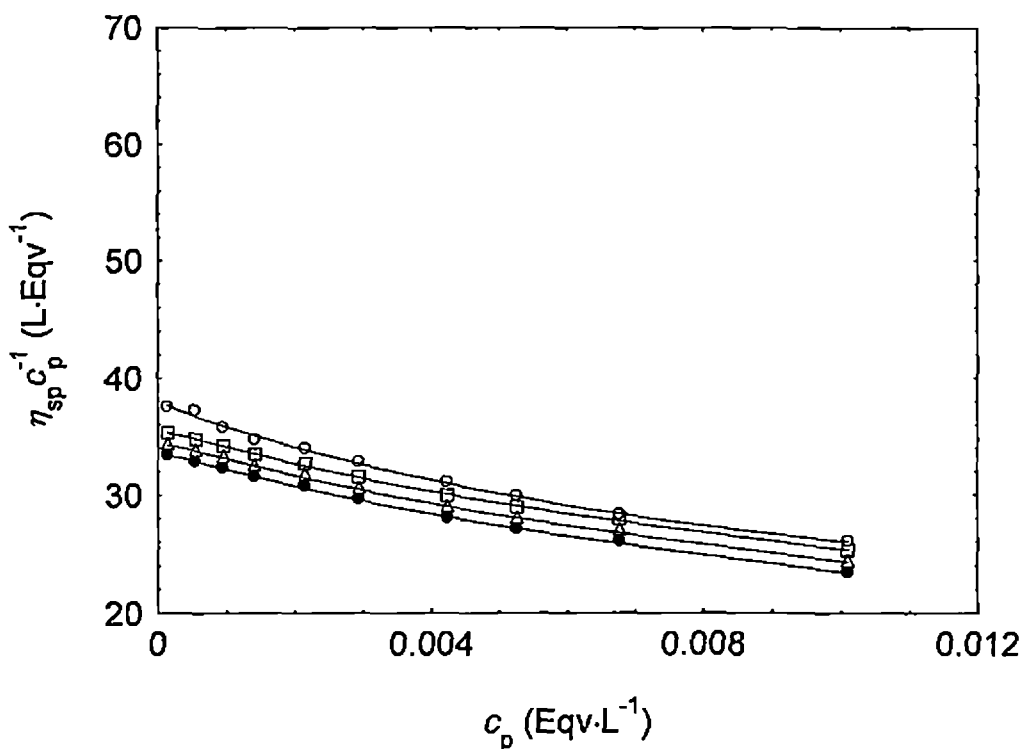


Figure 8.13 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 50 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. Lines are to guide the eye.

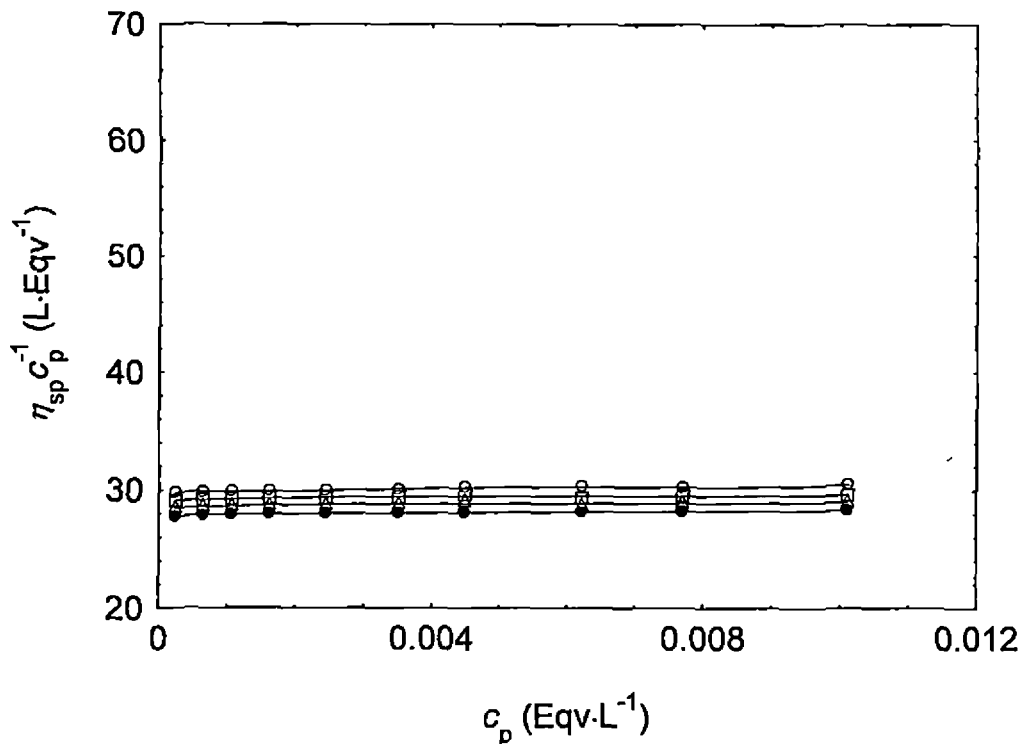


Figure 8.14 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp} / c_p) as a function of polyelectrolyte concentration (c_p) in 25 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$.

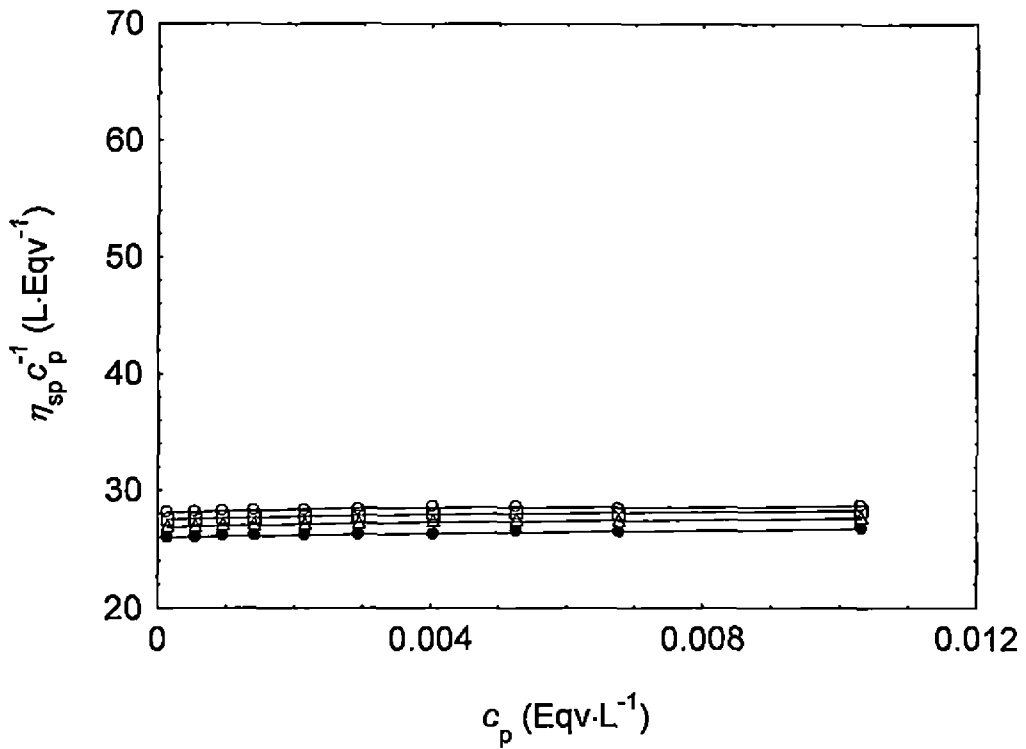


Figure 8.15 Temperature dependence (open circle: 308.15 K; open square: 313.15 K; triangle: 318.15 K and closed circle: 323.15 K) of reduced viscosity (η_{sp}/c_p) as a function of polyelectrolyte concentration (c_p) in 40 mass percent of 2-ethoxyethanol–water mixture in presence of the salt, NaCl, of concentration $1 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$.