Chapter 6

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

Introduction

Intrinsic viscosity has always been an important parameter in determining the conformation of a single polymer chain dissolved in solutions.

In case of uncharged polymer solutions, the reduced viscosity (η_{sp}/c; η_{sp} = specific viscosity and c = polymer concentration) varies linearly with concentration c in dilute solutions which led Huggins to propose the following equation[1,2]

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

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 $c = 0$.

Due to the presence of electric charges along the polymer chains in polyelectrolytes, the behavior of these species in solutions is entirely different from that of uncharged polymers which are characterized by complex interactions, structures, and dyanamics.[1,3-5] The reduced viscosity of polyelectrolyte solutions, particularly in salt-free and low-added-salt 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 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 of polyelectrolyte solutions 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.[8-13] Moreover, intrinsic viscosities obtained at different ionic strengths (and hence at different polyelectrolyte concentrations) in conjunction with the reduced viscosities as a function of concentrations of salt-free polyelectrolyte solutions have been shown to provide an opportunity to separate the conformational and electrostatic contributions to the reduced viscosities from experimental results.[13]

The principal objective of the present investigation is, therefore, to employ the method of isoionic dilution to obtain the intrinsic viscosities of sodium carboxymethylcellulose in aqueous and methanol-water mixed solvent media. The influences of the medium, and total ionic strength on the intrinsic viscosities and the Huggins constants will be interpreted in terms of the various phenomena occurring in polyelectrolyte solutions. A convenient method has recently been proposed by one of us to decompose the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components *from purely experimental considerations.*[13] A theoretical approach was proposed by Nishida *et al.*[14] for calculating the electrostatic contributions to the reduced viscosity of polyelectrolyte solutions. The investigation made by our group in aqueous ethylene glycol media[13] was the first attempt to separate the intermolecular and intramolecular contributions to reduced viscosity from experimental point of view. The present study carried out in another solvent mixture (methanol-water) using sodium chloride to maintain the ionic strength will thus also be a test of the validity of the model. Results of viscosity measurements in presence of potassium chloride and barium chloride in aqueous solutions have also been included for the purpose of comparison.

Experimental

Methanol (Acros Organics, 99% pure) was distilled twice. The purified solvent had a density of 0.77728 g.cm^{-3} and a coefficient of viscosity of 0.4747 mPa.s at 308.15 K; these values are in good agreement with the literature values.[15,16] 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.

Sodium carboxymethylcellulose used in these investigations was purchased from Aldrich Chemicals. The average molecular weight (*M*) of the sample was 90,000 with a degree of substitution (*DS*) of 0.70. It was characterized in a similar fashion as described earlier by us.[13] The average molecular weight of the sample was also estimated from the intrinsic viscosity value using the Mark-Houwink equation with the constants obtained from the literature.[17] DS was determined by a conductometric procedure as described by Eyler *et al.*[18] The viscometric measurements were performed at 308.15 K using a Schultz-Immergut-type viscometer[19] 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.[20,21] 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 carboxymethylcellulose solution in water and methanol-water mixtures with 10, and 20 vol. % of methanol at 308.15 K are shown, respectively, in Figs. 1 - 4. 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.[8-13] 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 carboxymethylcellulose solutions have been performed at four different total ionic strengths in water and two methanol-water mixtures containing 10 and 20 vol.% of methanol at 308.15 K with sodium chloride as the added salt. Three different ionic strengths of potassium chloride and barium chloride were investigated in water at the same temperature.

The reduced viscosity data as functions of polyelectrolyte concentration resulting from the isoionic dilution can be described by the well-known Huggins equation,[1,2] 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 Figs. 8 - 11. The universal trend of decreasing k_H values with increasing ionic strength is observed in all the cases investigated.

The effects of medium on the intrinsic viscosity and the Huggins constant obtained for constant total ionic strengths in the range (0.911 – 4.15) x 10^{-3} eqv.L^{-1} at 308.15 K are shown in the Figs. 5 and 7, respectively. The influences of ionic strength on the intrinsic viscosity and the Huggins constant in water and methanol-water mixtures, on the other hand, are displayed in Figs. 6 and 8 respectively.

From Figs. 5 and 6, it is apparent that the intrinsic viscosities for the present polyelectrolyte system vary with the total ionic strength and the relative permittivity of the medium. This observation, thus, indicates that the investigated polyelectrolyte sodium carboxymethylcellulose differs quite appreciably in its solvodynamic behavior under varying conditions.

For a given value of the total ionic strength, the values of intrinsic viscosities are found to decrease and those of the Huggins constants are found to increase as the medium becomes richer in methanol (*cf.* Figs. 5 and 7, respectively). Similar type of results has also been reported earlier.[12,13,22-24] The variation of the intrinsic viscosity of sodium carboxymethylcellulose with the amount of methanol present in methanol-water mixed solvent media at a fixed total ionic strength could be ascribed to the changed counterion condensation in solution. The relative permittivity of the medium decreases as the medium becomes richer in methanol resulting in stronger electrostatic interactions between the polyion and the counterions. This brings about more and more counterion condensation onto the polyion chain. Consequently, the Coulomb repulsive interactions between the ionized groups on the polyion chain would decrease which reduces the electrostatic persistence length, thus allowing the chain to coil more tightly. The coiling of the polyion chains is manifested by the decreasing intrinsic viscosity values with increasing amount of methanol in the mixed solvent media. Depletion of counterion concentration with decreasing relative permittivity results in a less effective screening between the polyion chains as the medium becomes richer in methanol. An enhanced intermolecular interaction manifested by the increasing values of the Huggins constants with increasing amount of methanol in the mixed media would thus occur.

For each solvent medium, on the other hand, both the intrinsic viscosities and the Huggins constants are found to decrease as the total ionic strength of the solution increases (*cf.* Figs. 6 and 8, respectively).

For different salts it was found that the values of intrinsic viscosity decreased whereas the values of Huggins constant increased in going from sodium carboxymethylcellulose-sodium chloride, sodium carboxymethylcellulose-potassium chloride and sodium carboxymehyl-cellulose-barium chloride systems of equal ionic strengths. As we go from sodium chloride to barium chloride through potassium chloride, the effect of counterion condensation increased due to smaller solvated size and higher charge density of the cations. The greater difference in the intrinsic viscosity values between sodium chloride and barium chloride as compared to that between sodium chloride and potassium chloride clearly indicates that the charge effect may play a vital role in counterion condensation which results in coiling of the macromolecular chains.

As the concentration of the ions in the solution increases, counterion binding onto the polyion chain is enhanced considerably. This causes coiling of the macromolecules which is reflected in a decrease in the intrinsic viscosity of the polyelectrolyte solution. Greater screening with increasing ionic strength also causes reduced intermolecular electrostatic interactions and hence gradually lower values of the Huggins constants as the total ionic strength of the solution increases.

Here, we have decomposed the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components from the experimental results following a method developed earlier by one of us.[13] As pointed out earlier, 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 other words, this means that the intrinsic viscosity obtained for a given ionic strength (and hence for a given concentration) of a salt-free polyelectrolyte solution by the method of isoionic dilution corresponds to its conformational state in salt-free situation and thus could be considered as the conformational contribution to the reduced viscosity $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{conformation}}$.

Now, in the limit of weaker interactions the influence of polymer conformation and the influence of electrostatic interactions on the intrinsic viscosity of linear polyelectrolytes may be simply additive,[25,26] *i.e.*,

$$\eta_{\mathrm{sp}}/c_{\mathrm{P}} = (\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{conformation}} + (\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}} \qquad (4)$$

where $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}}$ is the electrostatic contribution to the reduced viscosity. This could easily be understood since when interactions are small, contributions of the cross terms are negligible and hence decoupling of these two contributions is possible..

The electrostatic contribution to the reduced viscosity $(\eta_{\mathrm{sp}}/c_{\mathrm{p}})_{\mathrm{electrostatic}}$ could, therefore, be readily obtained by subtracting the conformational part from the experimental reduced viscosity at the salt-free polyelectrolyte concentration where the isoionic dilution was performed. We have, thus, been able to quantify the conformational and electrostatic contributions of the reduced viscosity of a polyelectrolyte solution using the isoionic dilution method. The electrostatic reduced viscosity thus computed is shown graphically in Fig. 11 as a function of sodium carboxymethylcellulose concentration in water and methanol-water mixed solvent media. It is directly evident from this figure that the electrostatic contribution to the reduced viscosity decreases sharply with increasing polyelectrolyte concentration (and hence the ionic strength) in a given medium. This also verifies quantitatively the conclusions obtained from the Huggins constants as described above. Moreover, a monotonous growth of the electrostatic part on the addition of methanol to water in the medium at a given polyelectrolyte concentration has been clearly demonstrated in this figure in conformity with our earlier contention derived from Huggins constants (see above). The electrostatic contribution is always found to predominate over the conformational part for the present system.

Conclusions

The present chapter reported precise measurements on the viscosities of the solutions of an anionic polyelectrolyte sodium carboxymethylcellulose in water as well as in methanol–

water mixed solvent media containing 10, and 20 vol. % of methanol at 308.15 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 of the solutions at constant level using sodium chloride, potassium chloride, and barium chloride of equal strength. 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. A convenient method has been used to decompose the reduced viscosity of a polyelectrolyte solution into its conformational and electrostatic components. The electrostatic contributions to the reduced viscosities obtained here purely from experimental considerations quantitatively corroborate the conclusions derived from Huggins constants.

Overall, the results obtained in this work are quite useful for understanding the viscometric behaviour of polyelectrolyte solutions and the experimental values of the electrostatic contributions to the reduced viscosity are found to be consistent with the theoretical calculations presented here.

References

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Table 1. Intrinsic Viscosities $[\eta]$, Huggins Constants k_H, and the Correlation Coefficients of Fits (as r^2) of Sodium Carboxymethylcellulose in Water and Methanol–Water Mixtures Containing 10 and 20 vol. % of Methanol at the Polyelectrolyte Concentrations where Isoionic Dilution was performed at 308.15 K

Salt	Vol.% of methanol	c_p (Eqv.L^{-1})	$[\eta]$ (L.Eqv^{-1})	k_H	r^2
NaCl	0	9.11×10^{-4}	134	13.42	0.999
		1.25×10^{-3}	130	9.23	0.999
		2.02×10^{-3}	127	4.28	0.996
		4.15×10^{-3}	114	1.78	0.998
	10	9.11×10^{-4}	107	21.05	0.996
		1.25×10^{-3}	104	14.98	0.998
		2.02×10^{-3}	97.7	8.06	0.999
		4.15×10^{-3}	86.8	3.58	0.996
	20	9.11×10^{-4}	80.7	41.00	0.999
		1.25×10^{-3}	77.1	30.45	0.999
		2.02×10^{-3}	73.5	15.94	0.999
		4.15×10^{-3}	64.5	7.60	0.996
KCl	0	9.11×10^{-4}	123	16.79	0.999
		2.02×10^{-3}	118	5.34	0.998
		4.15×10^{-3}	107	2.19	0.999
$BaCl_2$	0	9.11×10^{-4}	62.1	85.57	0.987
		2.02×10^{-3}	54.4	36.16	0.992
		4.15×10^{-3}	39.9	26.19	0.995

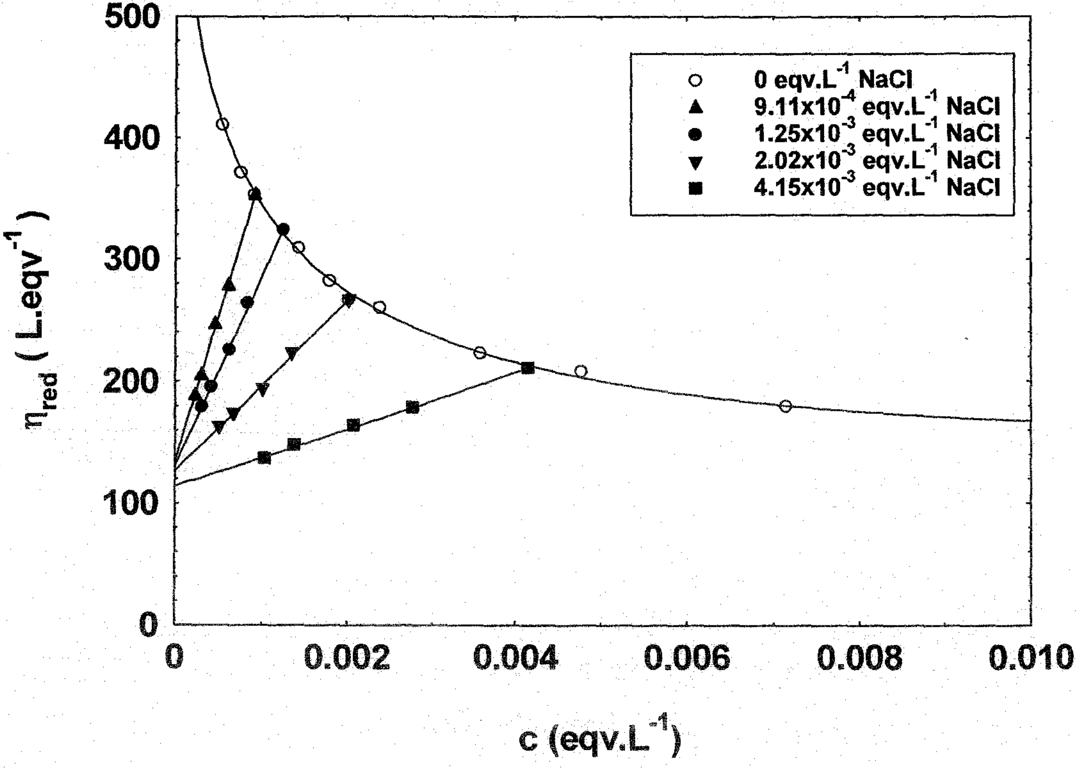

Fig. 1. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using NaCl.

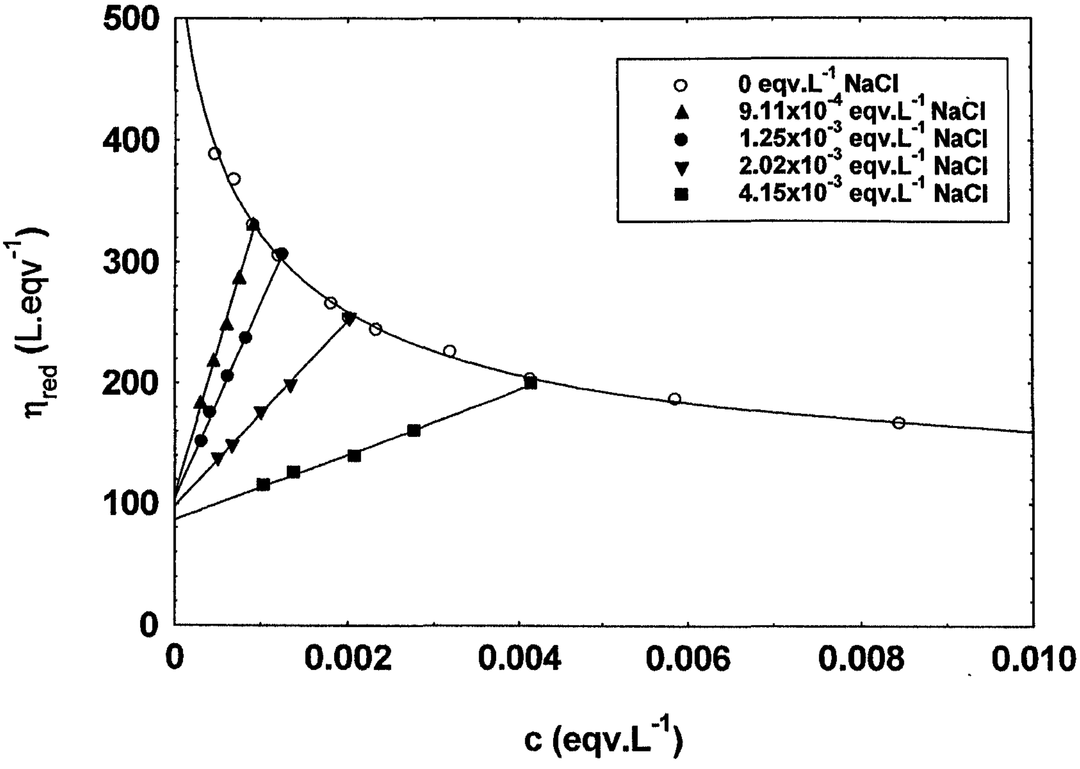

Fig. 2. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in methanol-water mixture containing 10 vol. % of methanol. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using NaCl.

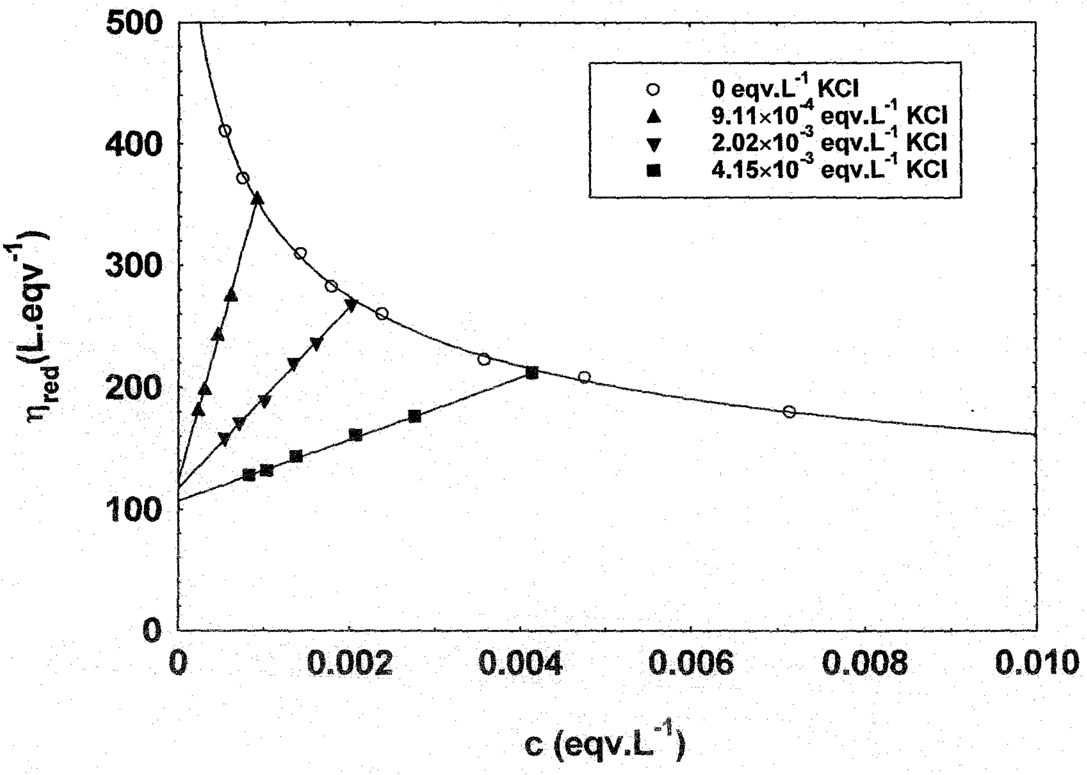

Fig. 3. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at different total ionic strengths where isoionic dilutions were performed by using KCl.

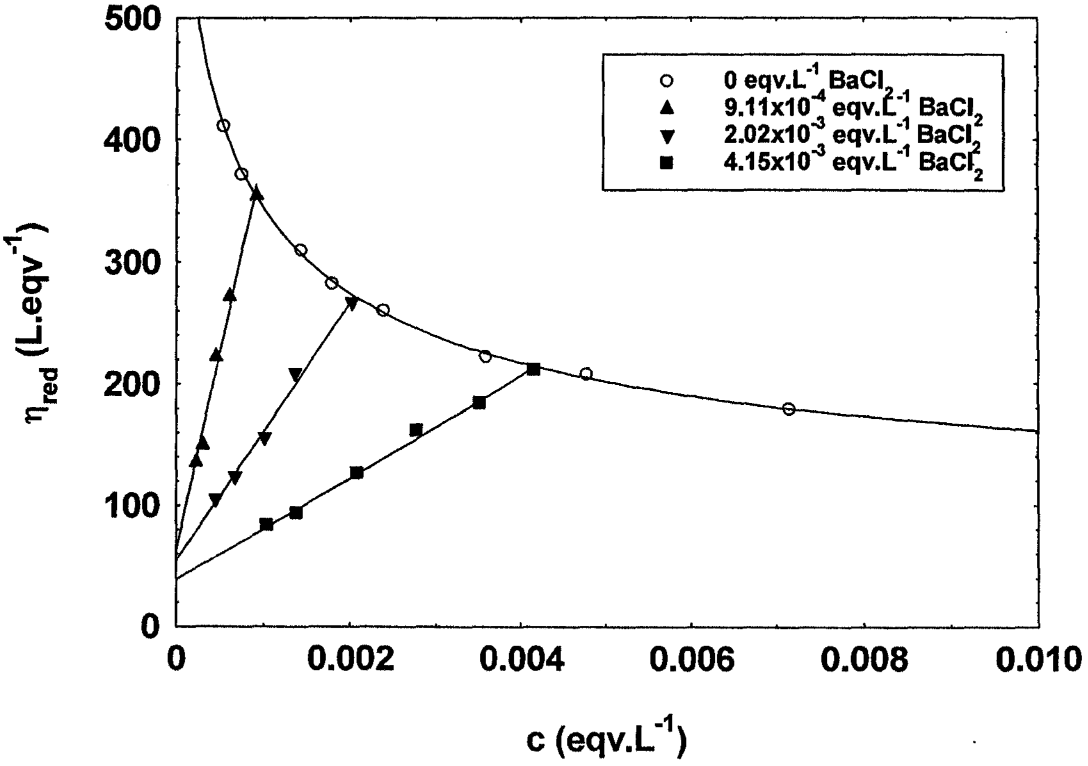

Fig. 4. The variation of the reduced viscosity for sodium carboxymethylcellulose with the polyelectrolyte concentration in water. Also included in this figure are the straight lines obtained at diiferent total ionic strengths where isoionic dilutions were performed by using $BaCl_2$.

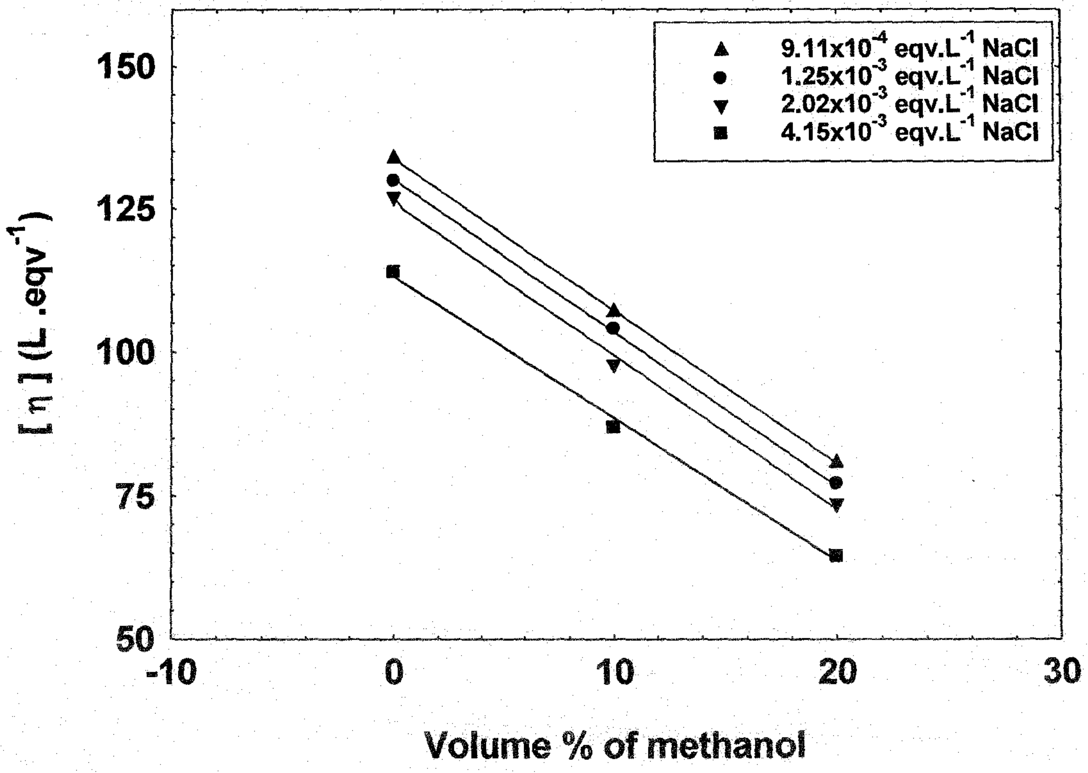

Fig. 5. The effect of medium on the intrinsic viscosity of sodium carboxymethylcellulose in methanol-water mixtures at different total ionic strengths where isoionic dilutions were performed by using NaCl.

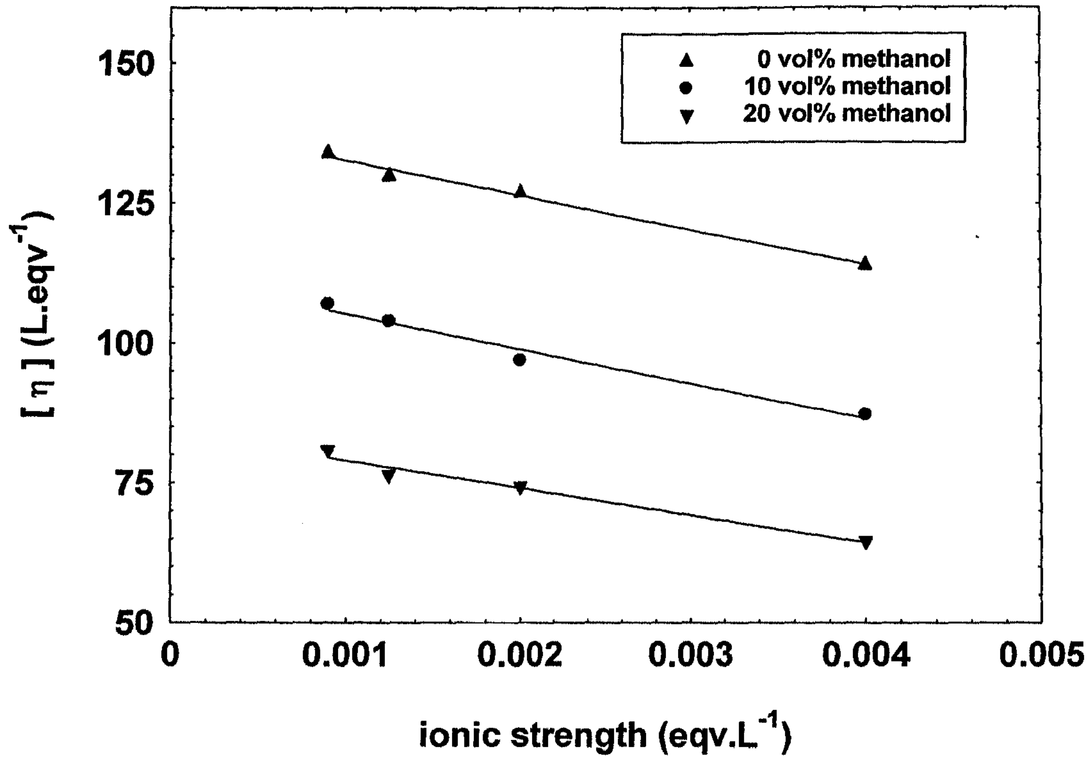

Fig. 6. The effect of total ionic strength on the intrinsic viscosity of sodium carboxymethylcellulose in different methanol-water mixtures, where isoionic dilutions were performed by using NaCl.

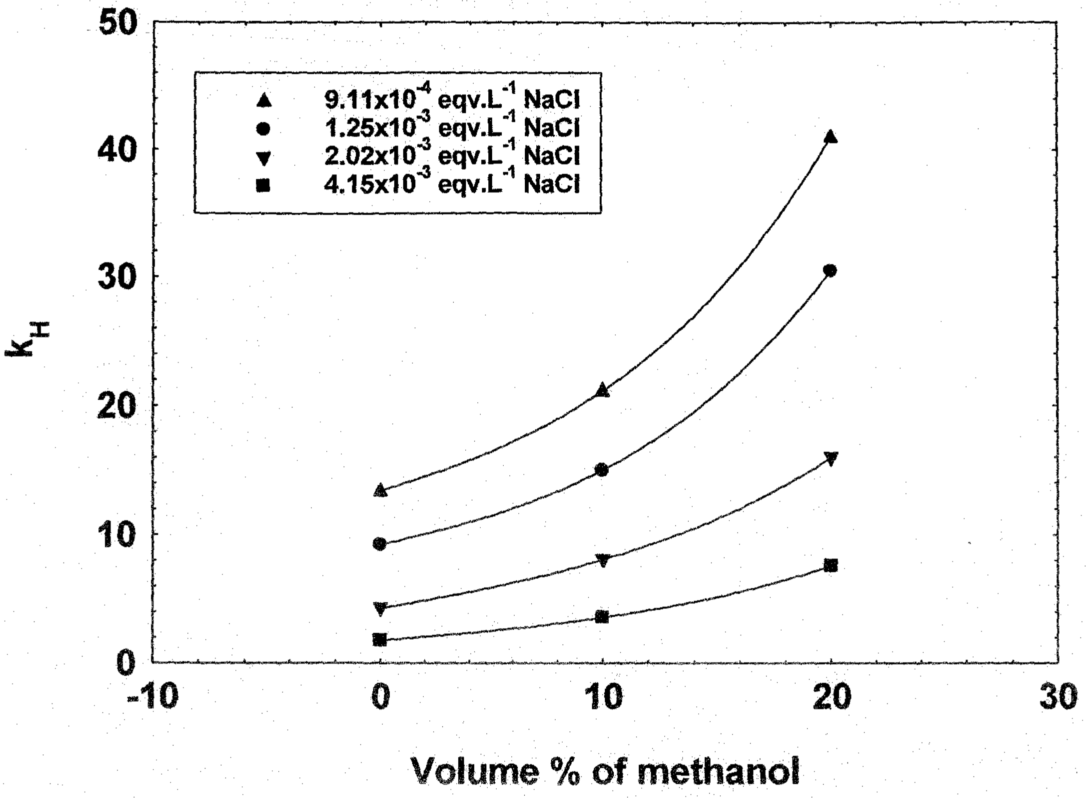

Fig. 7. The effect of medium on the Huggins constant of sodium carboxymethylcellulose in methanol-water mixtures at different total ionic strengths where isoionic dilutions were performed by using NaCl.

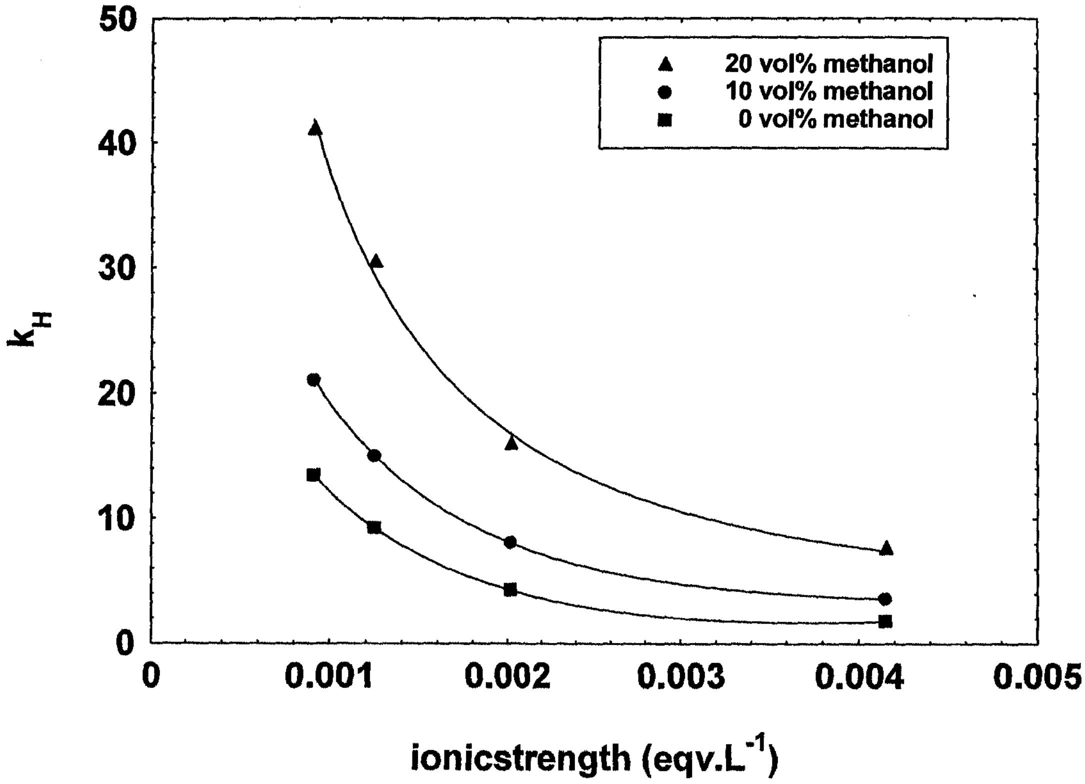

Fig. 8. The effect of total ionic strength on the Huggins constant of sodium carboxymethylcellulose in methanol-water mixtures containing different vol. % of methanol, where isoionic dilutions were performed by using NaCl.

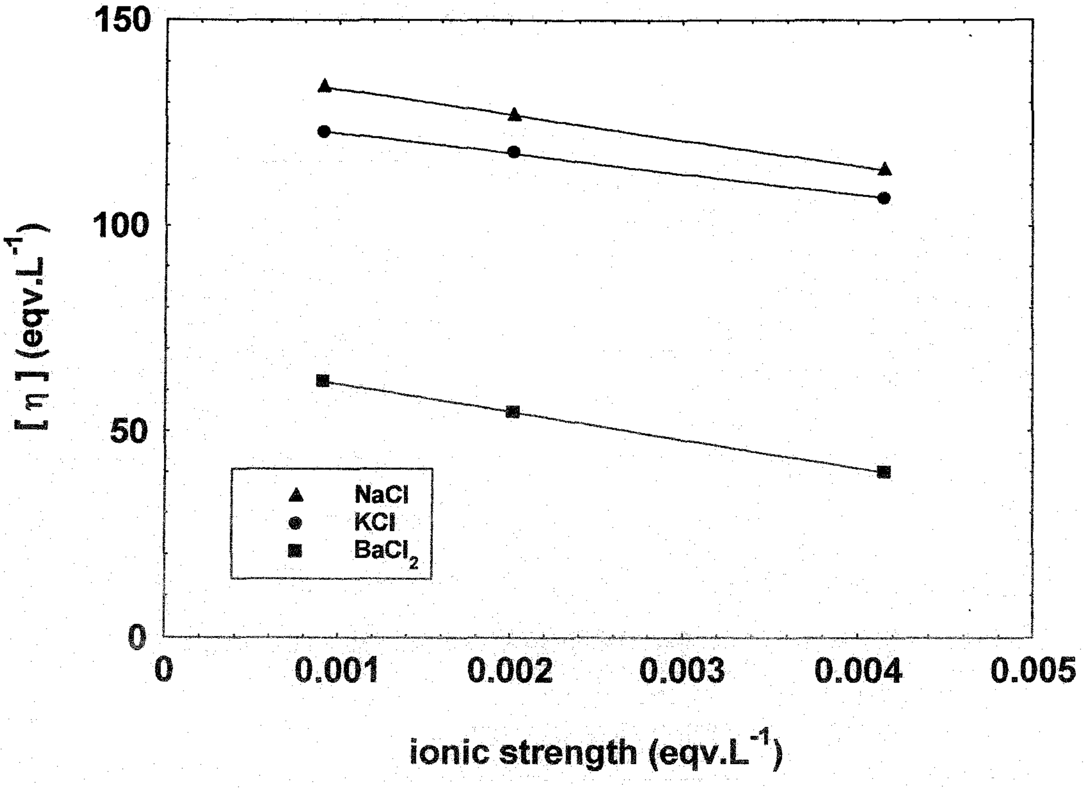

Fig. 9. The effect of different salt on intrinsic viscosity of sodium carboxymethylcellulose by using different salts in water.

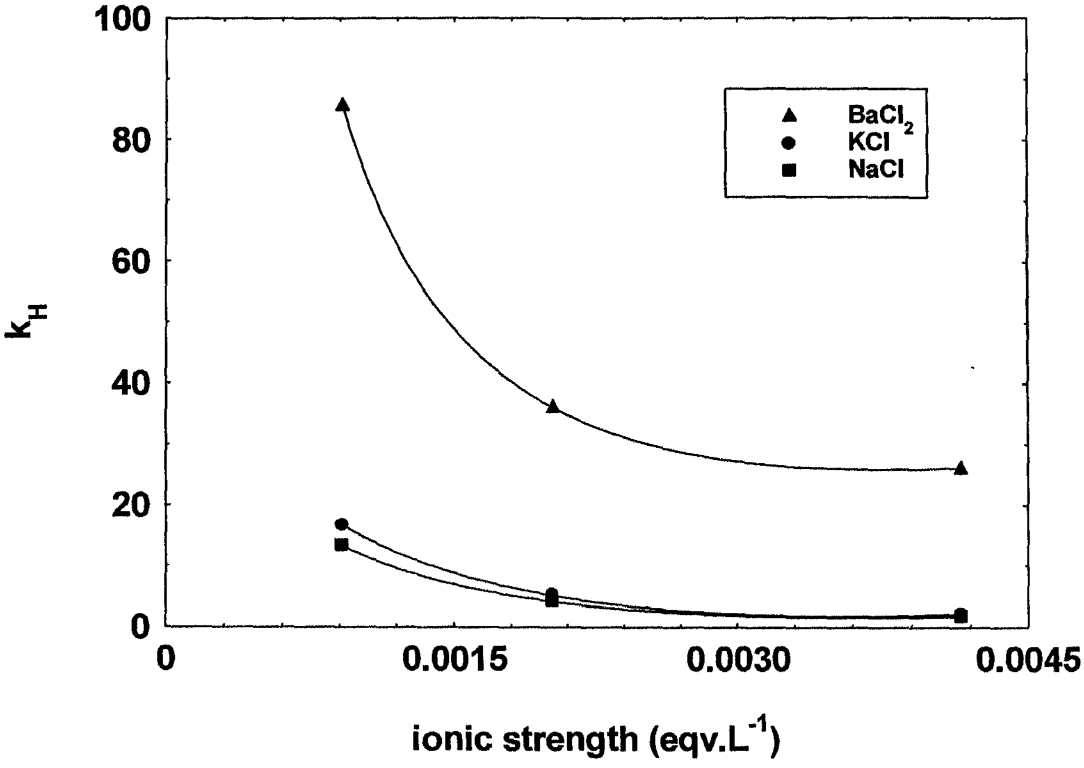

Fig. 10. The effect of different salts on Huggins constant of sodium carboxymethylcellulose by using NaCl, KCl, and $BaCl_2$.

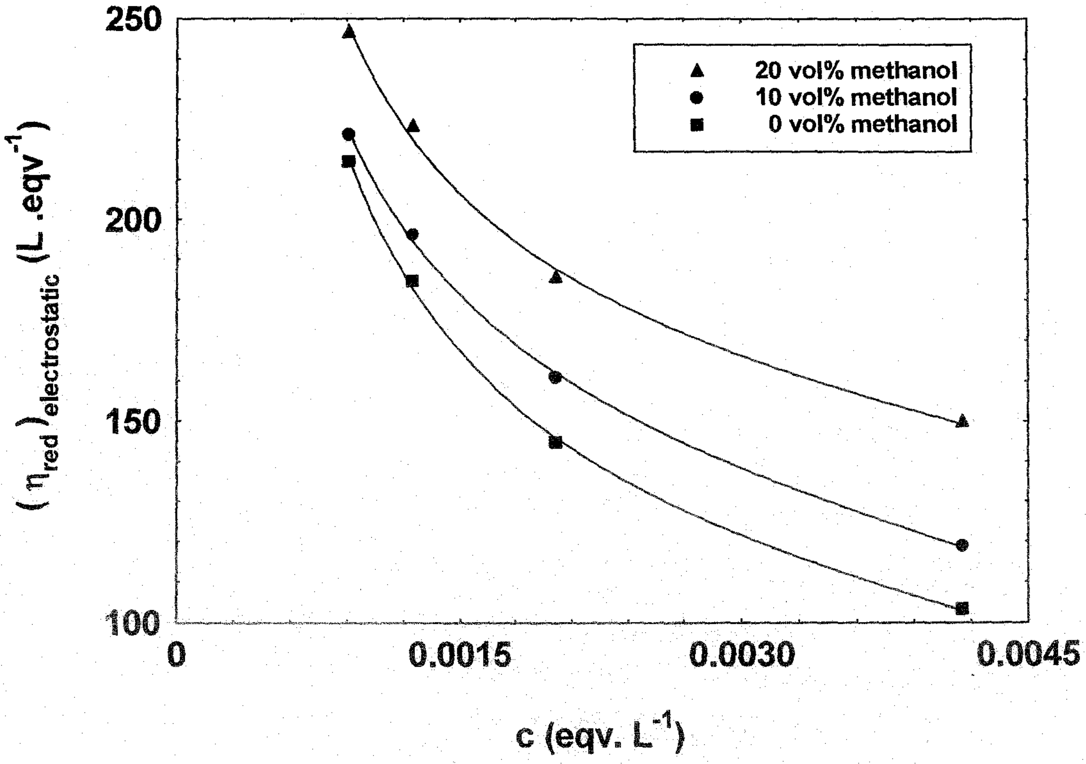

Fig. 11. Electrostatic contribution to the reduced viscosity as a function of polyelectrolyte concentration for sodium carboxymethylcellulose in different methanol-water mixtures.