Chapter VI

Intrinsic Viscosities of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixed Solvent Media Using the Isoionic Dilution Method

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 behavior 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 ; $\eta_{sp}=$ specific viscosity and c = polymer concentration) varies linearly with concentration c in dilute solutions which led Huggins to propose the following equation[2,5]

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \tag{1}$$

where $[\eta]$ is the intrinsic viscosity describing the solvodynamic behavior 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 vs. c values to $c = 0$. On the other hand, the reduced viscosity of salt-free polyelectrolyte solutions exhibits an anomalous behavior.

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 behavior revealed that the apparent unbounded rise in the reduced viscosity is always followed by a maximum, and normal polymer behavior 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 vs. c 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. 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.[8-12]

The principal objective of the present contribution is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium polysytrenesulfonate (NaPSS) in acetonitrile-water mixed solvent media. The influences of the medium, total ionic strength, and temperature on the counterion condensation behavior and on the changes in the conformation, if any, of the polyion will also be investigated.

Experimental

Acetonitrile (E. Merck, India, 99%) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 g.cm^{-3} and a co-efficient of viscosity of 0.3126 mPa.s at 308.15 K; these values are in good agreement with the literature values.[13] Triply distilled water with a specific conductance of less than 10^{-6} S.cm^{-1} at 308.15 K was used for the preparation of the mixed solvents.

NaPSS used in these investigations was purchased from Aldrich Chemical. The average molecular weight (M_w) of the sample was $70,000$ with a degree of substitution (DS) of 1, and these values agree well with those obtained from physiochemical characterization in the present study.

The viscometric measurements were performed at 298.15, 308.15, and 318.15 K using a Schultz-Immergut-type viscometer[14] 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 ± 0.005 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.[15,16] 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

$$\frac{\eta_{sp}}{c} = \frac{t - t_0}{t_0} \frac{1}{c} \qquad (2)$$

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.

Results and Discussion

The typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free sodium polystyrenesulfonate solution in acetonitrile-water mixtures with 10, 20, and 40 vol% of acetonitrile at 298.15, 308.15, and 318.15 K are shown, respectively, in Figures 1 to 9. In absence of an added salt, the reduced viscosity is found to increase as the polyelectrolyte concentration decreases, for all systems investigated, bending up at low concentrations thus manifesting the typical polyelectrolyte behavior. No maximum was, however, detected in the η_{sp}/c versus c profiles within the concentration range studied here.

Isoionic dilution was proposed to avoid the conformational change of the polyion thus eliminating the anomalous polyelectrolyte behavior and to determine the intrinsic viscosity of solution.[8-12] As we know that the intrinsic viscosity is the parameter which enables characterization of dimension and configuration of polymer, this may play a crucial role in the discussion of polyelectrolyte behavior in dilute solutions.

Isoionic dilution of sodium polystyrenesulfonate solutions have been performed at two different total ionic strengths (at polyelectrolyte concentrations of 0.0065 and 0.0125 equiv L^{-1}) in acetonitrile-water mixtures containing 10, 20 and 40 vol % of acetonitrile at 298.15, 308.15, and 318.15 K using sodium chloride as the added salt. Figures 1-9 also include the experimental data for the isoionic dilutions.

The reduced viscosity data as functions of polyelectrolyte concentration resulting from the isoionic dilution can be described by the well-known Huggins equation,[2,5] Eq. (1).

From the present experimental η_{sp}/c versus c data, the intrinsic viscosities and the Huggins constants have been determined by the method of least-squares using Eq. (1) and these are displayed in Figures 10 - 13.

Influence of Total Ionic Strength, Medium and Temperature on the Intrinsic Viscosities and the Huggins Constants

The intrinsic viscosities and the Huggins constants for the present polyelectrolyte system vary with the total ionic strength, the medium, and the experimental temperature (*cf.* Table 1 and Figures 10-13). This observation, thus, indicates that the polyelectrolyte NaPSS differs quite appreciably in its solvodynamic and thermodynamic behaviours under varying experimental conditions.[17,18]

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 2.

Influence of Medium

At 298.15, 308.15 and 318.15 K, and at a given value of the total ionic strength, the intrinsic viscosities are found to decrease as the medium becomes richer in acetonitrile (Table 1 and Figure 10). Moreover, the Huggins constants are found to increase with increasing amount of acetonitrile in the mixed solvent media (Table 1 and Figure 11). It is thus apparent that the polyion chain swells differently in different solvents and it would be interesting to relate the intrinsic viscosities to the parameters of thermodynamic affinity of a solvent for a polymer as described by Alfrey *et. al.*[17,18] The above observation demonstrates that the solvent interacts poorly with the polymer (*i.e.*, with less thermodynamic affinity) as the medium gets richer in acetonitrile and hence the polymer-polymer contacts are becoming more probable than the polymer-solvent contacts, and therefore the solvodynamic dimension of the chain will be gradually reduced. This explains both the lower intrinsic viscosity and the higher values of the Huggins constants in a solvent richer in acetonitrile. This is consistent with the general view that high k_H values are the characteristics of the poor solvents.

Influence of Ionic Strength

The intrinsic viscosities are found to decrease as the total ionic strength of the solution increases as reported in Table 1 at a particular solvent composition and at a particular

temperature. Counterion binding onto the polyion chain is considerably enhanced, as the concentration of the ions in the solution increases. This causes more effective screening of the chain charges in high ionic strength solution, decreasing the intramacromolecular electrostatic repulsions (and hence decreasing k_H, cf. Table 1) and resulting in partial coiling of the macromolecules, and hence, in a decrease in the intrinsic viscosity of the solution.

Influence of Temperature

Intrinsic viscosity values are found to increase regularly with temperature a given solvent medium when the total ionic strength is maintained at a constant level (Table 1, and Figure 12). The Huggins constant, on the other hand, decreases with temperature in these cases (Table 1, and Figure 13). This is directly connected to the temperature coefficient of the second Virial coefficient (A_2). The present observation points to the fact that the thermodynamic affinity of the solvent for the polymer (i.e., the polymer-solvent interaction) improves as the temperature rises (i.e., A_2 increases) in a given solvent, and hence the chain expands more resulting in an increase in the intrinsic viscosity values with an elevation of temperature. Increase in the polymer-solvent interaction results in a decrease in the polymer-polymer interaction,[19] manifested by the decreasing Huggins constant values as a function temperature. Studies on the temperature dependence of Huggins constants for polyelectrolytes are, to the best of our knowledge, not available in the literature. However, k_H values reported[18] for a polystyrene sample are found to decrease with the increase in temperature as observed in the present work.

Conclusions

The present chapter reported precise measurements on the viscosities of the solutions of an anionic polyelectrolyte sodium polystyrenesulfonate in acetonitrile–water mixed solvent media containing 10, 20, and 40 vol percent of acetonitrile at 298.15, 308.15, and 318.15 K. The intrinsic viscosities and the Huggins constants of the polyelectrolyte solutions were obtained using the Huggins equation through isoionic dilution whereby maintaining the total ionic strengths at polyelectrolyte concentrations of 0.0065, and 0.0125 equiv L^{-1} with sodium chloride. The influences of medium and the total ionic strength on the intrinsic viscosities have been interpreted in terms of counterion condensation and coiling behaviour in the investigated solutions. The variations of Huggins constants, on the other hand, provided information on the intermolecular interactions.

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Table 1. Intrinsic viscosities $[\eta]$, Huggins Constants k_H, and Correlation Coefficient of Fits (as r^2) of Sodium Polystyrenesulfonate in Acetonitrile-Water Mixtures Aontaining 10, 20, and 40 volume percent of acetonitrile at 298.15, 308.15 and 318.15 K

Vol Percent of acetonitrile in acetonitrile –water mixed media	Polyelectrolyte concentration where isoionic dilutions were performed (equiv L^{-1})	$[\eta]$ (L equiv^{-1})	k_H	r^2
		$T = 298.15$ K		
10	0.0065	11.60 ± 0.09	9.88 ± 0.14	0.9991
10	0.0125	9.43 ± 0.19	6.62 ± 0.26	0.9954
		$T = 308.15$ K		
10	0.0065	12.27 ± 0.22	7.44 ± 0.30	0.9934
10	0.0125	10.06 ± 0.12	4.83 ± 0.13	0.9976
		$T = 318.15$ K		
10	0.0065	13.05 ± 0.22	5.17 ± 0.29	0.9903
10	0.0125	10.68 ± 0.17	3.27 ± 0.18	0.9881
		$T = 298.15$ K		
20	0.0065	9.51 ± 0.13	14.48 ± 0.32	0.9980
20	0.0125	7.75 ± 0.17	10.39 ± 0.33	0.9960
		$T = 308.15$ K		
20	0.0065	10.45 ± 0.20	10.34 ± 0.43	0.9930
20	0.0125	8.41 ± 0.18	7.82 ± 0.31	0.9937
		$T = 318.15$ K		
20	0.0065	11.16 ± 0.11	8.02 ± 0.20	0.9976
20	0.0125	9.12 ± 0.14	5.80 ± 0.21	0.9949
		$T = 298.15$ K		
40	0.0065	8.63 ± 0.23	17.95 ± 0.68	0.9942
40	0.0125	6.46 ± 0.18	16.56 ± 0.53	0.9958

Table 1. continued

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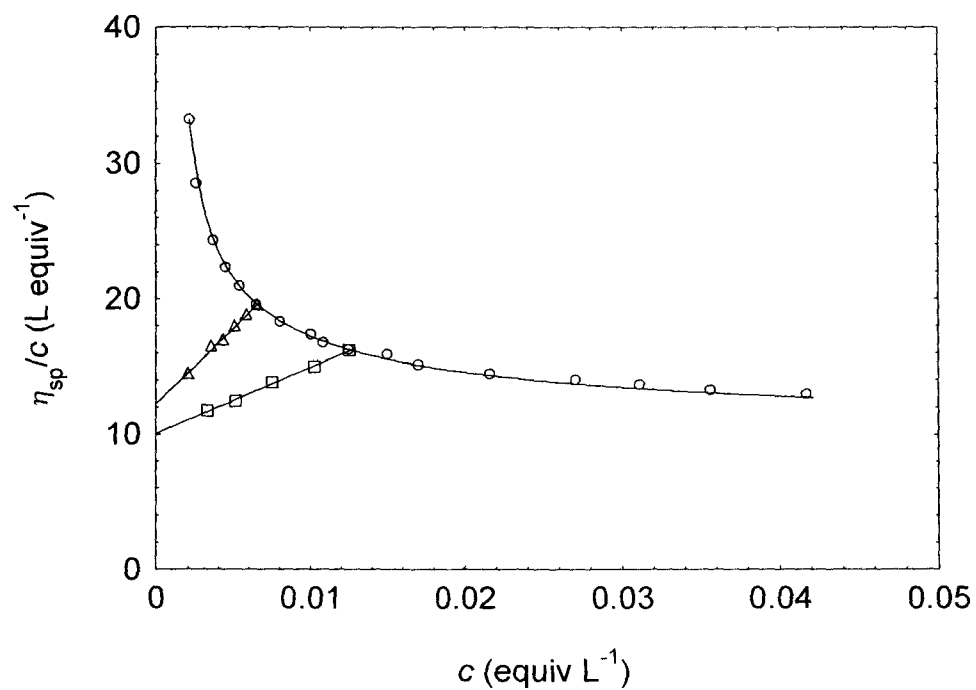|		$T = 308.15$ K		
40	0.0065	9.00 ± 0.15	15.36 ± 0.41	0.9972
40	0.0125	6.98 ± 0.14	13.12 ± 0.36	0.9969
		$T = 318.15$ K		
40	0.0065	9.75 ± 0.20	11.09 ± 0.45	0.9934
40	0.0125	7.56 ± 0.18	10.13 ± 0.40	0.9939

Table 2. Parameters of Eq. (3) and the Correlation Coefficients of Fits (as r^2) for Sodium Polystyrenesulfonate in Acetonitrile-Mater mixtures Containing 10, 20, and 40 vol percent of Acetonitrile

| c (equiv L^{-1})	A	B	r^2
10 Vol Percent of Acetonitrile			
0.0065	0.00048	-2966	0.992
0.0125	0.00013	-3235	0.994
20 Vol Percent of Acetonitrile			
0.0065	0.00097	-2864	0.997
0.0125	0.00109	-2733	0.999
40 Vol Percent of Acetonitrile			
0.0065	0.01410	-2138	0.951
0.0125	0.00749	-2297	0.998
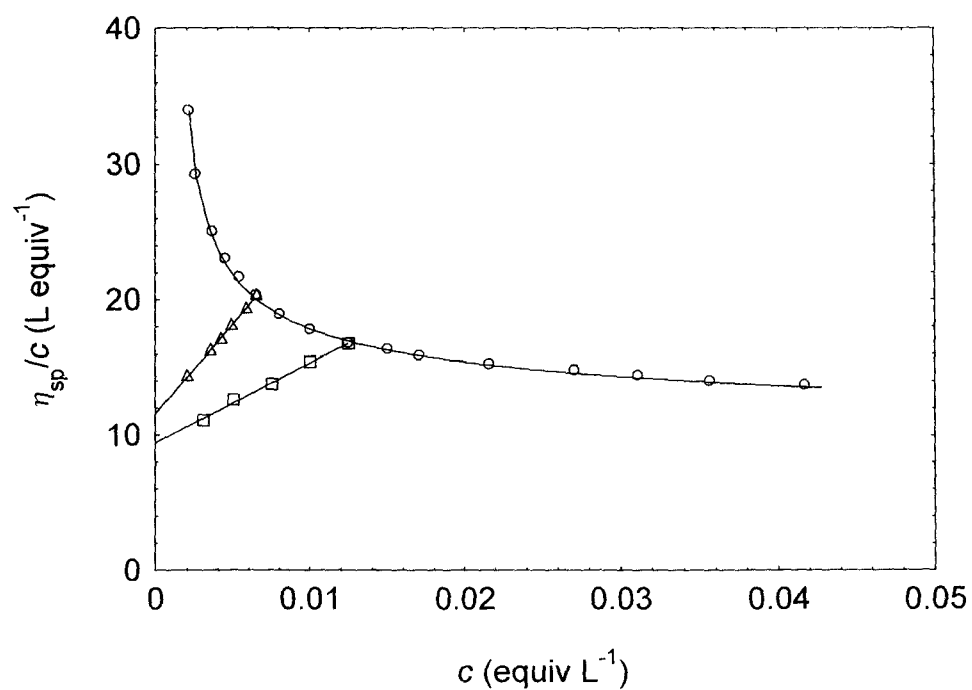
Figure 1. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 298.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} (△), and 0.0125 equiv L^{-1} (□) where isoionic dilutions were performed.
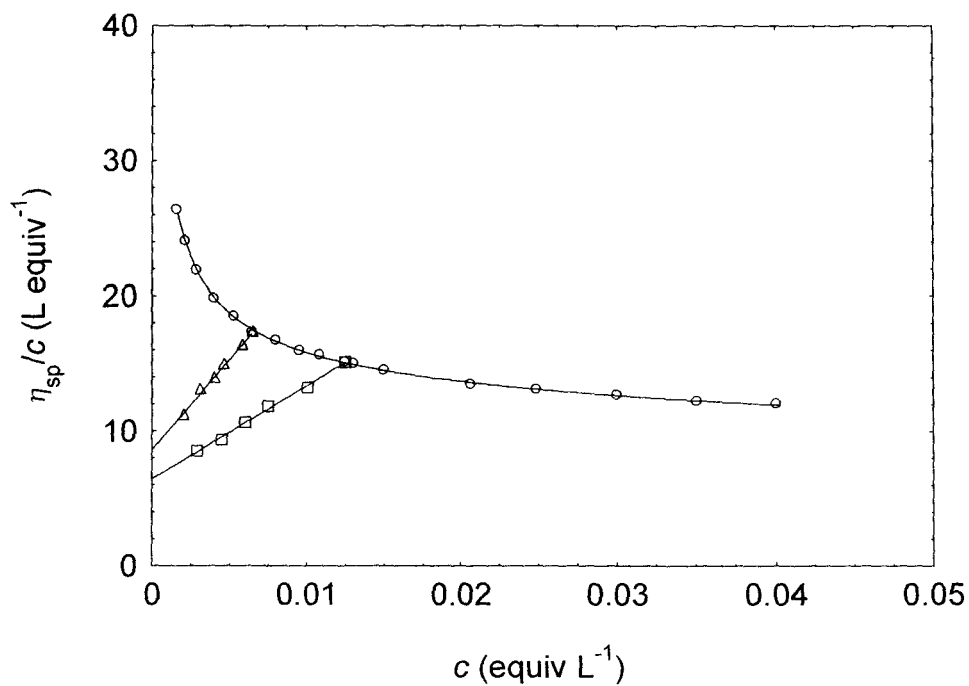
Figure 2. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 308.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.
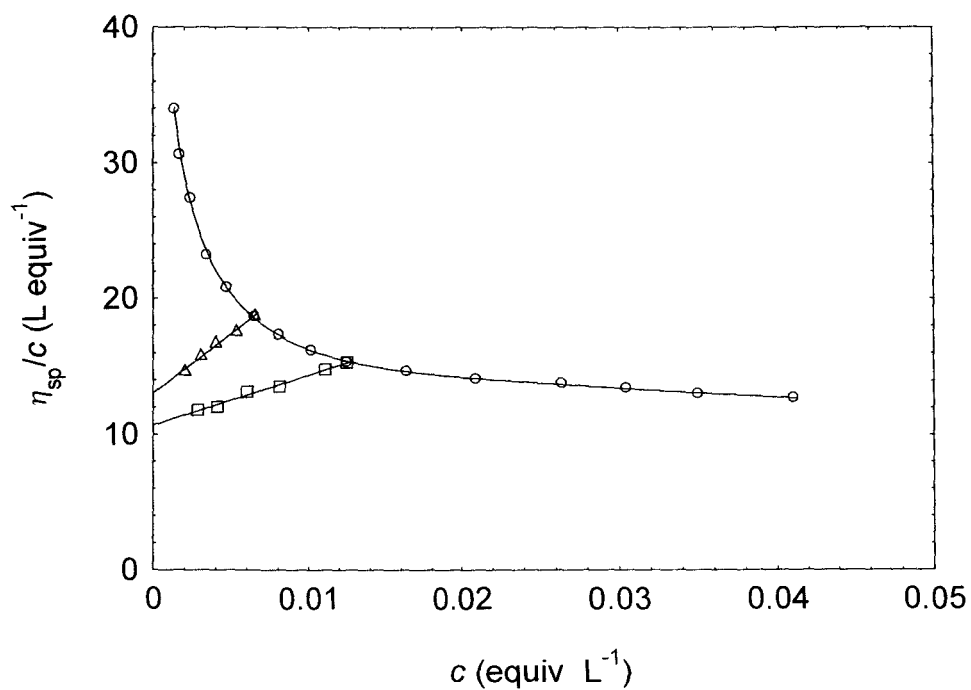
Figure 3. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 10 vol percent acetonitrile-water mixture at 318.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.
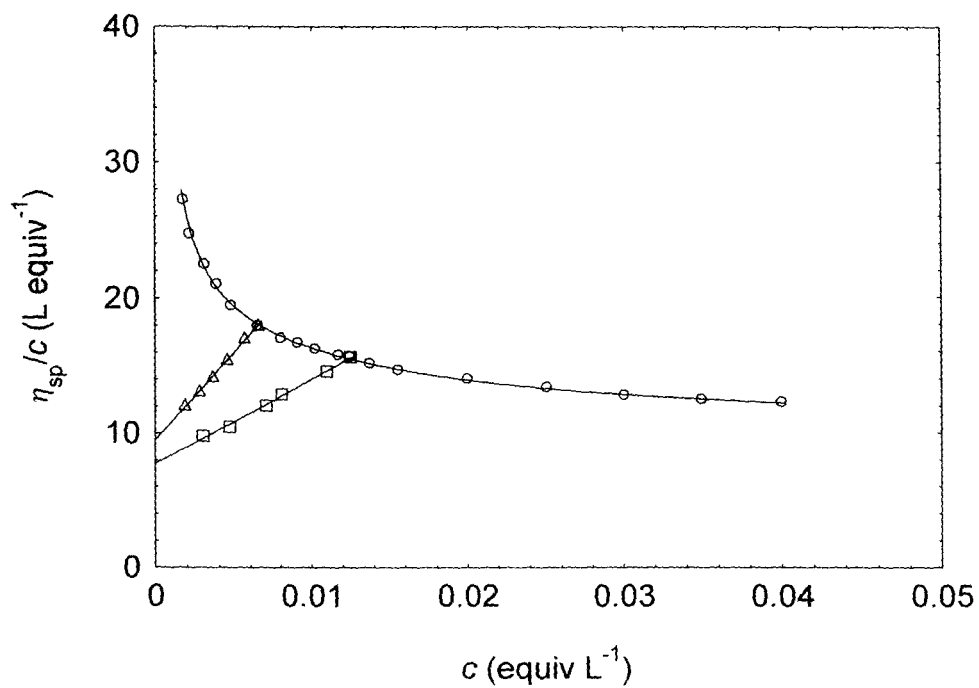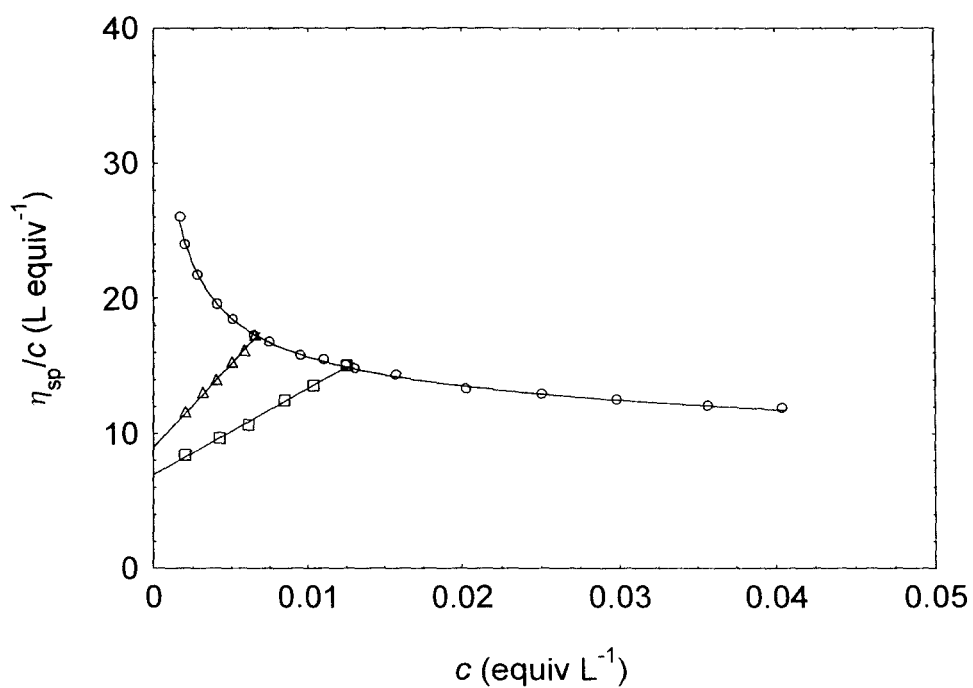
Figure 4. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 298.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.
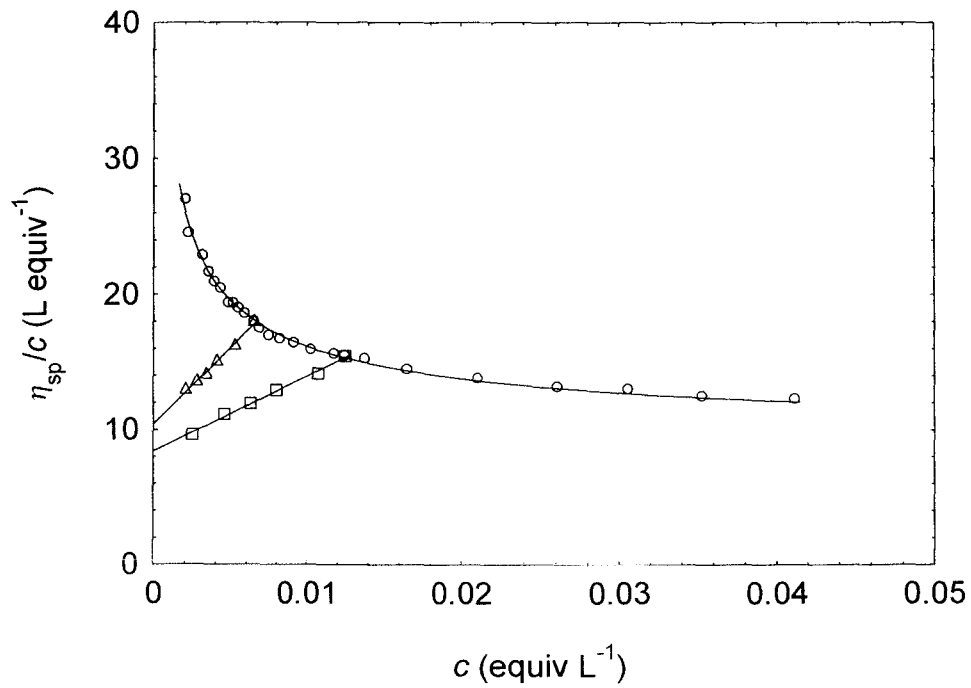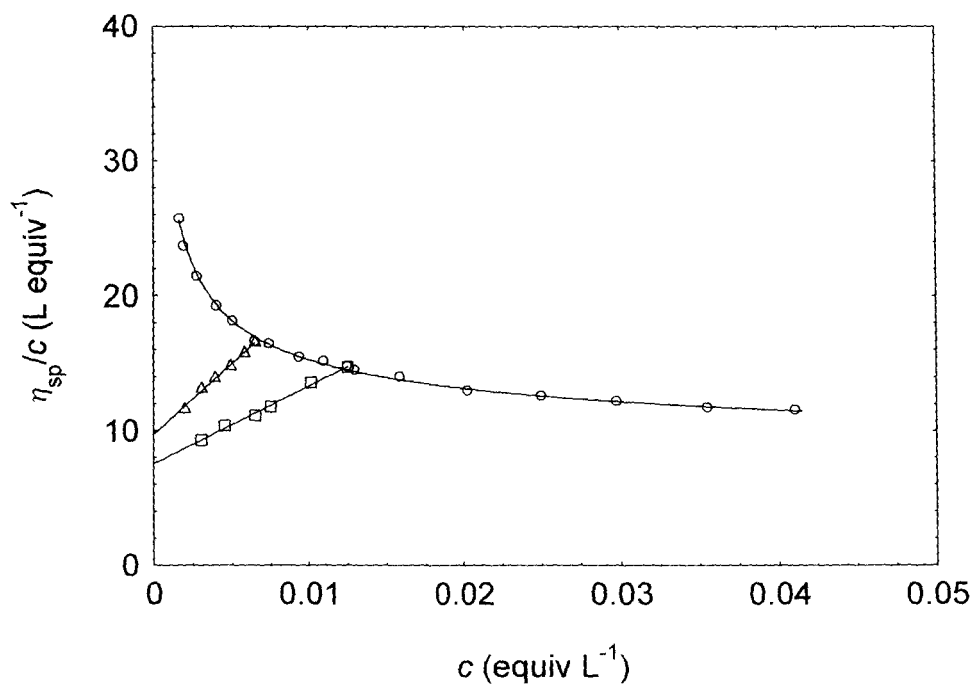
Figure 5. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 308.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.
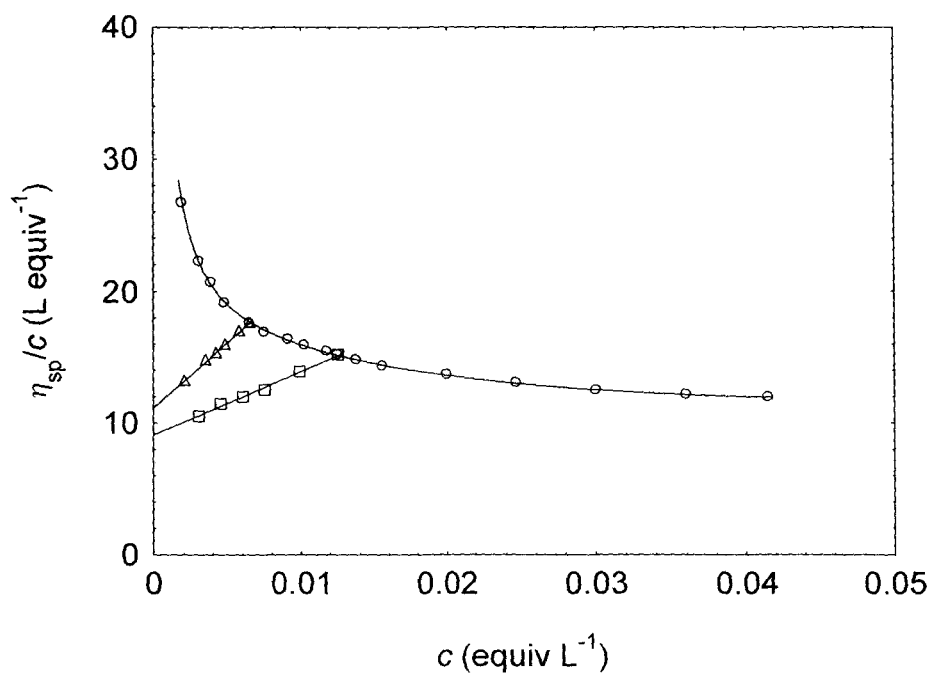
Figure 6. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 20 vol percent acetonitrile-water mixture at 318.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.

Figure 7. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 298.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.

Figure 8. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 308.15 K ($\circ$). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} ($\triangle$), and 0.0125 equiv L^{-1} ($\square$) where isoionic dilutions were performed.

Figure 9. The variation of the reduced viscosity for sodium polystyrenesulfonate with the polyelectrolyte concentration in 40 vol percent acetonitrile-water mixture at 318.15 K (○). Also included in this figure are the straight lines obtained at polyelectrolyte concentrations of 0.0065 equiv L^{-1} (△), and 0.0125 equiv L^{-1} (□) where isoionic dilutions were performed.
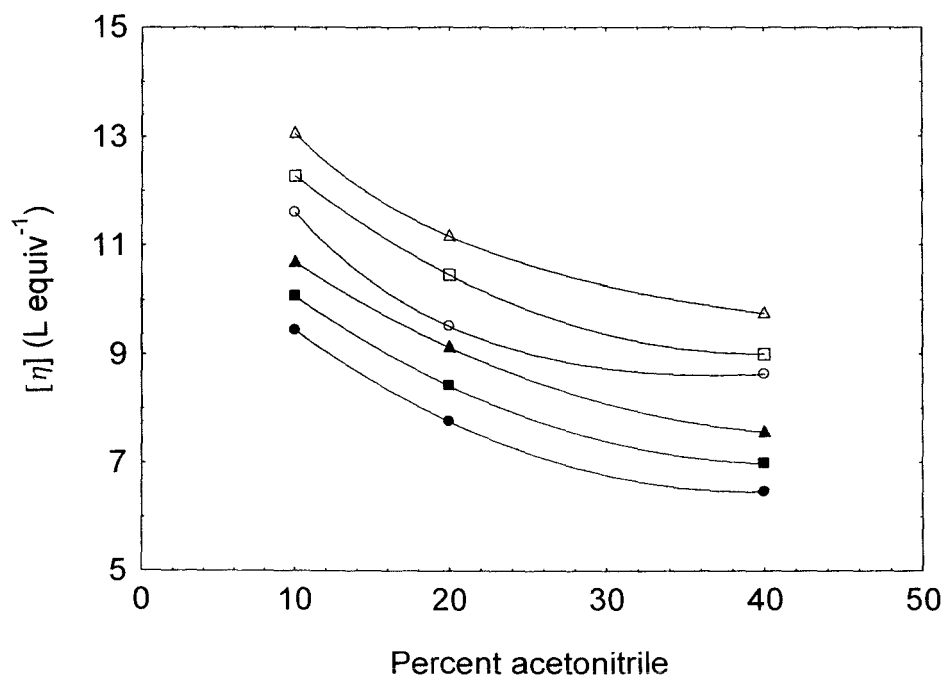
Figure 10. Effect of medium on the intrinsic viscosity for a polyelectrolyte concentration of 0.0065 equiv L^{-1} at 298.15 K (○), 308.15 K (□), and 318.15 K(△); and for a polyelectrolyte concentration of 0.0125 equiv L^{-1} at 298.15 K (●), 308.15 K (■), and 318.15 K(▲).
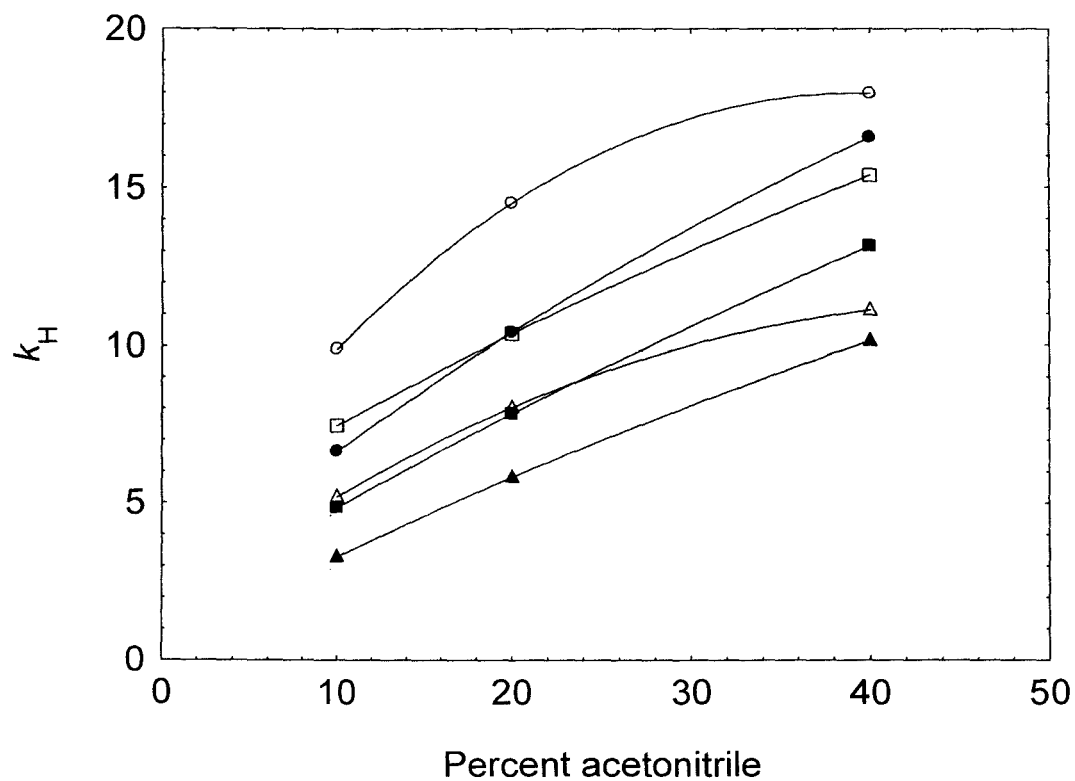
Figure 11. Effect of medium on the Huggins constant for a polyelectrolyte concentration of 0.0065 equiv L^{-1} at 298.15 K ($\circ$), 308.15 K ($\square$), and 318.15 K($\triangle$); and for a polyelectrolyte concentration of 0.0125 equiv L^{-1} at 298.15 K ($\bullet$), 308.15 K ($\blacksquare$), and 318.15 K($\blacktriangle$).
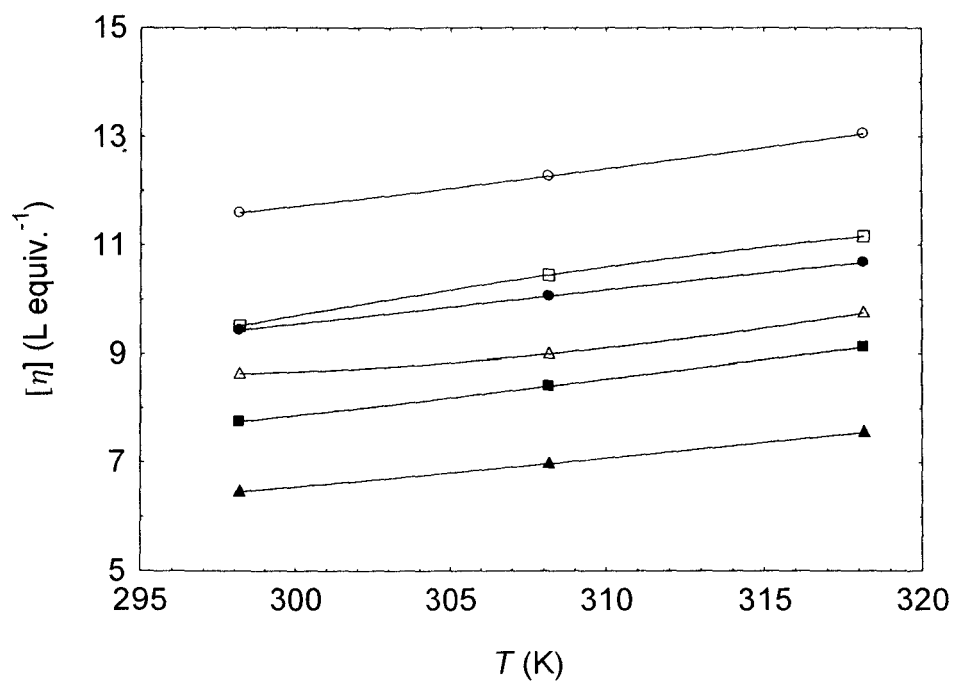
Figure 12. Effect of temperature on the intrinsic viscosity for a polyelectrolyte concentration of 0.0065 equiv L^{-1} in 10 vol percent acetonitrile-water mixture (○), 20 vol percent acetonitrile-water mixture (□), and 40 vol percent acetonitrile-water mixture (△); and for a polyelectrolyte concentration of 0.0125 equiv L^{-1} in 10 vol percent acetonitrile-water mixture (●), 20 vol percent acetonitrile-water mixture (■), and 40 vol percent acetonitrile-water mixture (▲).
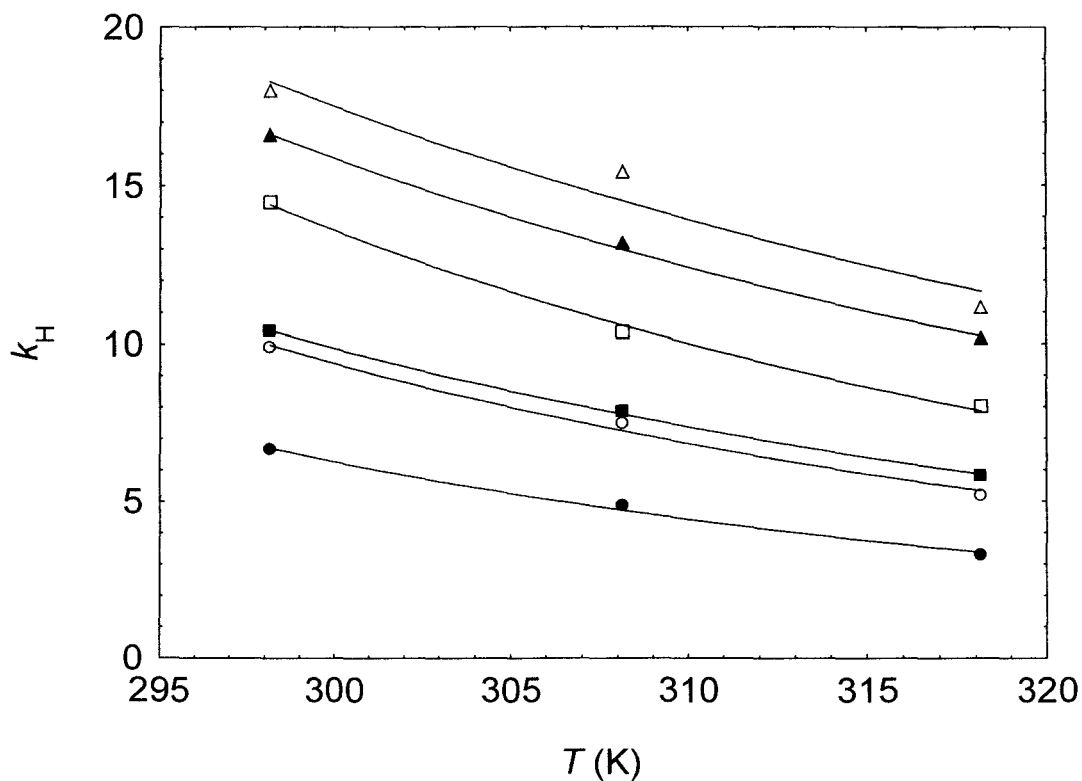
Figure 13. Effect of temperature on the Huggins constant for a polyelectrolyte concentration of 0.0065 equiv L^{-1} in 10 vol percent acetonitrile-water mixture (○), 20 vol percent acetonitrile-water mixture (□), and 40 vol percent acetonitrile-water mixture (△); and for a polyelectrolyte concentration of 0.0125 equiv L^{-1} in 10 vol percent acetonitrile-water mixture (●), 20 vol percent acetonitrile-water mixture (■), and 40 vol percent acetonitrile-water mixture (▲).