

Chapter VI

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

Introduction

It is well known that the intrinsic viscosity $[\eta]$ is the parameter which enables characterization of the dimension and configuration of a polymer in solution. For salt-free polyelectrolyte solutions, however, the determination of this parameter presents a great challenge.

The anomalous concentration dependence of viscosity of polyelectrolyte solutions with no added salt has been known for a long period. Early investigations appeared to suggest an unbound rise in the reduced viscosity (η_{sp}/c_p ; η_{sp} = specific viscosity and c_p = polymer concentration) of salt-free polyelectrolyte solutions as one lowers the polyion concentration.^{1,2} In these studies, which are summarized in the pioneering work of Fuoss,^{1,2} a straight line is obtained when the reciprocal of reduced viscosity is plotted against the square root of the concentration. It was usually assumed that this line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero concentration gives the inverse of the intrinsic viscosity. However, careful investigations on the dilute solution behaviour revealed that the apparent unbound rise in the reduced viscosity is always followed by a maximum,³ and normal polymer behaviour is recovered at the extrapolated limit of zero polyelectrolyte concentration. Thus the method of Fuoss could not be used 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 observed behaviour is a consequence of the screening of long-range intermolecular interactions by the residual electrolytes in the solution.³ Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentration and, therefore, was close to the limit of accuracy of the measuring systems. Therefore, it is virtually impossible to obtain the intrinsic viscosity of polyelectrolyte solutions without added salt since the concentrations beneath the viscosity maximum are in the very low-concentration region difficult to reach experimentally.

The determination of the intrinsic viscosity is more straightforward if the isoionic dilution method^{4,5} is applied. Following 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 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 conditions 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.

In spite of the success of this method for the determination of intrinsic viscosity in a convenient manner, very little attention was paid in this direction.⁴⁻⁷ The aim of the present contribution is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of NaCMC in water as well as acetonitrile-water mixed solvent media. Furthermore, the influence of the medium, total ionic strength and temperature on the polymer-solvent and polymer-polymer interactions 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 $0.76570 \text{ gm.cm}^{-3}$ 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.⁸ Triply distilled water with a specific conductance of less than $10^{-6} \text{ S.cm}^{-1}$ at 308.15 K was used for the preparation of the mixed solvents.

NaCMC used in these investigations was purchased from Aldrich Chemical. The average molecular weight (M_w) of the sample was 90,000 with a degree of substitution (DS) of 0.70, and

these values agree well with those obtained from physicochemical characterization in the present study.

The viscometric measurements were performed at 308.15, 313.15 and 323.15 K using a Schultz-Immergut-type viscometer⁹ 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.^{10,11} 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.

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

Representative plots for the typical dependence of the reduced viscosity with the polyelectrolyte concentration for salt-free NaCMC solution in water and 20 percent of acetonitrile-water mixture at 323.15 K are shown, respectively, in Figures 1 and 2. In absence of added salt, the reduced viscosity is found to increase as the polymer concentration decreases, for all systems investigated, bending up at low concentrations. No maximum was, however, detected in the η_{sp}/c_p versus c_p graph within the concentration range studied here.

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 solution.⁴⁻⁷ As we know that the intrinsic viscosity is the parameter which enables characterization of dimension and configuration of polymer, this data may play a crucial role in the discussion of polyelectrolyte behaviour in dilute solutions.

We have performed the isoionic dilution of NaCMC solutions at two different total ionic strengths ($\sim 4.20 \times 10^{-4}$ and 1.45×10^{-3} mol.l⁻¹ of NaCl, these ionic strengths are evenly poised around the midpoint of the investigated polymer concentration region) in water and in two acetonitrile-water mixtures containing 10 and 20 volume percent of acetonitrile at three different temperatures, namely, 308.15, 313.15 and 323.15 K. The representative Figures (Figures 1 and 2) also include the experimental data for isoionic dilution for the two total ionic strengths mentioned above.

The reduced viscosity data as functions of polymer concentration can be described by the well-known Huggins equation.^{12,13}

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

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.

From the present experimental η_{sp} / c_p versus c_p data, the intrinsic viscosities and the Huggins constants were determined by method of least-squares using Eq. (1) and these are listed in Table 1 along with their standard errors and the correlation coefficients of fits (as r^2).

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

From Table 1 and Figures 3-6, 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 NaCMC differs quite appreciably in its solvodynamic and thermodynamic behaviours under varying conditions.^{14,15} Although, investigations on isoionic dilutions of polyelectrolytes are

completely absent in mixed solvent media, a report⁷ on such a study in aqueous solution also indicated a significant variation in the coil size of NaCMC with the total ionic strength. A direct comparison of these results with those of the present work is not possible since the molar mass and the degree of substitution of the polyelectrolyte sample are different in these two cases. However, our results in aqueous solution are found to be consistent with the earlier findings.⁷

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

$$k_H = Ae^{-B/T} \quad (2)$$

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 308.15 and 313.15 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 3). Moreover, the Huggins constants are found to increase with increasing acetonitrile-content of the media (Table 1 and Figure 4). 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.*^{14,15} The above observation demonstrates that the solvent interacts with the polymer gradually poorly (*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.¹⁶ At 323.15 K, on the other hand, the intrinsic viscosity values pass through a minimum while those of the Huggins constants go through a minimum (Table 1 and Figures 3 and 4). This indicates that at this temperature, the polymer-polymer

interactions reach a maximum whereas the polymer-solvent interactions reach a minimum in the mixture containing 10 volume percent acetonitrile. A similar behaviour was also noticed earlier by Palit *et. al.*¹⁷ for a solution of polystyrene in a mixture of acetone and methylcyclohexane.

Influence of Ionic Strength

For each solvent medium and at each temperature, the intrinsic viscosities are found to decrease as the total ionic strength of the solution increases (Table 1). As the concentration of the ions in the solution increases, counterion binding onto the polyion chain is considerably enhanced. This causes more effective screening of the chain charges in high ionic strength solution, decreasing the intramacromolecular electrostatic repulsions (and hence decreasing k_H , 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 in a given solvent medium when the total ionic strength is maintained at a constant level (Table 1 and Figure 5). The Huggins constant, on the other hand, decreases with temperature in these cases (Table 1 and Figure 6). 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,¹⁶ 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 reported¹⁵ for a polystyrene sample are found to decrease with the increase in temperature as observed in the present work.

Conclusions

The present chapter reported the precise measurements on the viscosities of the solutions of NaCMC in water and in two acetonitrile-water mixtures containing 10 and 20 volume percent of acetonitrile at 308.15, 313.15 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 $\sim 4.20 \times 10^{-4}$ and $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$ with sodium chloride. The Huggins constants were also obtained from the experimental results. The influences of the medium, the temperature and the total ionic strength on the intrinsic viscosities as well as on the Huggins constants have been interpreted to elucidate the solvodynamic and thermodynamic interactions occurring in solution.

References

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Table 1. Intrinsic Viscosity Values, $[\eta]$ (ml.gm⁻¹), and Huggins Constants k_H and the Correlation Coefficients of Fits (as r^2) for NaCMC in Water, 10 and 20 Volume Percent Acetonitrile-Water Mixtures at 308.15, 313.15 and 323.15 K

Solvent	Ionic Strength (mol.dm ⁻³)	$[\eta]$ (ml.gm ⁻¹)	k_H	r^2
T = 308.15 K				
Water	1.45×10^{-3}	271 ± 8	3.88 ± 0.11	0.9938
	4.20×10^{-4}	336 ± 8	15.72 ± 0.24	0.9984
10 Vol% Acetonitrile	1.45×10^{-4}	249 ± 9	4.22 ± 0.14	0.9842
	4.20×10^{-4}	258 ± 7	24.91 ± 0.35	0.9984
20 Vol% Acetonitrile	1.45×10^{-3}	230 ± 8	5.07 ± 0.16	0.9865
	4.20×10^{-4}	240 ± 9	30.69 ± 0.47	0.9970
T = 313.15 K				
Water	1.45×10^{-3}	289 ± 7	3.20 ± 0.10	0.9955
	4.20×10^{-4}	346 ± 8	14.15 ± 0.22	0.9987
10 Vol% Acetonitrile	1.45×10^{-3}	255 ± 8	4.06 ± 0.14	0.9914
	4.20×10^{-4}	272 ± 7	22.70 ± 0.31	0.9990
20 Vol% Acetonitrile	1.45×10^{-3}	241 ± 9	4.64 ± 0.16	0.9885
	4.20×10^{-4}	253 ± 10	28.25 ± 0.52	0.9945

Table 1. Contd.

Solvent	Ionic Strength (mol.dm⁻³)	[η] (ml.gm⁻¹)	k_H	r^2
T = 323.15 K				
Water	1.45×10^{-3}	330 ± 5	1.98 ± 0.05	0.9972
	4.20×10^{-4}	471 ± 7	6.15 ± 0.10	0.9984
10 Vol% Acetonitrile	1.45×10^{-3}	304 ± 4	2.11 ± 0.04	0.9983
	4.20×10^{-4}	435 ± 4	6.34 ± 0.08	0.9993
20 Vol% Acetonitrile	1.45×10^{-3}	339 ± 1	1.57 ± 0.10	0.9998
	4.20×10^{-4}	509 ± 5	4.08 ± 0.06	0.9987

Table 2. Parameters of Eq. (2) and the Correlation Coefficients of Fits (as r^2) for NaCMC in Water, 10, and 20 Volume Percent Acetonitrile–Water Mixtures

Solvent	Ionic Strength (mol.dm⁻³)	ln <i>A</i>	<i>B</i>	r^2
Water	1.45×10^{-3}	-13.354	-4538.3	0.9956
	4.20×10^{-4}	-18.404	-6549.2	0.9409
10 Vol% Acetonitrile	1.45×10^{-3}	-14.334	-4887.2	0.9134
	4.20×10^{-4}	-27.863	-9626.8	0.9196
20 Vol% Acetonitrile	1.45×10^{-3}	-24.964	-8234.6	0.9234
	4.20×10^{-4}	-42.612	-14267.0	0.9057

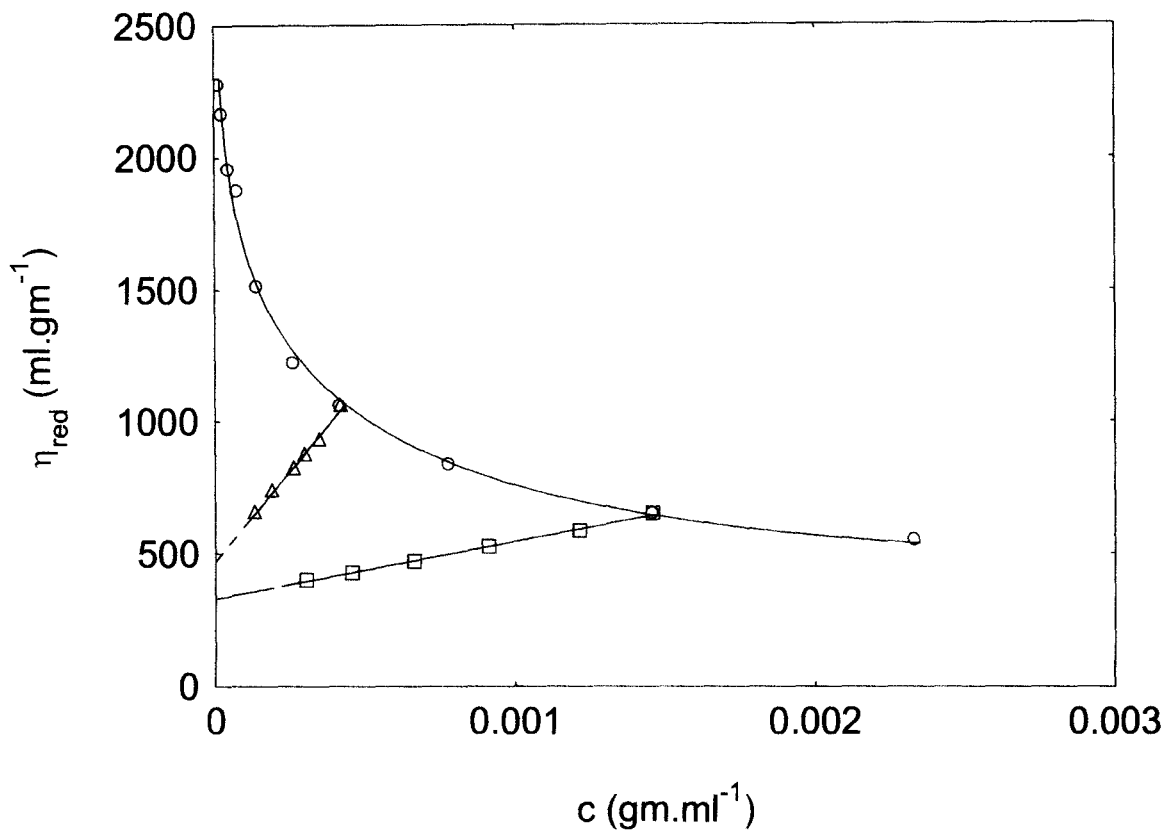


Figure 1. The change of the reduced viscosity for NaCMC with the polyelectrolyte concentration in water at 323.15 K, Open circles; Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with total ionic strengths $\sim 4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open triangles; and $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Open squares.

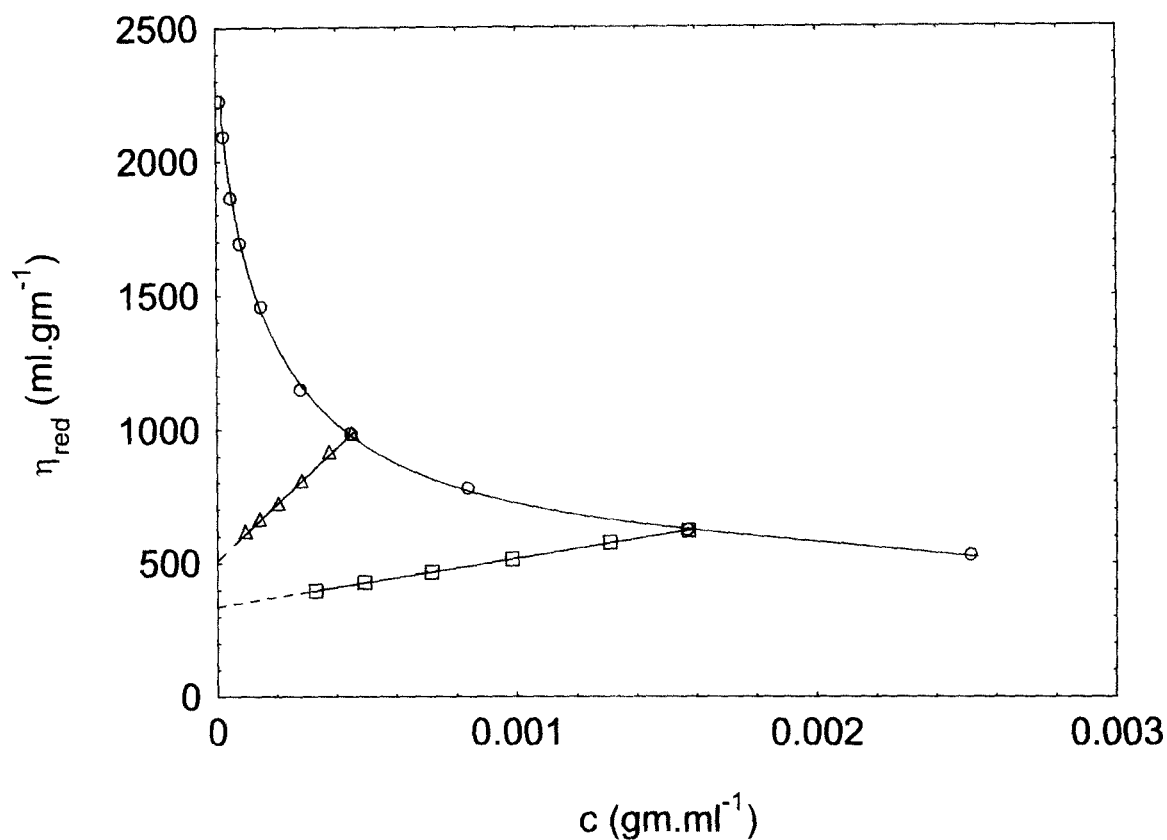


Figure 2. The change of the reduced viscosity for NaCMC with the polyelectrolyte concentration in 20 volume percent acetonitrile-water mixture at 323.15 K , Open circles; Also included in this figure are the straight lines obtained in accordance with the isoionic dilution technique with total ionic strengths $\sim 4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open triangles; and $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Open squares.

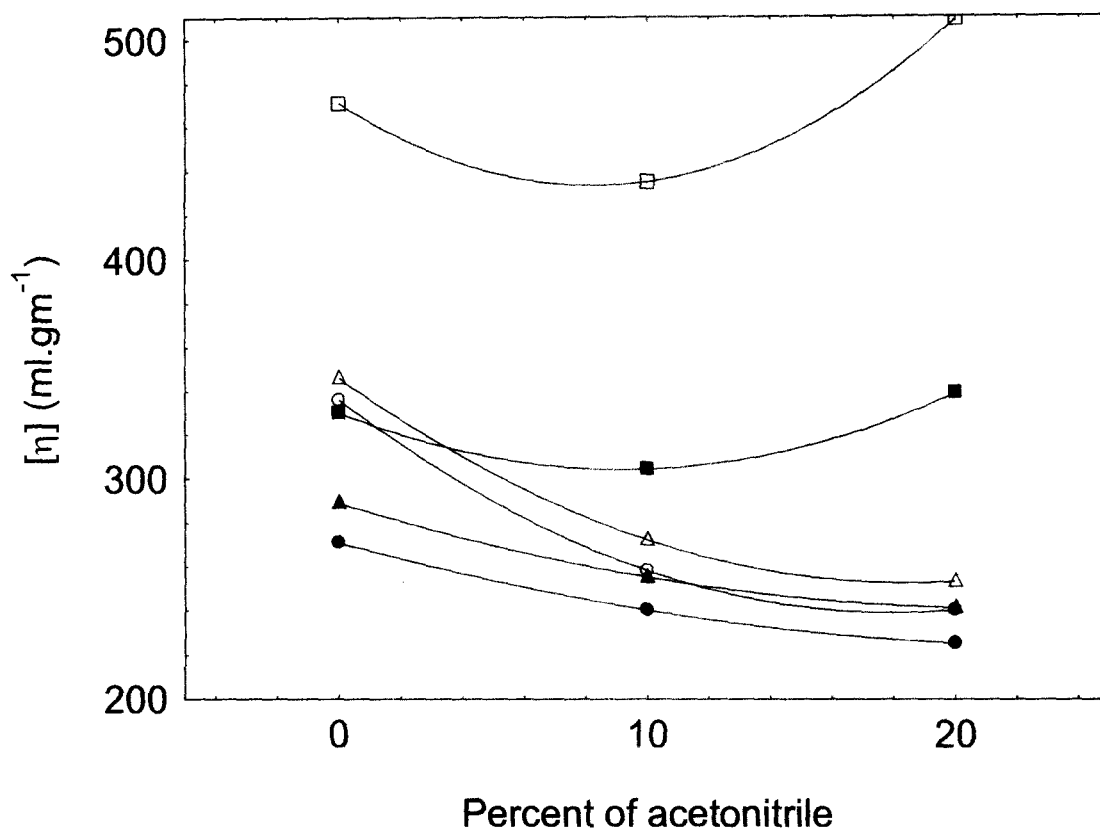


Figure 3. Effect of medium on the intrinsic viscosity at 308.15 K [for total ionic strength $4.2 \times 10^{-4} \text{ mol.dm}^{-3}$, Open circles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled circles], 313.15 K [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open triangles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled triangles], and 323.15 K [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open squares; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled squares].

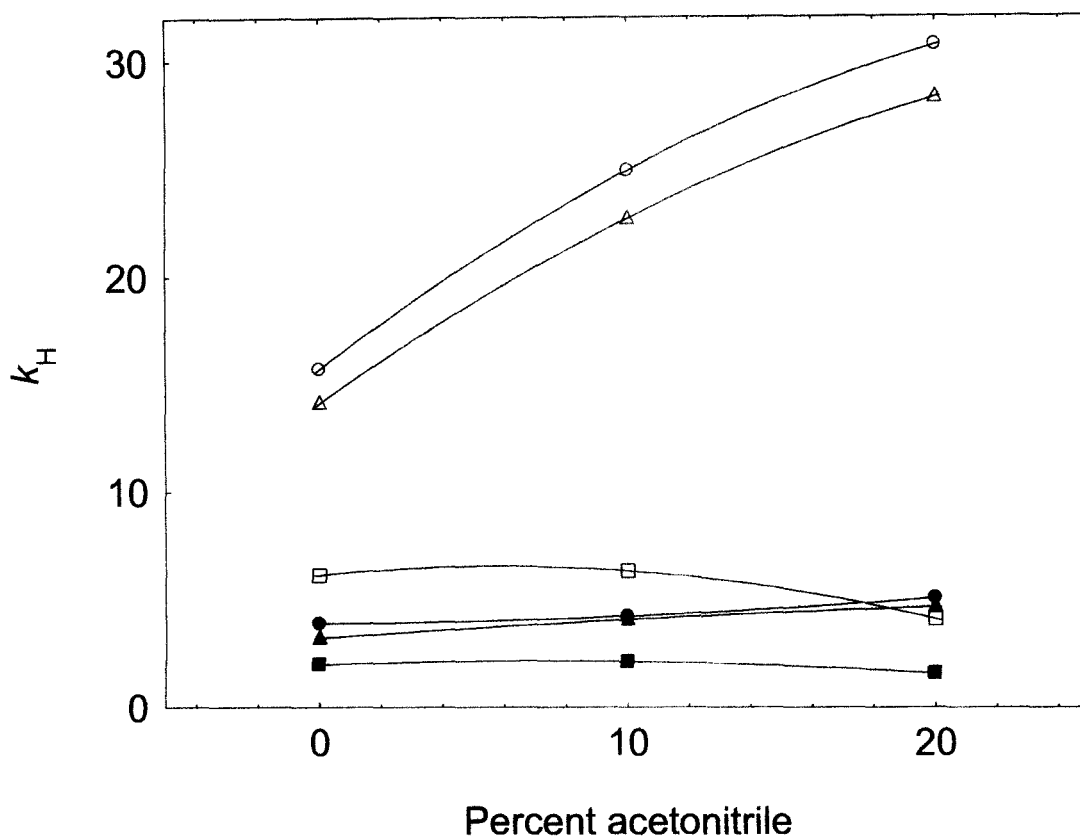


Figure 4. Effect of medium on the Huggins constant at 308.15 K [for total ionic strength 4.2×10^{-4} mol.dm⁻³, Open circles; and for total ionic strength 1.45×10^{-3} mol.dm⁻³, Filled circles], 313.15 K [for total ionic strength 4.20×10^{-4} mol.dm⁻³, Open triangles; and for total ionic strength 1.45×10^{-3} mol.dm⁻³, Filled triangles], and 323.15 K [for total ionic strength 4.20×10^{-4} mol.dm⁻³, Open squares; and for total ionic strength 1.45×10^{-3} mol.dm⁻³, Filled squares].

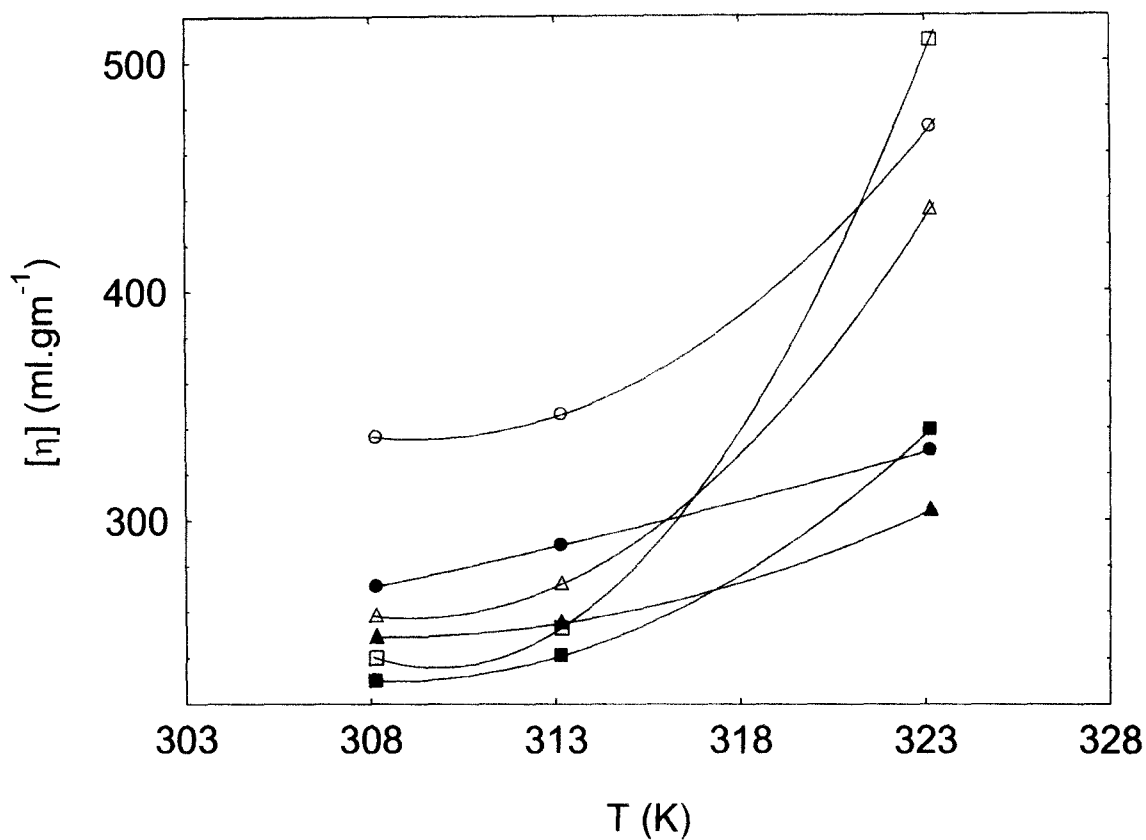


Figure 5. Effect of temperature on the intrinsic viscosity in water [for total ionic strength $4.2 \times 10^{-4} \text{ mol.dm}^{-3}$, Open circles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled circles], in 10 volume percent acetonitrile-water mixture [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open triangles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled triangles], and in 20 volume percent acetonitrile-water mixture [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open squares; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled squares].

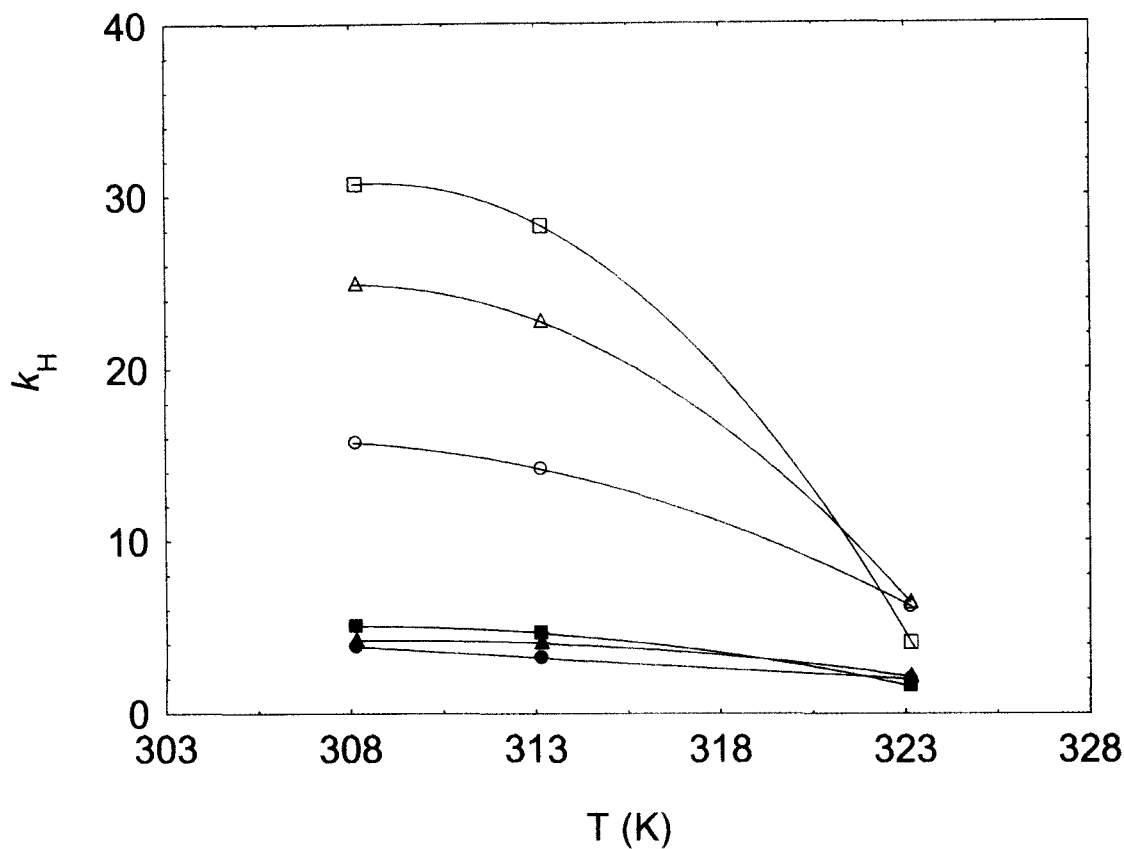


Figure 6. Effect of temperature on the Huggins constant in water [for total ionic strength $4.2 \times 10^{-4} \text{ mol.dm}^{-3}$, Open circles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled circles], in 10 volume percent acetonitrile-water mixture [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open triangles; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled triangles], and in 20 volume percent acetonitrile-water mixture [for total ionic strength $4.20 \times 10^{-4} \text{ mol.dm}^{-3}$, Open squares; and for total ionic strength $1.45 \times 10^{-3} \text{ mol.dm}^{-3}$, Filled squares].