Chapter 7

Intrinsic Viscosities of Sodium Polystyrenesulphonate in 2-Ethoxyethanol–Water Mixed Solvent Media Using the Isoionic Dilution Method

7.1 Introduction

In discussing the conformation of a single polymer chain from viscometric data, information about the intrinsic viscosity $[\eta]$ is indispensable. Because of the presence of electric charges along the polymer chains in polyelectrolytes, the behaviour of these species in solutions is entirely different from that of the uncharged (neutral) polymers and these are characterized by complex interactions, conformations, structures and dynamics.[1-4] It is thus not surprising that although the experimental determination of the intrinsic viscosity $[\eta]$ of uncharged polymers is rather straightforward, that of salt-free polyelectrolyte solutions or of polyelectrolyte solutions with small amount of added salts presents a great challenge.

In case of uncharged polymer solutions, the reduced viscosity (η_{sp}/c_p; η_{sp} = specific viscosity and c_p = polymer concentration) varies linearly with concentration c_p in dilute solutions which led Huggins to propose the following equation[2,5]

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

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behaviour of the polymer molecules in solution and k_H is the Huggins constant which is a characteristic for a given polymer-solvent system. This well-known relation has been extensively used for determining the intrinsic viscosity of uncharged polymers simply by extrapolating η_{sp}/c_p vs. c_p values to $c_p = 0$. On the other hand, the reduced viscosity of salt-free polyelectrolyte solutions exhibits an anomalous behaviour.

Early investigations appeared to suggest a monotonous increase in the reduced viscosity of polyelectrolyte solutions with no-added salt as one lowers the polyion concentration.[6,7] In

these studies, which are summarized in the pioneering work of Fuoss,[6,7] a straight line is obtained when the reciprocal of reduced viscosity is plotted as a function of the square root of the polyelectrolyte concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the reciprocal intrinsic viscosity. However, careful investigations on the dilute solution behaviour revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum, and normal polymer behaviour is recovered as the polyelectrolyte concentration approaches zero. Thus, the method of Fuoss could not be employed to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in polyelectrolyte history. It has been argued that the maximum in the η_{sp}/c_p vs. c_p profiles results from a competition between screening of electrostatic interactions and decreasing intermolecular distances. At the maximum, the pair potential attains its maximum value – it decreases upon dilution because of an increase in intermolecular distances and it 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 polyelectrolyte concentration and, therefore, was close to the limit of the accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations below the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

Isoionic dilution[8,9] is the most straightforward method for the determination of the intrinsic viscosity of a polyelectrolyte in solution. In accordance with this method, a polyelectrolyte solution in the pure solvent (in absence of any low-molar mass salt) is diluted with solutions of increasing concentration of a salt. The dilution of the solution is performed in such a way that after each addition of the salt solution, the total ionic strength of the solution remains the same and equal to the original value due to the polyelectrolyte alone. The remarkable fact about the isoionic dilution is that under these circumstances the reduced viscosity decreases linearly as one lowers the polyelectrolyte concentration and thus extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength, *i.e.*, at each of the polyelectrolyte concentration where isoionic dilution were performed. 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.

Despite the success of this method for the determination of intrinsic viscosity of polyelectrolytes in solution in a convenient manner, very little attention has been paid in this direction.[8-13]

The principal objective of the present contribution is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium polystyrenesulphonate in aqueous and binary aqueous 2-ethoxyethanol mixed solvent media. Further, the influences of the medium and the total ionic strength on the counterion condensation behaviour and on the changes in the conformation, if any, of the polyion will also be investigated.

7.2 Experimental

Sodium polystyrenesulphonate 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).

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 g·cm^{-3} and a coefficient of viscosity as 1.8277 mPa·s at 298.15 K ; these values are in good agreement with the literature values.[14] For the preparation of the mixed solvents, triply distilled water with a specific conductance less than 10^{-6} S·cm^{-1} at 308.15 K was used.

The viscometric measurements were performed at the experimental temperature using a Schultz-Immergut-type viscometer[15] 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 ±0.01 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.[16,17] 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.

The reduced viscosity is obtained from

$$\frac{\eta_{sp}}{c_p} = \frac{t - t_0}{t_0} \frac{1}{c_p} \tag{2}$$

where t and t_0 are the measured flow times of the polyelectrolyte solution and of the pure solvent, respectively.

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.

7.3 Results and Discussion

7.3.1 Dependence of Reduced Viscosity with Polyelectrolyte Concentration

The typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free sodium polystyrenesulphonate solution in water at 308.15 K and in 2-ethoxyethanol–water mixtures containing 10 mass percent of 2-ethoxyethanol at 318.15 K are shown in Figures 1 and 2 respectively. In the absence of an added salt, the reduced viscosity is found to increase as the polyelectrolyte concentration decreases, for all the systems investigated here, bending up at low concentrations thus manifesting the typical polyelectrolyte behaviour. No maximum was, however, detected in the η_{sp}/c_p versus c_p profiles within the concentration range studied here.

7.3.2. Isoionic Dilution

Isoionic dilution was proposed to avoid the conformational change of the polyion thus eliminating the anomalous polyelectrolyte behaviour and to determine the intrinsic viscosity of the polyelectrolyte solution.[8-13] Since intrinsic viscosity is a parameter which enables characterization of dimension and configuration of a polymer, this may play a crucial role in the discussion of polyelectrolyte behaviour in dilute solutions.

We have performed isoionic dilution on sodium polystyrenesulphonate solutions at three different polyelectrolyte concentrations (0.0033, 0.0054 and 0.0080 Eqv·L^{-1}) using NaCl 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. The representative figures (Figures 1

and 2) also include the experimental data for isoionic dilution for the three different polyelectrolyte concentrations.

The reduced viscosity values as functions of polyelectrolyte concentration resulting from the isoionic dilution are found to decrease linearly as we lower the polyelectrolyte concentration and hence extrapolation to reasonable values for the intrinsic viscosity becomes possible for each value of the total ionic strength using the well-known Huggins equation[2,5] [Eq. (1)].

From the present experimental η_{sp}/c_P versus c_P data, the intrinsic viscosities and the Huggins constants have been determined by the method of least-squares using Eq. (1) and these are listed in Table 7.1.

7.3.3. Solvodynamic and Thermodynamic Behaviour

From Table 7.1 and Figures 7.3 to 7.8, it is apparent that the intrinsic viscosities and the Huggins constants for the present polyelectrolyte system vary with the total ionic strength, the medium and the experimental temperature. This observation, thus, indicates that the polyelectrolyte sodium polystyrenesulphonate differs quite appreciably in its solvodynamic and thermodynamic behaviours under varying conditions.

7.3.3.1. Variation of the Intrinsic Viscosity with the Solvent Medium at a Given Temperature and a Given Polyelectrolyte Concentration

At a given temperature and at a given polyelectrolyte concentration, the intrinsic viscosities are found to decrease as the medium becomes richer in 2-ethoxyethanol (Table 7.1 and Figure 7.3). With the addition of 2-ethoxyethanol to water, the relative permittivity of the medium decreases which results in a greater counterion condensation onto the polyion chain as the medium becomes richer in 2-ethoxyethanol. Greater counterion condensation leads to a smaller effective charge on the polyion with a concomitant reduction in the size of the polyion.

7.3.3.2. Variation of Intrinsic Viscosity with Temperature in a Given Solvent Medium and a Given Polyelectrolyte Concentration

In a given solvent medium and at a given polyelectrolyte concentration, the intrinsic viscosity is found to decrease with increasing temperature (Table 1 and Figure 7.5). With the increase of temperature, an expansion of the polyion chain is expected. On the other hand, an increase in temperature should also cause a reduction in the relative permittivity of the medium

leading to a contraction of the polyion chain due to more counterion condensation. The present observation indicates that the later effect predominates over the former in controlling the intrinsic viscosity of the polyelectrolyte as a function of temperature in a given solvent medium.

7.3.3.3. Variation of Huggins Constant with Solvent Medium at a Given Temperature and a Given Polyelectrolyte Concentration

At a given temperature and at a given polyelectrolyte concentration, the Huggins constants are found to increase as the medium becomes richer in 2-ethoxyethanol (Table 7.1 and Figure 7.4). This clearly demonstrates that the solvent medium becomes poorer towards the polyelectrolyte with the addition of 2-ethoxyethanol to water at a given temperature and at a given polyelectrolyte concentration. This is consistent with the general view that high k_H values are the characteristics of the poor solvents.[16]

7.3.3.4. Variation of Huggins Constants with Temperature in a Given Solvent Medium and a Given Polyelectrolyte Concentration

In a given solvent medium and at a given polyelectrolyte concentration, the Huggins constant value are found to increase with increasing temperature (Table 7.1 and Figure 7.6). This is an indication of the fact that the medium becomes poorer with increasing temperature and is consistent with the view pointed out in section 7.3.3.3.

7.3.4. Temperature Dependence of the Huggins Constants

The temperature dependence of the Huggins constant values can be conveniently described by the following equation:

$$k_H = Ae^{-B/T} \tag{3}$$

The values of the constants A and B, obtained by the method of least-squares analysis, along with the correlation coefficients of fits (as r^2) are listed in Table 7.2.

7.4. Conclusions

The present investigation reported the 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. The intrinsic viscosities of the polyelectrolyte solutions were obtained through isoionic dilution maintaining the total ionic strengths of the solutions at polyelectrolyte concentrations 0.0033, 0.0054, and 0.0080 $Eqv \cdot L^{-1}$ with sodium chloride. The Huggins constants were also obtained from the experimental results. The influences of the medium and the temperature on the intrinsic viscosities as well as on the Huggins constants have been interpreted in order to elucidate the solvodynamic and thermodynamic interactions occurring in solution.

7.5 References

1.   F. Oosawa, In *Polyelectrolytes*, Marcel Dekker, New York (1993).

2.   H. Dautzenberg, W. Jaeger, J. Koetz, B. Philipp, C. Seidel, and D. Stscherbina, *In Polyelectrolytes: Formation, Characterization and Application*, Hanser Publishers, Munich, Chapter 5 (1994).

3.   K. S. Schmitz (Ed.), *Macro-ion Characterization. From Dilute Solutions to Complex Fluids*. ACS Symposium Series 548, American Chemical Society, Washington DC (1994).

4.   J. Cohen and Z. Priel, *Trends in Macromol. Res.*, **1**, 201 (1994).

5.   H. L. Huggins, *J. Phys. Chem.* **42**, 911 (1938).

6.   R. M. Fuoss, *J. Polym. Sci.*, **3**, 603 (1948).

7.   R. M. Fuoss, *J. Polym. Sci.*, **4**, 96 (1949).

8.   D. T. E. Pals and J. J. Hermans, *J. Polym. Sci.*, **5**, 773(1950).

9.   D. T. E. Pals and J. J. Hermans, *Rec. Trav. Chim. Pays-Bas*, **71**, 458 (1952).

10. I. Roure, M. Rinaudo and M. Milas, *Ber Bunsenges Phys. Chem.*, **100**, 703 (1996).

11. M. Moan, *Thesis*, University of Brest, France, (1976).

12. P. Nandi, A. Bhattarai and B. Das, *J. Polym. Sci., Polym. Phys. Ed.*, **45**, 1765 (2007).

13. R. Sharma, B. Das, P. Nandi and C. Das, *J. Polym. Sci., Polym. Phys. Ed.*, **48**, 1196 (2010).

14. G. Douheret and A. Pal, *J. Chem. Eng. Data*, **33**, 40 (1988).

15. J. Schulz and E. H. Immergut, *J. Polym. Sci.*, **9**, 279 (1952).

16. B. Das and D. K. Hazra, *Bull. Chem. Soc. Jpn.*, **65**, 3470 (1992).

17. B. Das and D. K. Hazra, *J. Phys. Chem.* **99**, 269 (1995).

Table 7.1 Intrinsic Viscosities $[\eta]$, Huggins Constants k_H, and the Correlation Coefficients of Fits (as r^2) of Sodium Polystyrenesulphonate in Water and 2-Ethoxyethanol–Water Mixtures Containing 10, 25, 40, and 50 mass percent of 2-Ethoxyethanol at the Polyelectrolyte Concentrations where Isoionic Dilution was performed at 308.15, 313.15, 318.15, and 323.15 K

T (K)	Mass % of Cosolvent	c_p (Eqv·L^{-1})	$[\eta]$ (L·Eqv^{-1})	k_H	r^2
308.15	0	0.0033	43.7 ± 0.3	4.52 ± 0.09	0.997
		0.0054	40.0 ± 0.2	1.68 ± 0.04	0.995
		0.0080	35.6 ± 0.3	1.02 ± 0.05	0.980
	10	0.0033	37.9 ± 0.1	6.08 ± 0.06	0.999
		0.0054	35.9 ± 0.2	2.28 ± 0.05	0.996
		0.0080	30.8 ± 0.1	1.45 ± 0.04	0.995
	25	0.0033	34.4 ± 0.3	7.52 ± 0.13	0.997
		0.0054	31.8 ± 0.1	2.83 ± 0.07	0.995
		0.0080	28.8 ± 0.2	1.46 ± 0.07	0.979
	40	0.0033	32.7 ± 0.2	7.61 ± 0.12	0.998
		0.0054	29.8 ± 0.2	3.05 ± 0.06	0.996
		0.0080	26.6 ± 0.3	1.59 ± 0.11	0.963
	50	0.0033	31.7 ± 0.2	7.65 ± 0.18	0.996
		0.0054	26.8 ± 0.4	3.69 ± 0.21	0.974
		0.0080	24.4 ± 0.2	1.81 ± 0.07	0.988
313.15	0	0.0033	41.2 ± 0.2	5.15 ± 0.07	0.999
		0.0054	38.9 ± 0.2	1.78 ± 0.04	0.996
		0.0080	34.1 ± 0.2	1.13 ± 0.04	0.990
	10	0.0033	36.8 ± 0.2	6.51 ± 0.09	0.998
		0.0054	34.5 ± 0.2	2.38 ± 0.06	0.995
		0.0080	30.0 ± 0.2	1.52 ± 0.05	0.990
	25	0.0033	33.7 ± 0.3	7.89 ± 0.17	0.996
		0.0054	31.2 ± 0.2	3.00 ± 0.06	0.997
		0.0080	28.2 ± 0.3	1.57 ± 0.06	0.986
	40	0.0033	31.5 ± 0.3	7.94 ± 0.19	0.996
		0.0054	28.7 ± 0.2	3.11 ± 0.08	0.994
		0.0080	25.6 ± 0.2	1.62 ± 0.09	0.986
	50	0.0033	30.2 ± 0.3	7.99 ± 0.19	0.995
		0.0054	25.9 ± 0.2	3.73 ± 0.09	0.996
		0.0080	23.4 ± 0.1	1.90 ± 0.05	0.994
318.15	0	0.0033	39.3 ± 0.1	5.83 ± 0.06	0.999
		0.0054	37.4 ± 0.2	2.01 ± 0.06	0.993
		0.0080	32.8 ± 0.2	1.25 ± 0.05	0.985
	10	0.0033	35.7 ± 0.2	6.87 ± 0.10	0.998
		0.0054	33.4 ± 0.2	2.57 ± 0.06	0.996
		0.0080	29.2 ± 0.3	1.64 ± 0.08	0.980

Table 7.1 (Continued)

T (K)	Mass % of Cosolvent	c_p (Eqv·L^{-1})	$[\eta]$ (L·Eqv^{-1})	k_H	r^2
	25	0.0033	32.4 ± 0.3	7.93 ± 0.30	0.989
		0.0054	30.7 ± 0.2	3.08 ± 0.06	0.995
		0.0080	27.0 ± 0.1	1.66 ± 0.07	0.985
	40	0.0033	31.0 ± 0.3	7.97 ± 0.15	0.997
		0.0054	28.0 ± 0.3	3.22 ± 0.10	0.992
		0.0080	25.1 ± 0.2	1.68 ± 0.08	0.982
	50	0.0033	28.9 ± 0.3	8.07 ± 0.22	0.994
		0.0054	24.8 ± 0.3	3.88 ± 0.15	0.989
		0.0080	21.9 ± 0.1	2.15 ± 0.06	0.994
323.15	0	0.0033	38.1 ± 0.3	5.93 ± 0.12	0.997
		0.0054	35.9 ± 0.2	2.08 ± 0.06	0.993
		0.0080	31.3 ± 0.2	1.32 ± 0.05	0.987
	10	0.0033	34.1 ± 0.2	6.89 ± 0.14	0.997
		0.0054	32.1 ± 0.2	2.60 ± 0.08	0.992
		0.0080	28.0 ± 0.2	1.65 ± 0.04	0.994
	25	0.0033	31.1 ± 0.3	7.98 ± 0.16	0.997
		0.0054	30.3 ± 0.1	3.18 ± 0.05	0.997
		0.0080	26.7 ± 0.2	1.70 ± 0.08	0.984
	40	0.0033	30.2 ± 0.3	8.05 ± 0.15	0.997
		0.0054	27.3 ± 0.2	3.33 ± 0.09	0.994
		0.0080	24.2 ± 0.2	1.91 ± 0.08	0.986
	50	0.0033	27.6 ± 0.3	8.13 ± 0.24	0.995
		0.0054	23.6 ± 0.2	3.91 ± 0.15	0.992
		0.0080	20.7 ± 0.1	2.64 ± 0.06	0.996

Table 7.2 Parameters of Eq. (2) and the Correlation Coefficients of Fits (as r^2) for Sodium Polystyrenesulphonate in Water, 10, 25, 40, and 50 mass percent 2-Ethoxyethanol–Water Mixtures

| Mass % of Cosolvent	c_p (Eqv·L^{-1})	$\ln A$	B	r^2
0	0.0033	-4.25	-0.019	0.922
	0.0054	-4.18	-0.015	0.958
	0.0080	-5.36	-0.017	0.983
10	0.0033	-0.82	-0.008	0.890
	0.0054	-2.07	-0.009	0.938
	0.0080	-2.48	-0.009	0.922
25	0.0033	0.90	-0.004	0.759
	0.0054	-1.27	-0.007	0.967
	0.0080	-2.77	-0.010	0.956
40	0.0033	0.98	-0.003	0.803
	0.0054	-0.73	-0.006	0.986
	0.0080	-3.17	-0.012	0.840
50	0.0033	0.86	-0.004	0.832
	0.0054	-0.01	-0.004	0.925
	0.0080	-7.19	-0.025	0.928
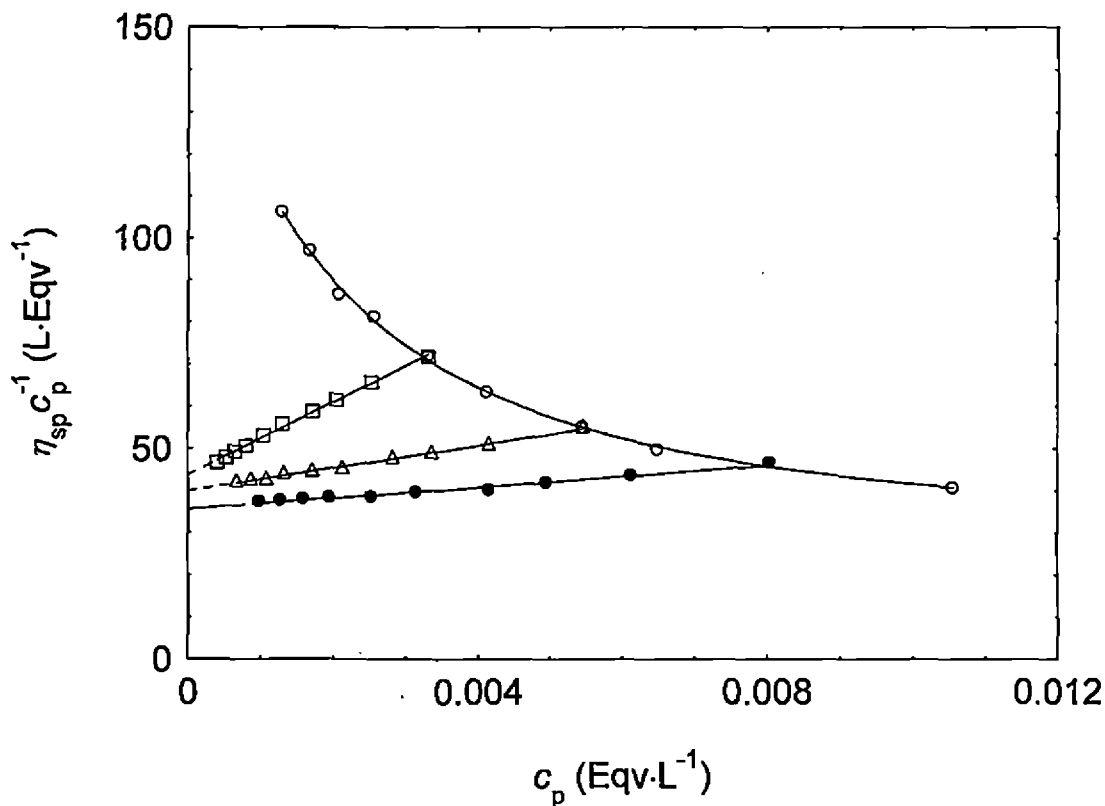
Figure 7.1 The variation of the reduced viscosity for sodium polystyrenesulphonate with polyelectrolyte concentration in water at 308.15 K (o). Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with constant total ionic strengths at polyelectrolyte concentrations 0.0033 ($\square$), 0.0054 ($\triangle$), and 0.0080 ($\bullet$) Eqv·L^{-1}.
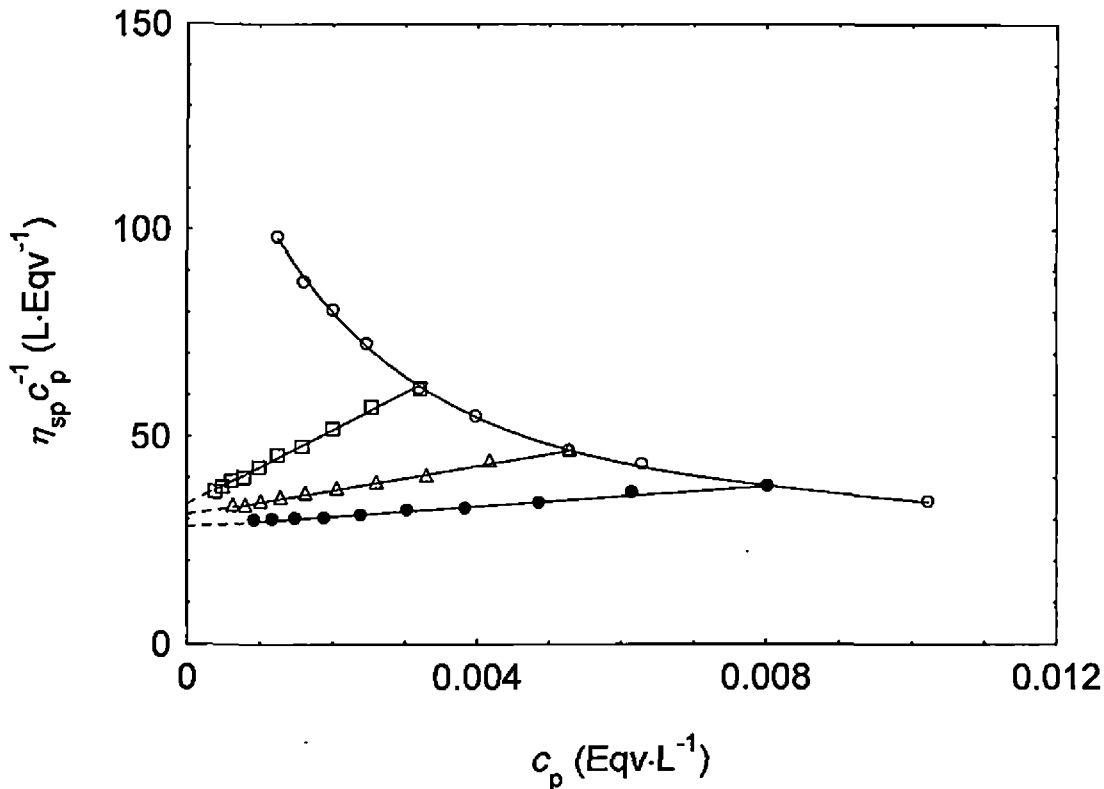
Figure 7.2 The variation of the reduced viscosity for sodium polystyrenesulphonate with polyelectrolyte concentration in 2-ethoxyethanol–water mixture containing 25 mass percent 2-ethoxyethanol at 313.15 K (o). Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with total ionic strengths 0.0033 (□), 0.0054 (Δ), and 0.0080 (•) Eqv·L⁻¹.
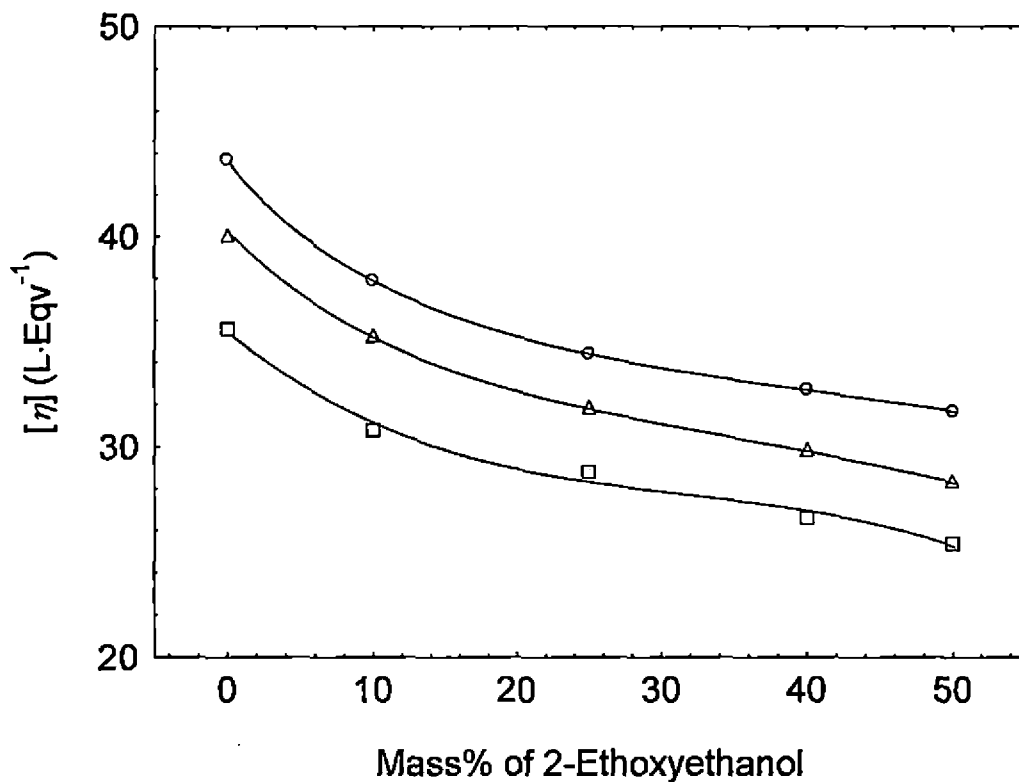
Figure 7.3 The effect of medium on the intrinsic viscosity of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media at 308.15 K obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (o), 0.0054 (△), and 0.0080 (□) $Eqv \cdot L^{-1}$.
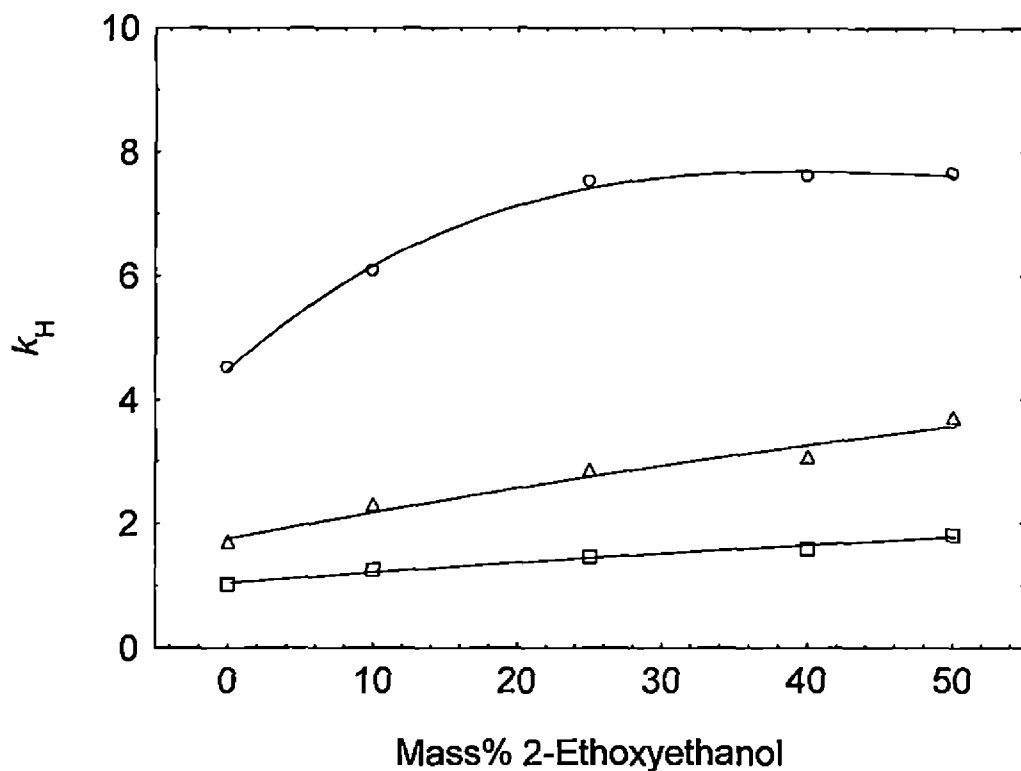
Figure 7.4 The effect of medium on the Huggins constant of sodium polystyrenesulphonate in 2-ethoxyethanol–water mixed solvent media at 308.15 K obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (Δ), and 0.0080 (□) Eqv·L^{-1}.
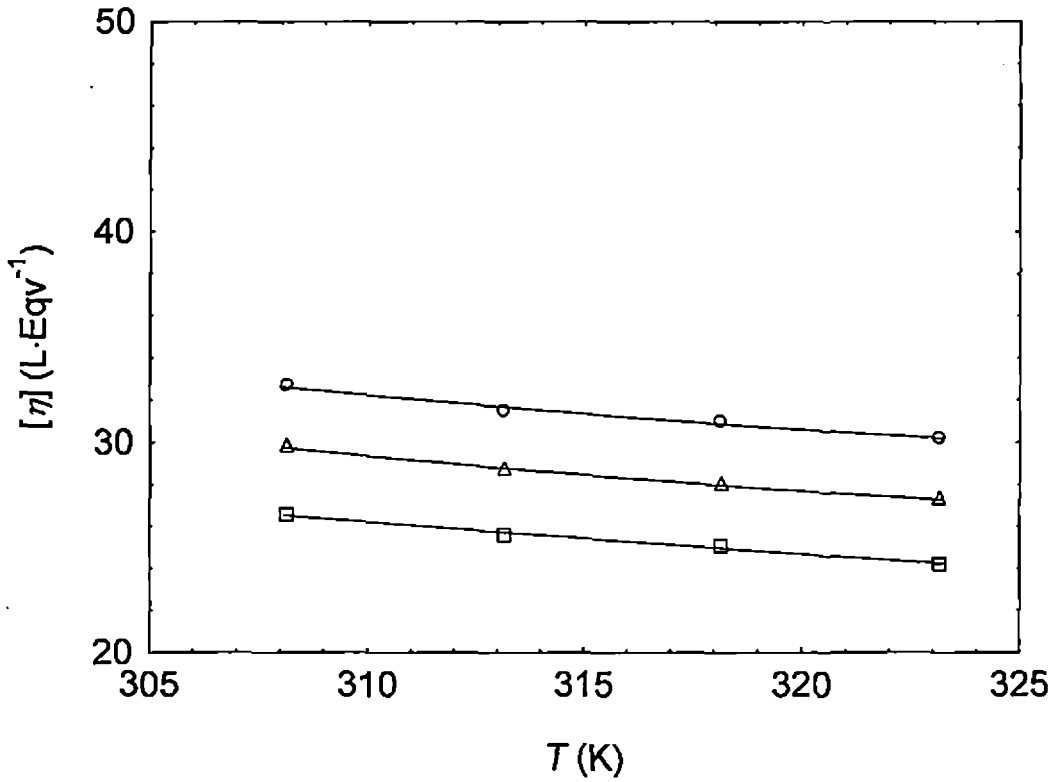
Figure 7.5 The effect of temperature on the intrinsic viscosity of sodium polystyrenesulphonate in 40 mass percent 2-ethoxyethanol–water mixed solvent media obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (o), 0.0054 (△), and 0.0080 (□) Eqv·L⁻¹.
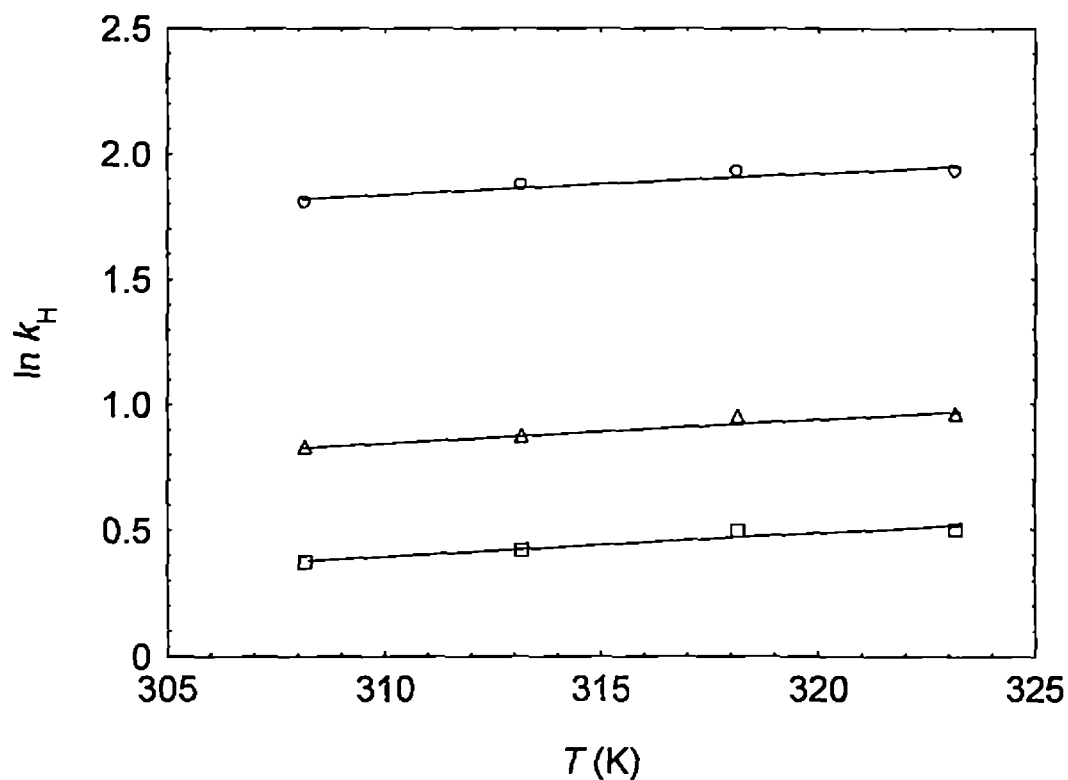
Figure 7.6 The effect of temperature on the Huggins constant of sodium polystyrenesulphonate in 10 mass percent 2-ethoxyethanol–water mixed solvent media obtained by the method of isoionic dilution at polyelectrolyte concentrations 0.0033 (○), 0.0054 (△), and 0.0080 (□) Eqv·L⁻

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