

Chapter 5

Conductance of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media: An Analysis using the Scaling Theory Approach

5.1 Introduction

In Chapter 4 it has been observed that the Manning counterion condensation model could not explain the conductivity behaviour of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media. The disagreement indicates that this theory provides comparatively small values for the fraction of uncondensed counterions for this system. Possible reasons for the observed disagreement have also been analyzed. However, very significant conclusions regarding the structures of the polyion and its counterions are achieved through an analysis of the results.

Later Colby *et al.*¹ using the scaling description for the configuration of a polyion chain according to Dobrynin *et al.*² put forward an equation (with one adjustable parameter) to describe the conductivity of a semidilute polyelectrolyte solution. It would be of interest to apply this model for the analysis of the conductivity data which are in the semidilute concentration region since the application of the Manning model to these systems is, however, less straightforward because these semidilute macroions do not assume a fully stretched conformation in solution.

In the semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bears an electric charge of $q_\xi = zefg$ (z being the counterion valence and e is the electronic charge) and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge of $Q_p = N_\xi q_\xi = zefgN_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is in a fully extended conformation of g_e electrostatic blobs of size ξ_e . This means that for length scales less than ξ_0 , the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0 , the hydrodynamic interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Under the condition of $g/g_e = \xi_0/\xi_e$ and making use of the fact that the electrostatic blobs are space filling ($g = c_p \xi_0^3$, c_p being the number density of monomers), the specific conductivity of a polyelectrolyte in a semidilute solution in absence of an added salt is, within this model, given by

$$\kappa = f c_p \left[\lambda_c^0 + \frac{c_p \xi_0^2 e^2 f}{3\pi\eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (1)$$

where λ_c^0 is the limiting equivalent conductivity of the counterions and η_0 is the coefficient of viscosity of medium.

The above expression given by Colby *et al.*¹ is derived taking into account the scaling arguments proposed by Dobrynin *et al.*² neglecting the hydrodynamic interactions (Kirkwood model) between the single structural units *i.e.*, the correlation blobs and neglecting the asymmetry field effect. As can be seen the above model has a single free (adjustable) parameter f , the fraction of uncondensed counterions that defines the degree of the effectively ionized groups along the chain, in the scheme of the Manning counterion condensation theory.

This new model for semidilute polyelectrolyte conductivity has been applied, so far, to a limited number of aqueous polyelectrolytes^{1,3,4} and good agreement with the experiment was observed. This model, however, has not been applied to polyelectrolyte solutions in solvents besides water with the exception of an attempt by one of us for sodium polystyrenesulphonate in acetonitrile–water mixed solvent media.⁵

5.2 Results and Discussion

Graphical representation of the experimental equivalent conductance (Λ) values (points), and the Manning predictions (continuous lines) are shown in Figure 4.5 (Chapter 4) at 308.15, 313.15, 318.15 and 323.15 K in 2-ethoxyethanol–water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated following the Manning model. Possible reasons for the deviation and their implication for the elucidation of the structure of the polyelectrolyte solutions have been adequately discussed in the previous chapter. The deviation probably arises from the fact that the polyelectrolyte solutions investigated here are different from the model that underlies the Manning counterion condensation model. By

estimating the overlap concentration (c^*) for the polymer chain investigated using the following equation,⁶ one can understand the reason for the failure of the Manning model.

$$c^* = \frac{1}{N_A L^2 a} \quad (2)$$

where N_A is the Avogadro's Number, L the contour length and a the monomer length. It is observed that the polymer solutions used in the present study are mostly in the semidilute regime ($c_p > c^* \approx 1 \times 10^{-3} \text{ Eqv} \cdot \text{L}^{-1}$) where the Manning limiting law does not apply.

For semidilute polyelectrolyte solutions we, therefore, have made an effort to analyse the present conductivity data using the scaling theory approach as proposed by Colby *et al.*¹ for semidilute polyelectrolyte solutions.

Since the present 2-ethoxyethanol–water mixtures are poor-solvents for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule and hence we use a value of 5 \AA^0 as the effective monomer size (b) as suggested by Colby *et al.*¹ while analyzing the data on the basis of the Colby model.

The electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) under poor solvent condition are given by¹

$$\xi_e = b \left(\frac{f}{f^2} \right)^{-1/3} \quad (3)$$

and

$$\xi_0 = (cb)^{-1/2} \left(\frac{f}{f^2} \right)^{-1/3} \quad (4)$$

Therefore, an estimate of polyelectrolyte equivalent conductivity in the semidilute regime is provided by Eq. (1) in conjunction with Eq. (3) and Eq. (4).

In Figures 5.1 to 5.5, the predictions of the Colby model (dashed lines) for the semidilute regime have been compared with the experimental data. The dashed lines in Figures 5.1 to 5.5 display the results of the calculation using the optimum values of f . The fractions of uncondensed counterion (f) which describe the experimental results best along with the respective standard deviations of fits are given in Table 5.1. Figures 5.1 to 5.5 reveal an excellent agreement of the experimental results with those predicted by the scaling theory approach using only one adjustable parameter f .

5.3 Conclusions

We have, thus, been able to quantitatively describe the electrical conductivity data of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media with the help of the scaling concept of polyelectrolyte solutions. The values of f listed in Table 5.1 indicate a lower level of counterion condensation as compared to the Manning model.

5.4 References

1. R. H. Colby, D. C. Boris, W. E. Krause and J. S. Tan, *J. Polym. Sci. Part B: Polym. Phys.*, **35**, 2951 (1997).
2. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28**, 1859 (1995).
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Table 5.1 Fraction of Uncondensed Counterions (f) and the Standard Deviations(σ) of Fit for Sodium Polystyrenesulphonate in the Absence of an Added Salt at 308.15, 313.15, 318.15 and 323.15 K in 2-Ethoxyethanol–Water mixed Solvent Media as Obtained According to Eq. (1)

T (K)	Mass % of Cosolvent	f	$\sigma \times 10^6$
308.15	10	0.45	3.78
	25	0.41	4.20
	40	0.26	7.78
	50	0.25	5.35
313.15	10	0.43	3.44
	25	0.41	7.66
	40	0.25	3.48
	50	0.24	3.97
318.15	10	0.40	3.37
	25	0.39	5.65
	40	0.26	5.15
	50	0.24	5.04
323.15	10	0.38	3.36
	25	0.35	5.67
	40	0.24	3.86
	50	0.23	4.45

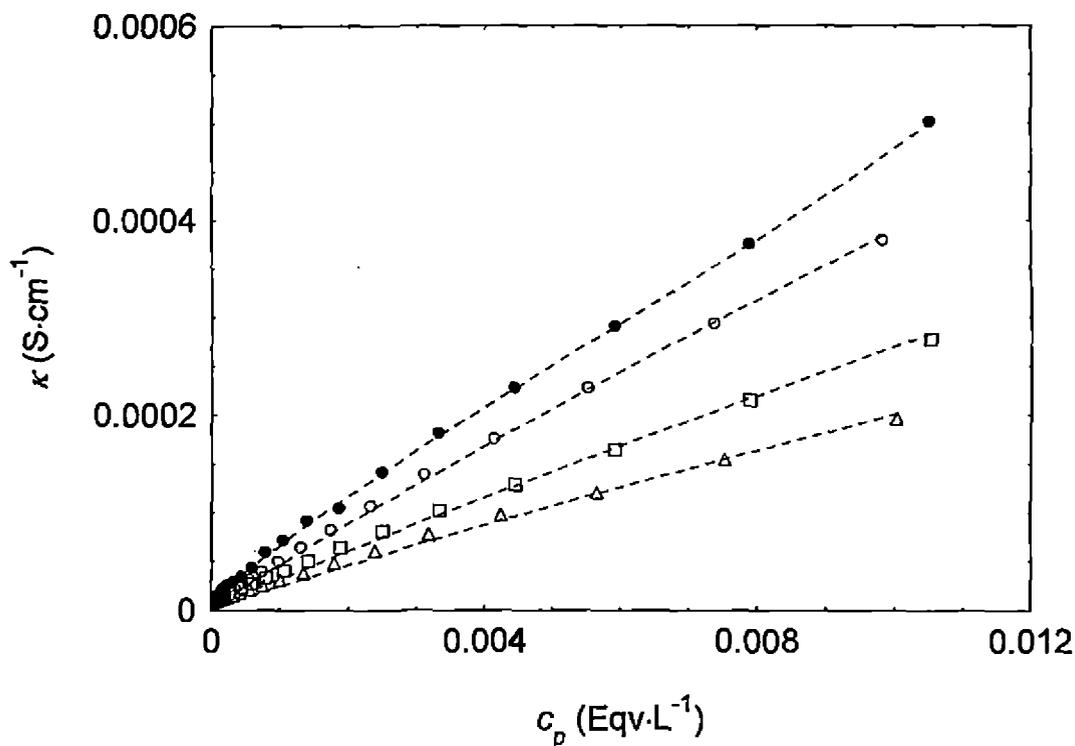


Figure 5.1 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 308.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (△) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

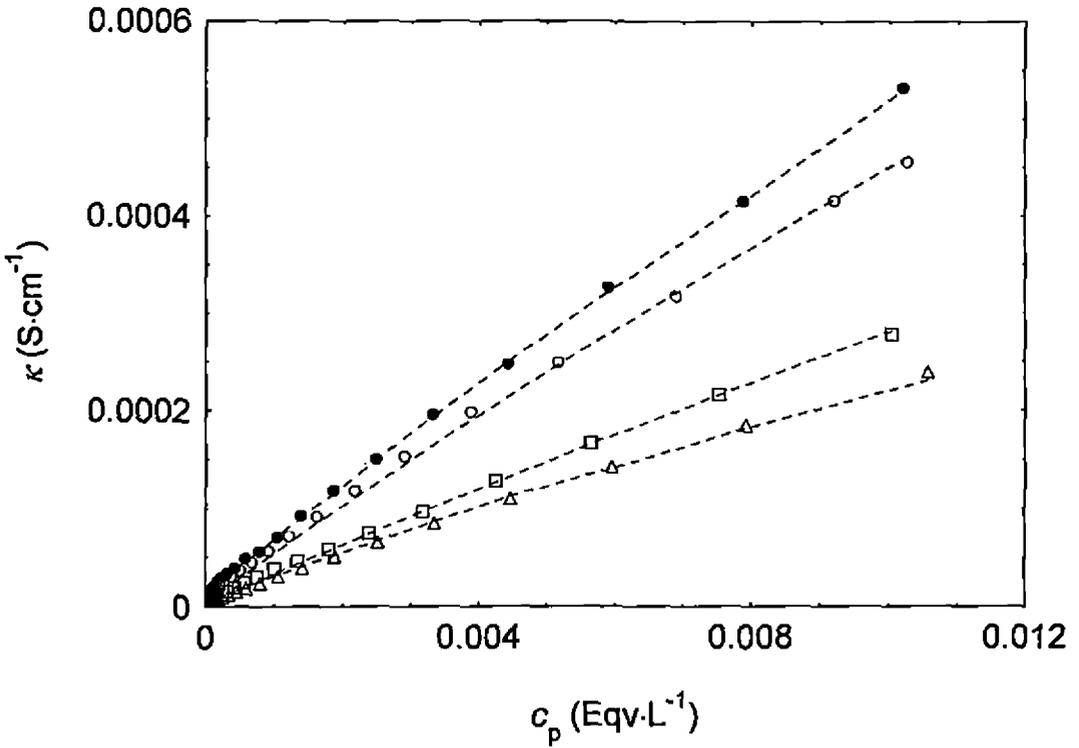


Figure 5.2 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 313.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (△) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

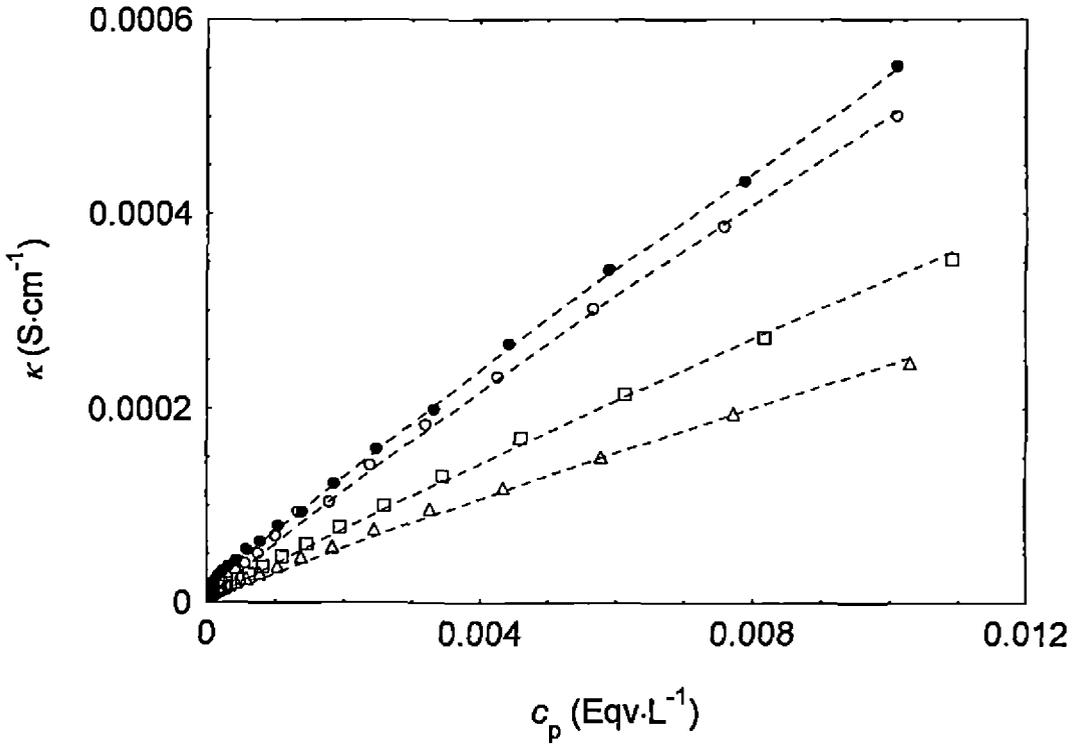


Figure 5.3 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 318.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (Δ) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

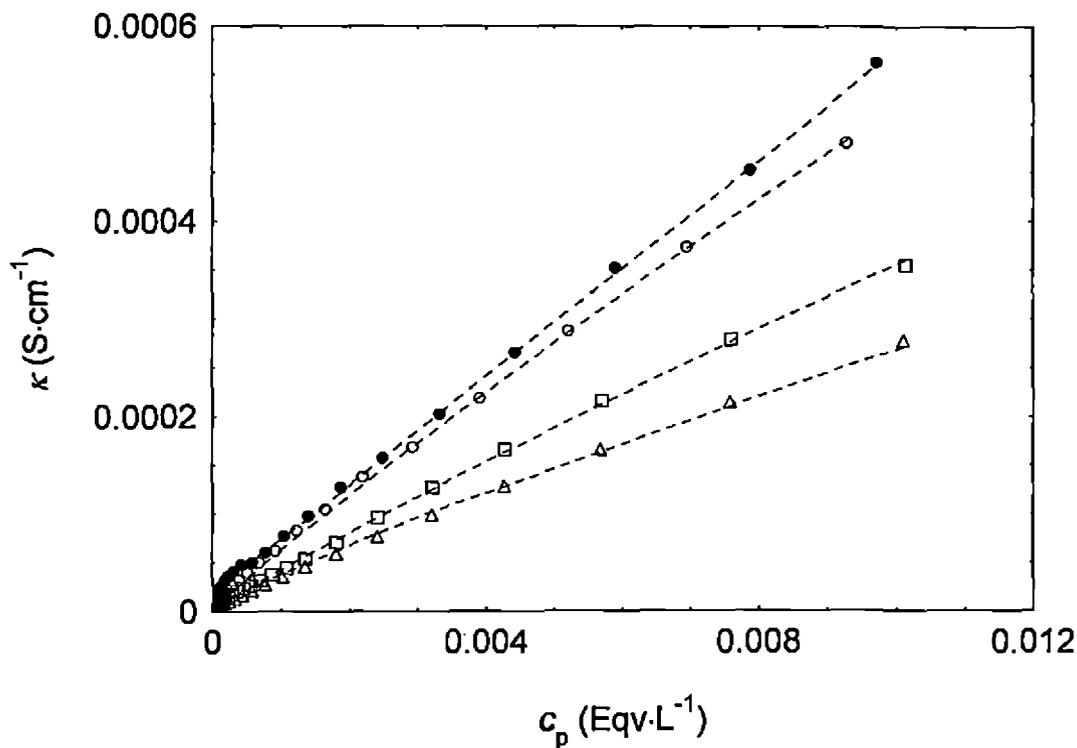


Figure 5.4 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at a temperature of 323.15 K in 2-ethoxyethanol–water mixtures with 10 (●), 25 (○), 40 (□) and 50 (△) mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).

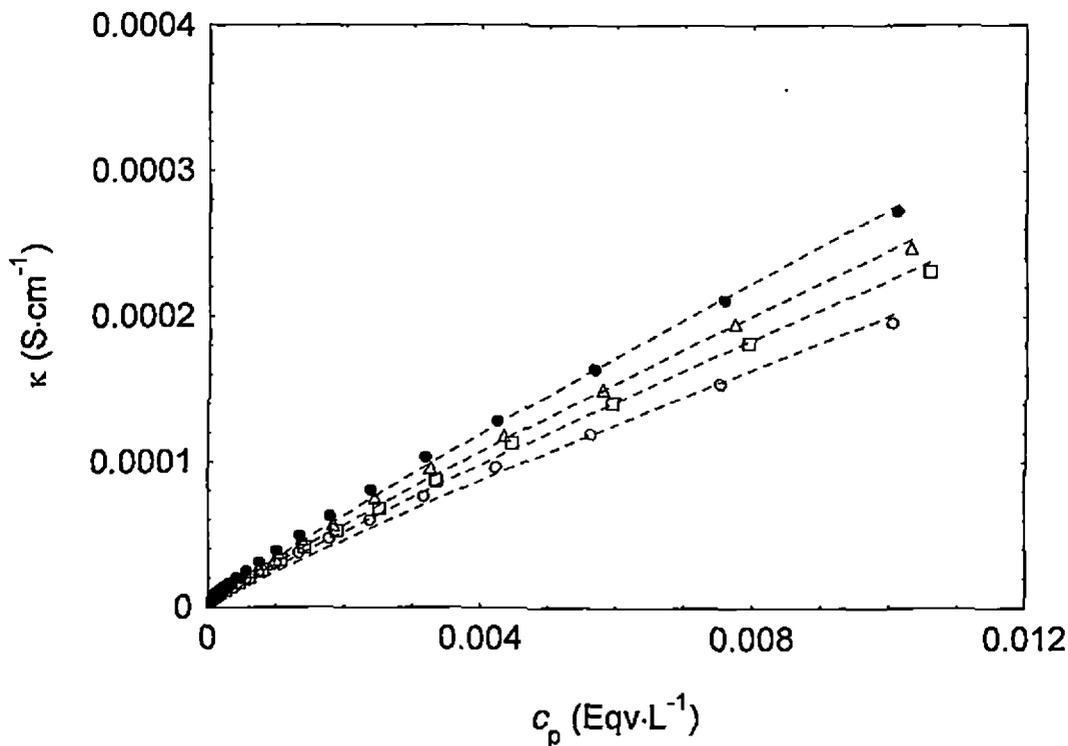


Figure 5.5 Specific conductivities of sodium polystyrenesulphonate as a function of the polymer concentration (c_p) at temperatures of 308.15(○), 313.15(□), 318.15(△) and 323.15 K (●) in 2-ethoxyethanol–water mixtures with 50 mass percent of 2-ethoxyethanol. Experimental: symbols represent experimental values whereas the dashed lines are according to Eq. (1).