

Chapter 4

The Effects of Concentration, Relative Permittivity, and Temperature on the Transport Properties of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media

4.1 Introduction

Polyelectrolytes are polymers having ionizable groups, which in polar solvents, can dissociate into charged polymer chains and small counterions of opposite charge.¹⁻² Solution properties of polyelectrolytes, both in the presence and in the absence of an added salt, differ considerably from those of neutral macromolecular solutions or those of simple electrolytes. The origin of this specificity lies in the combination of properties derived from long-chain molecules with those derived from charge interactions. The high charge density on the macroion produces a strong ionic field which attracts counterions. This strong ionic interaction is the source of the characteristic properties of polyelectrolytes. Current interest in charged polymer solutions, in particular, in high-molecular weight ionic macromolecules, is supported by the needs of biophysics since biopolymers are usually charged under physiological conditions and many of their biological functions are governed by the polyelectrolyte behaviour.³ In accounting for the solution behaviour of biological and synthetic polyelectrolytes, elucidation of the interactions between counterions and charged groups on the polyion are of essential importance. Polyelectrolyte effect includes both deviations from the behaviour of neutral polymers caused by the existence of charges along the polymer chain and deviations from the behaviour of the electrolytes caused by the fixation of one sort of charges on the polymer chain. Therefore, in addition to the method of macromolecular characterization, electrochemical techniques have also been applied to investigate the solution behaviour of polyelectrolytes. The specific conductance and the equivalent conductivity, Λ , are experimentally determined parameters which are suitable to describe the electrolytic transport properties of polyelectrolyte solutions because these properties take into account the movement of any charged entity present in the system under the influence of an externally applied electric field. In spite of various attempts by different investigators, a completely satisfactory theory to provide a priori description of the electrolytic conductivity of polyelectrolyte solutions has not yet been developed.⁴⁻⁶

However, the description of different electrical properties of polyions in aqueous solutions and of their interactions with counterions is generally based on the Manning counterion condensation theory⁷⁻¹⁰ that, under some aspects, can be considered equivalent to the Poisson-Boltzmann cylindrical cell model.¹¹⁻¹⁵ Within this model, the polyion is represented as an infinitely long charged line, small ions (counterions) are assumed to form an ionic atmosphere whose density depends on the frame of the polyion and their interactions with the charged polyions groups are purely Coulombic, so that the screening effect extends over the Debye length. The uncondensed mobile ions are treated in the Debye-Hückel approximation. The solvent is assumed to be a continuous medium characterized by a spatially uniform dielectric constant. Interactions among polyions are neglected, the theory being addressed to highly diluted solutions. The basic idea is that if the charge density (ξ) of the rod exceeds a critical value, some charges on the chain can be partially neutralized by one of the free ions in the solution, which means that the repulsion Coulombic energy of two adjacent unit charges on the chain must be smaller than the thermal energy $k_B T$. On the basis of these assumptions, this approach has been successfully applied to different polyelectrolyte systems, and numerous experiments have strongly suggested the validity of this model.¹⁶⁻²²

According to the Manning counterion condensation theory, polyelectrolytes can be characterized by the linear charge density parameter defined by^{7,23,24}

$$\xi = \frac{e^2}{bDk_B T} \quad (1)$$

where e is the protonic charge, D the relative permittivity of the medium, b the spacing between charged groups taken along the axis of the polyion chain, k_B the Boltzman constant and T the temperature in absolute scale. This theory states that if $\xi > 1$, enough counterions condense on to the polyion to yield the critical value $\xi = 1$. If, on the other hand, $\xi < 1$, ionization takes place to reach this critical value. A limiting law of electrical conductivity for a salt-free polyelectrolyte solution is related to ξ by the following equation.^{8,23,25}

$$\Lambda = f(\lambda_c^0 + \lambda_p) \quad (2)$$

where λ_c^0 and λ_p are the limiting ionic equivalent conductivity of the counterion and the equivalent conductivity of the polyion at a finite concentration, respectively, and f is counterion-polyion interaction parameter given by^{7,23,24}

$$f = \frac{0.866}{\xi} \quad (3)$$

In contrast to Huizenga,²⁶ where the counterions are regarded either as “bound” or as “free” implying that they are not influenced by the polyion, Manning assumed that while the condensed counterions, certainly qualify as bound, the fraction of such ions is $1-\xi^{-1} \neq 1-f$, the uncondensed counterions may, in no way, be thought of as free, being subjected to the Debye-Hückel potential of the polyions. Thus f does not have the significance of free counterions rather it represents the fraction of uncondensed counterions. Considering electrophoretic and relaxation contributions to the equivalent conductivity, λ_p has been derived theoretically for the cylinder model of polyelectrolyte,⁹ and it follows for counterions with a charge of z_c

$$\lambda_p = \frac{279A|z_c|^{-1}|\ln \kappa a|}{1 + 43.2A(|z_c|\lambda_c^0)^{-1}|\ln \kappa a|} \quad (4)$$

where the parameter a is the radius of the polymer chain, while

$$A = \frac{Dk_B T}{3\pi\eta_0 e} \quad (5)$$

with η_0 being the coefficient of viscosity of the solvent. In Eq. (5), κ is the Debye screening constant, which is defined by

$$\kappa^2 = \frac{4\pi e^2}{Dk_B T} \xi^{-1} n_e |z_c| \quad (6)$$

where n_e is the stoichiometric equivalent polyion concentration (monovalent charged groups per unit volume).

As far as we know there is very little work in the literature dealing with the effect of the medium and temperature on the interaction between a polyion and its counterions.^{1,27,28} In this chapter, the results are reported for conductivity measurements on sodium polystyrenesulphonate, an anionic polyelectrolyte, in 2-ethoxyethanol–water mixed solvent media with varying relative permittivity at different temperatures. The aim of the present work is to analyze the influence of concentration, medium and temperature on the extent of polyion-counterion interaction and on the mobility of the polyelectrolyte species. The

experimentally determined equivalent conductivity values have also been compared with those obtained theoretically from the Manning counterion condensation model. The solvent 2-ethoxyethanol has been chosen because it is soluble in water in all proportions and it has a low relative permittivity solvent ($D = 13.38$ at 298.15 K)²⁹ so that the relative permittivity of the mixed solvent media can be varied over a wide range.

4.2 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 $0.92497\text{ g}\cdot\text{cm}^{-3}$ and a coefficient of viscosity of $1.8277\text{ mPa}\cdot\text{s}$ at 298.15 K ; these values are in good agreement with the literature values.²⁹ Triply distilled water with a specific conductance less than $10^{-6}\text{ S}\cdot\text{cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The physical properties of 2-ethoxyethanol–water mixed solvents used in this study at 308.15 , 313.15 , 318.15 , and 323.15 K are reported in Table 4.1. The relative permittivity of 2-ethoxyethanol–water mixtures at the experimental temperatures were obtained with the equations as described in the literature³⁰ using the literature density and relative permittivity data of the pure solvents^{29,31} and the densities of the mixed solvents are given in Table 4.1.

Sodium polystyrenesulphonate employed in this investigation was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M) of the sample was *ca.* 70000 and this value agreed well with that determined in the present study (*cf.* Chapter 3 for purification and molecular weight determination).

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01% . The cell was calibrated by the method of Lind and co-workers³² using aqueous potassium chloride solution. The measurements were made in a water bath maintained within $\pm 0.005\text{ K}$ of the desired temperature. The details of the experimental procedure have been described earlier.^{33,34} Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results. The overall reproducibility of the conductance measurements was always found to be within $\pm 0.025\%$. Due correction was made for the specific conductance of the solvent by subtracting the specific conductance of the relevant solvent medium from those of the polyelectrolyte solutions.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

4.3 Results and Discussion

4.3.1 Experimental Equivalent Conductivity

The experimental equivalent conductivities for sodium polystyrenesulphonate as a function of the square root of the polymer concentration in four different 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 are shown in Figures 4.1 to 4.4. The equivalent conductivities exhibit, in general, a slight and monotonous increase with decreasing polymer concentration passing through a maximum in some cases within the concentration range investigated here. The experimental error associated with the measurements was found to be within $\pm 0.10\%$ which is always smaller than the concentration variation of the measured equivalent conductivities.

The effects of temperature and relative permittivity on the equivalent conductivity values are also evident from these figures. At each mass percent of 2-ethoxyethanol in 2-ethoxyethanol–water mixture, the Λ values are found to increase with increasing temperature over the entire concentration range investigated. This is quite expected because as the relative permittivity of the medium increases, interaction between polyion and counterions decreases which results in a higher mobility of the conducting species and hence the polyelectrolyte as a whole. Increasing temperature, on the other hand, is expected to increase the mobility as manifested in these figures.

4.3.2 Comparison with Manning Counterion Condensation Theory

Now we will compare the experimental values of equivalent conductivity with those calculated using the Manning counterion condensation theory, Eqs. (2) to (4). In order to calculate the theoretical equivalent conductivities, the required values for the limiting equivalent conductivity of the counterion, λ_c^0 in 10, 25, 40 and 50 mass percent of 2-ethoxyethanol mixtures were also measured and are given in Table 4.1. The charge density parameters, ξ , were calculated using a segment length²¹ of 2.52 \AA having one charged group and these are included in Table 4.2. The theoretical values of λ_p and hence of Λ , are dependent on a , the radius of the polyion cylinder. Obviously, the assignment of a cylindrical radius to any polymer chain can only be a rough approximation at best, but fortunately λ_p is not strongly dependent on a , and change in concentration dependence of λ_p upon varying a between realistic values is small. A cylindrical radius of 8 \AA was used for the present analysis.²¹

A graphical representation of the experimental values (points) along with the theoretical predictions (solid lines) is given in Figure 4.5 at a selected temperature in 2-ethoxyethanol–water mixtures. The experimentally obtained equivalent conductivities have always been found to be considerably higher than the theoretical values calculated using the charge density parameter, ξ , obtained from the molecular structure of the polyelectrolyte, (*cf.* Figure 4.5). The same situation of positive deviation^{35,36} as well as negative deviation^{20,28} from the experimental values was also noticed for other polyelectrolyte solutions. The discrepancy between the experimental and predicted Λ values for sodium polystyrenesulphonate in all 2-ethoxyethanol–water mixtures and at all temperatures investigated is very similar. Lower calculated equivalent conductivities are, therefore, a consequence of Manning theory which predicts too small values for the fraction of uncondensed counterions.

It is interesting to note that the equivalent conductivity calculated here is found to be highly sensitive towards ξ and a semiquantitative description of the experimental data is obtained only if the charge density parameter ξ is decreased from its structural value. The dashed lines in Figure 4.5 display the respective calculation using the optimum values of ξ which provide significant improvement over the Manning results although quantitative fits were not achieved. The charge density parameters, ξ , which describe the experimental results best along with the respective standard deviation of fits are given in Table 4.2. In the case of this flexible polyelectrolyte, this could be rationalized by assuming an “effective charge density parameter” which is lower than the value obtained from the structural data and adjusted to match the experimental data. The reason for a lower effective ξ was sought in the high charge density along the flexible polyion chain due to the higher dissociation of polyion than that predicated by the Manning theory. Hence the overall conductance value is increased. Other possible reasons for the observed differences between the experiment and theory include deviation from the rodlike model due to possible kinking in the structure of the polyelectrolyte, possible polyion-polyion interaction, interaction between the uncondensed counterions and specific interaction between polyion and the counterions.^{11,24,37-39} Another possible reason may be sought in a locally varying relative permittivity. The immediate neighbourhood of the macroion may exhibit a considerably higher relative permittivity than the bulk.⁴⁰ This must necessarily lead to a weaker interaction of the macroion with the counterions as observed in the present investigation. A further possibility is that the Manning theory, based on the assumption of an infinitely long polymer chain model, might be

inadequate for treating condensation phenomena, since in the limit of dilution, it was found that counterion condensation does not occur for polyion of finite length. Finally, it may be pointed out that even the “effective charge density parameter” does not quantitatively reproduce the experimental results indicating that there might be concentration dependent change in the parameter which has not been taken into account in the Manning theory.

4.3.3 Influences of Relative Permittivity and Temperature

The effects of relative permittivity and temperature on the equivalent conductivity values are directly evident from Figures 4.1 to 4.4. At each temperature, the Λ values are found to decrease with decreasing relative permittivity in going from 10 to 50 mass percent 2-ethoxyethanol–water mixtures over the entire concentration range investigated. An increase in temperature, on the other hand, is found to increase the polyelectrolyte solution conductivity in a given solvent medium as manifested in these figures.

At a given temperature, f values are found to decrease as the solvent medium gets richer in 2-ethoxyethanol (Figure 4.6). With the increase in the 2-ethoxyethanol content, the relative permittivity of the medium decreases at a given temperature. Lower relative permittivity promotes greater counterion-binding and hence results in a lower amount of uncondensed counterions in going from 10 to 50 mass percent of 2-ethoxyethanol in the mixed solvent media over the entire range of temperatures investigated.

4.4 Conclusions

Experimental results for the equivalent conductivity of salt-free solutions of an anionic polyelectrolyte, sodium polystyrenesulphonate, in 2-ethoxyethanol–water mixed solvent media have been presented as a function of polymer concentration and temperature. The equivalent conductivities are found to increase with increasing temperature over the entire concentration range investigated in a given mixed solvent medium whereas these values are found to decrease as the relative permittivity of the medium decreases. The conductivity theory, proposed by Manning, for salt-free polyelectrolyte solutions was applied to analyze the experimental data. The measured values of equivalent conductivity cannot be quantitatively described by this theory. Lower calculated equivalent conductivities are a consequence of Manning theory which predicts too small values for the fraction of uncondensed counterions. A semiquantitative description of the experimental data is, however, obtained if the charge density parameter is adjusted to a value lower than the structural value. The deviations indicate higher dissociation of the polyion than that predicted

by the theory, and / or a higher relative permittivity in the vicinity of the polyion chain. Other possible reasons for the observed deviation from the Manning theory have also been discussed. Counterion-binding onto the polyion chain is found to increase as the medium gets richer in 2-ethoxyethanol. The increase in the temperature, in general, has been shown to increase the fraction of uncondensed counterions in each of the mixed solvent medium investigated with minor exception in 10 mass percent 2-ethoxyethanol-water mixture. Finally, it should be pointed out that the Manning law applies only at exceedingly low concentrations which cannot be attained by experiments. Hence, the quantitative conclusion drawn from this law cannot be compared to experimental data in a quantitative manner. This might, however, provide a qualitative guideline.

4.5 References

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Table 4.1 Densities (ρ_0), coefficient of viscosities (η_0) and relative permittivities (D) of 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 and the Corresponding λ_c^0 Values of the Sodium Ion

T (K)	ρ_0 ($\text{g} \cdot \text{cm}^{-3}$)	η_0 ($\text{mPa} \cdot \text{s}$)	D	λ_c^0 ($\text{S} \cdot \text{cm}^2 \cdot \text{Eqv}^{-1}$)
10 mass % 2-ethoxyethanol				
308.15	0.98926	1.3099	69.87	46.63
313.15	0.99287	1.1017	68.13	50.33
318.15	0.99019	0.8961	66.55	52.17
323.15	0.99536	0.8943	65.08	55.47
25 mass % 2-ethoxyethanol				
308.15	0.99758	1.8430	60.13	37.42
313.15	0.99245	1.5293	58.70	40.13
318.15	0.98807	1.2738	57.37	42.87
323.15	0.98394	1.0923	56.11	45.80
40 mass % 2-ethoxyethanol				
308.15	0.99747	1.9545	50.54	29.82
313.15	0.99101	1.7015	49.28	32.04
318.15	0.98696	1.4274	48.14	35.30
323.15	0.98378	1.2317	47.10	38.16
50 mass % 2-ethoxyethanol				
308.15	0.99361	1.9234	44.30	25.61
313.15	0.98514	1.7195	43.03	27.81
318.15	0.98004	1.4552	41.95	31.30
323.15	0.97610	1.2762	40.96	34.26

Table 4.2 Calculated, from Eq. (1), and Best Fitted Charge Density Parameter, ξ , in 2-Ethoxyethanol–Water Mixtures at Temperatures 308.15, 313.15, 318.15, and 323.15 K

Mass % of cosolvent	ξ value							
	T = 308.15 K		T = 313.15 K		T = 318.15 K		T = 323.15 K	
	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)	Cal ^a (sd ^b)	Best Fitted (sd ^b)
10	3.08 (37.43)	1.08 (2.00)	3.11 (40.03)	1.14 (2.73)	3.13 (44.39)	1.12 (3.09)	3.15 (50.78)	1.03 (2.86)
25	3.58 (26.10)	1.19 (1.50)	3.61 (28.11)	1.21 (1.68)	3.63 (33.15)	1.15 (1.63)	3.66 (36.24)	1.15 (1.77)
40	4.26 (16.90)	1.48 (1.33)	4.30 (18.15)	1.50 (0.77)	4.33 (22.06)	1.42 (0.72)	4.36 (23.58)	1.44 (1.27)
50	4.86 (12.14)	1.74 (0.62)	4.92 (14.65)	1.64 (0.17)	4.97 (15.28)	1.74 (1.37)	5.01 (19.41)	1.58 (1.33)

^a Obtained assuming fully stretched polyion.

^b Standard deviation of fit.

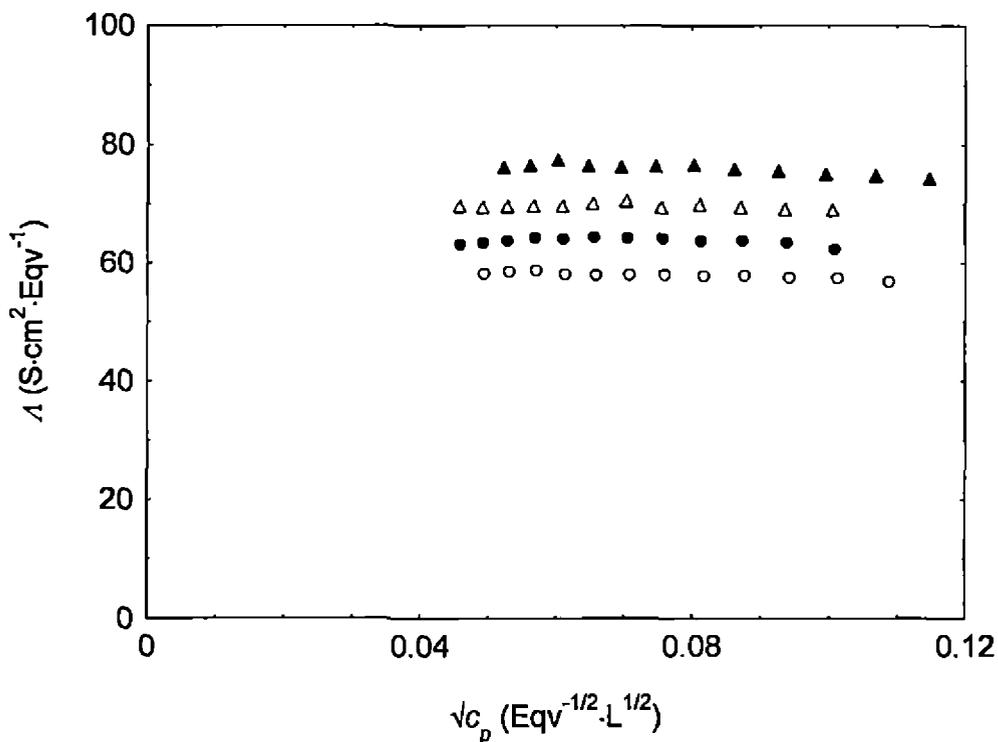


Figure 4.1 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 10 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

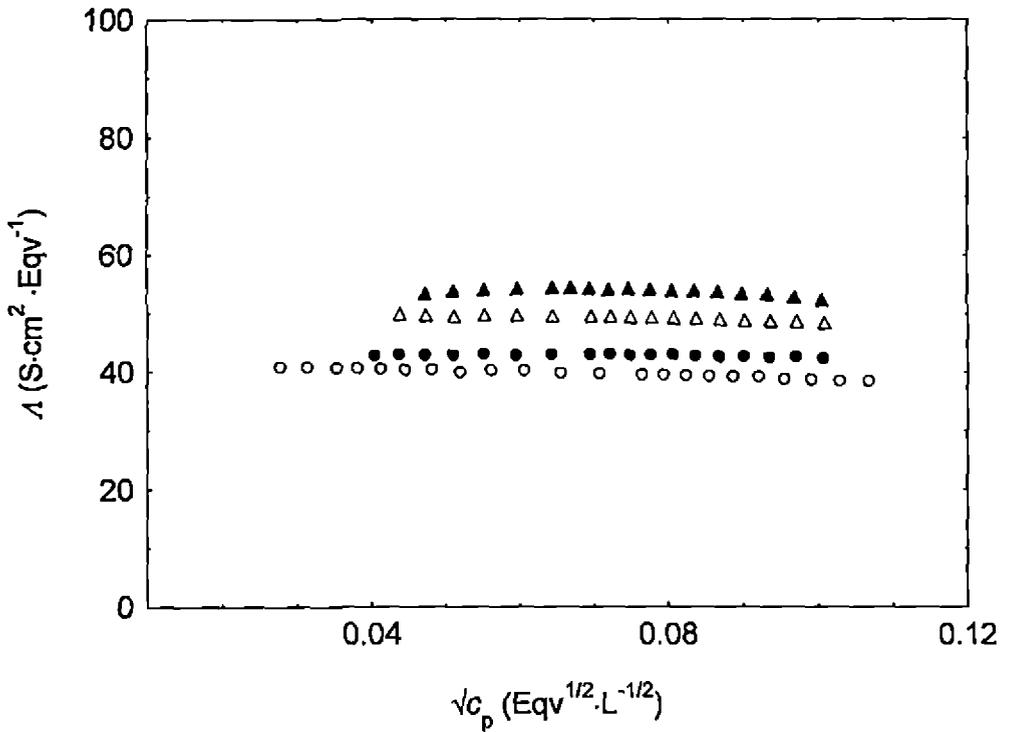


Figure 4.2 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

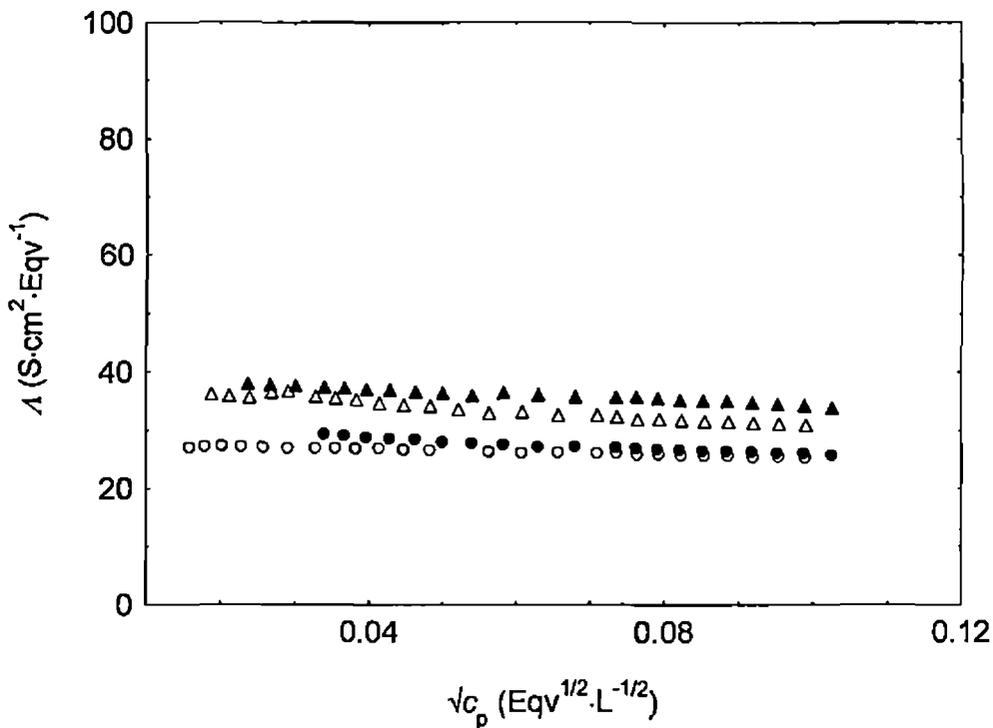


Figure 4.3 Equivalent conductivities (λ) of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

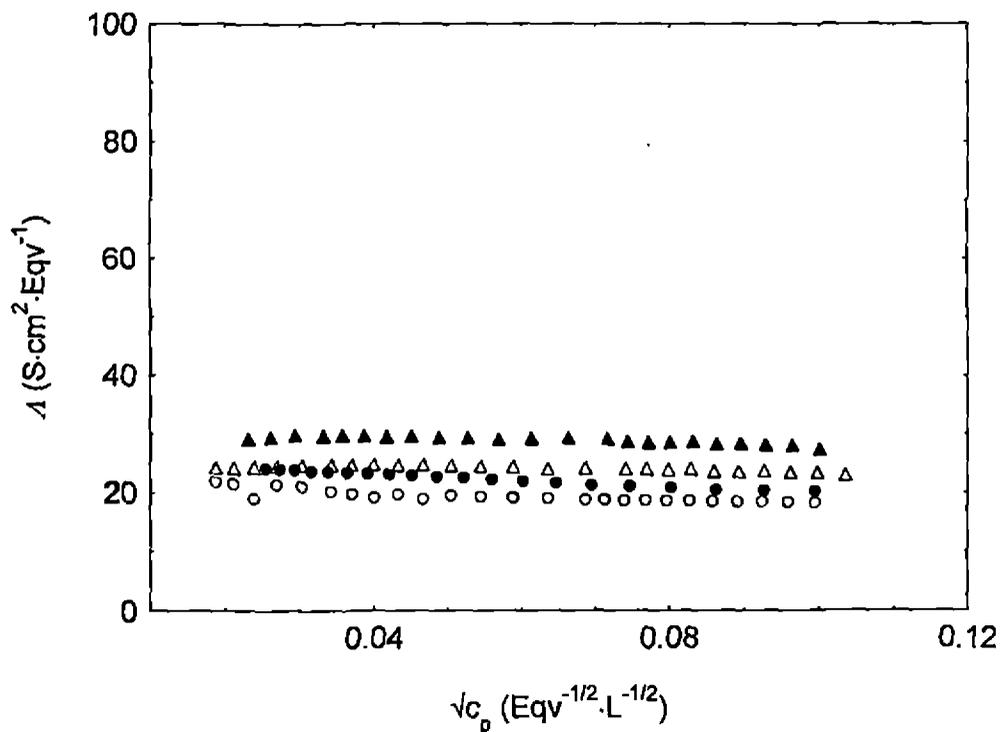


Figure 4.4 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 50 mass percent 2-ethoxyethanol–water mixture as a function of the square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles).

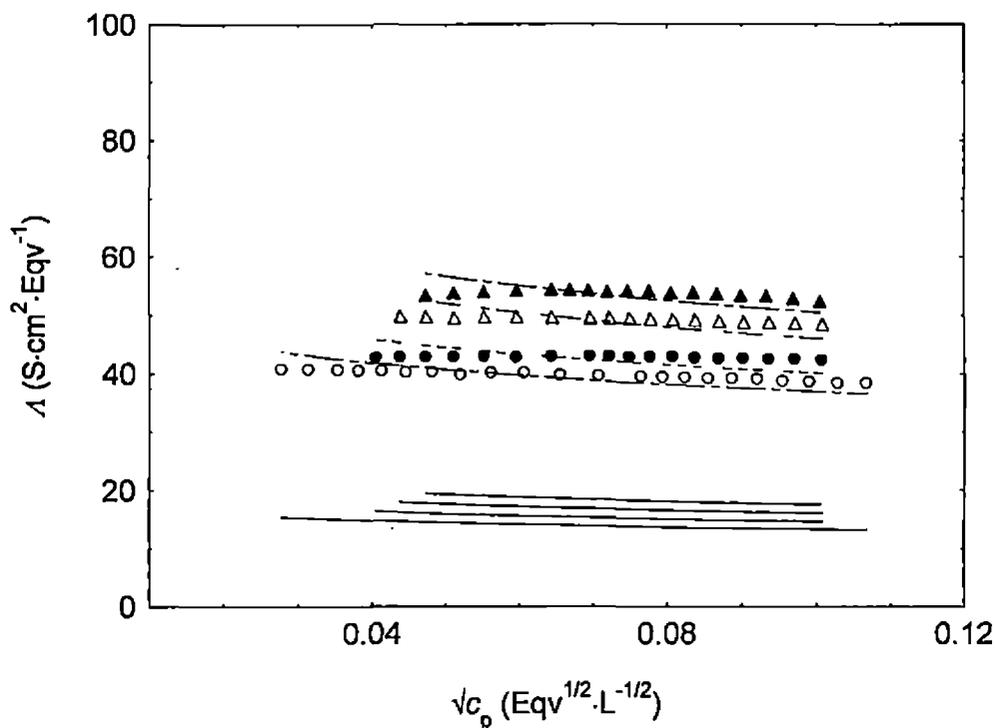


Figure 4.5 Equivalent conductivities (Λ) of sodium polystyrenesulphonate in 25 mass percent 2-ethoxyethanol–water mixture as a function of square root of the polymer concentration ($\sqrt{c_p}$) at 308.15 (open circles), 313.15 (closed circles), 318.15 (open triangles) and 323.15 K (closed triangles) along with those predicted by the Manning counterion condensation theory (continuous lines) and those obtained using the effective charge density parameter (broken lines) as described in the text.

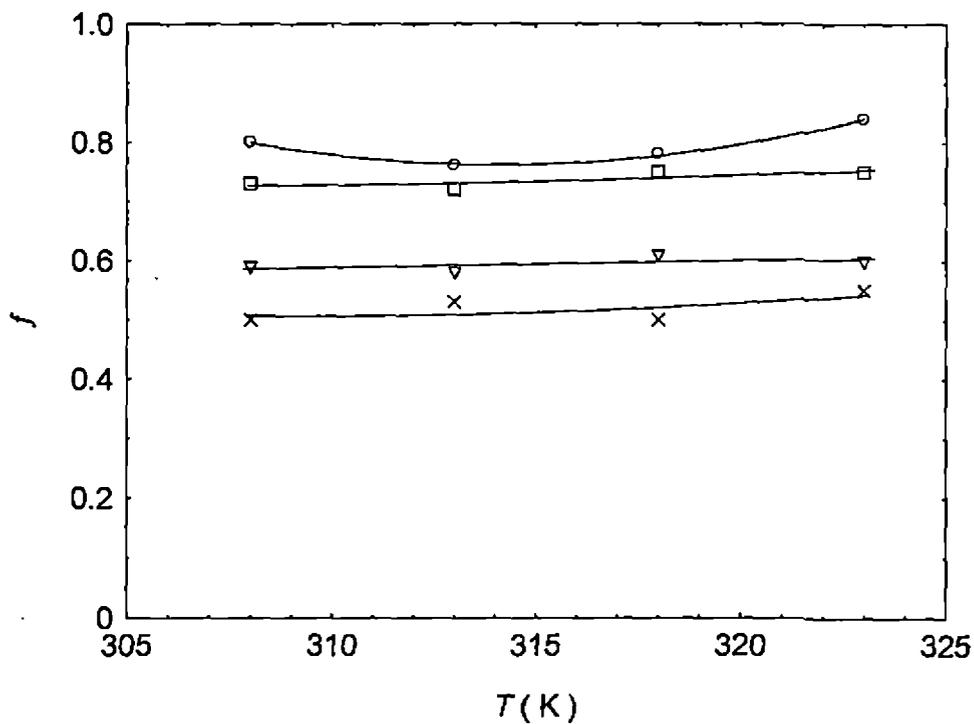


Figure 4.6 Fractions of uncondensed counterions of sodium polystyrenesulphonate in 2-ethoxyethanol-water mixtures as a function of the temperatures in 10 (open circle), 25 (square), 40 (triangle) and 50 (cross) mass percent of 2-ethoxyethanol.