Chapter 7

Intrinsic Viscosity and Radius of Gyration of Sodium Carboxymethylcellulose in the Absence and in the Presence of a Salt in Aqueous and Mixed Solvent Media

Introduction

A fundamental aspect in understanding the physical properties of a polymer involves determination of the dimension of the macromolecules in a solution. In this context, an accurate determination of the intrinsic viscosity $[\eta]$ and the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ of polymeric samples is of great importance.

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 this distinct polyelectrolyte behavior is 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 to the polymer scientists.

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[4]:

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

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 vs. c values to

$c = 0$. 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 the reduced viscosity is plotted as a function of the square root of the polyelectrolyte concentration. It was usually assumed that this straight line could be extrapolated to zero polyelectrolyte concentration and that the intercept at zero polyelectrolyte 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[6,7] could not be employed to obtain the intrinsic viscosity and, in fact, this is now known to be one of the capital errors in the history of polyelectrolyte. 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.

The problem, however, may be solved through screening of the chain charges by addition of an excess of low molar mass electrolytes. Under these circumstances, the values of the intrinsic viscosities depend on the concentration of the added salt. Other attempts to overcome the problem of the determination of the intrinsic viscosities of polyelectrolytes, in particular, under salt-free situations used semiempirical equations.[8-12] Tobitani & Ross-Murphy[13] revisited several models for predicting the polyelectrolyte intrinsic viscosities, and examined their validity by comparison with experiments, and no concurrence on the method which works best was arrived at.

Recently, Wolf presented a purely phenomenological approach to describe quantitatively the variation of the viscosity of polymer solutions as a function of polymer concentration in the range of pair interaction between the polymer coils, and hence to determine the intrinsic viscosities in a very convenient manner.[14] This model has been shown to be equally applicable for charged and uncharged, linear or non-linear macromolecules in salt-free solutions as well as in solutions containing an external low-molecular weight electrolytes.[14-17]

The principal aim of this study is to obtain accurate root-mean-square radii of gyration of a negatively charged polyelectrolyte sodium carboxymethylcellulose in water and methanol-water mixtures both in the absence and in the presence of salt in order to investigate the variation of the solvodynamic behaviour of this polyelectrolyte as a function of the relative permittivity of the medium and of the concentration of the added salt on the basis of a new method developed by us. The method exploits the experimentally determined intrinsic viscosity values obtained as a function of the ionic strength of the medium. Moreover, mixed solvent media provides an excellent opportunity to study the polyion solvodynamic behaviour from a more general point of view since the electrostatic interactions can be modulated conveniently by merely changing the composition of the solvent medium. For this purpose, precise viscosity measurements of the system mentioned above have been performed, and the derived intrinsic viscosity values were translated to the root-mean-square radius of gyration values of the polyion chains.

Cellulose derivatives are carbohydrate polymers which are well-known for their thickening and stabilizing properties, and carboxymethylcelluloses have been considered a "working horse" amongst the anionic polysachharide-based thickeners and stabilizers and find widespread applications in printing pastes and paints, ice creams, cosmetic creams etc.[18] Thus, with an accurate knowledge on their radii of gyration, their solution properties (for example their rheological behavior) and their efficacies in various applications can be predicted.

Theory

Recently, Wolf offered a purely phenomenological approach to depict quantitatively the variation of the viscosity of polymer solutions as a function of polymer concentration.

According to Wolf[14] the concentration dependence of the relative viscosity of a polyelectrolyte in solution can be conveniently expressed as

$$\ln \eta_{rel} = \frac{c\,[\eta] + Bc^2[\eta][\eta]^*}{1 + Bc\,[\eta]} \tag{2}$$

where B and $[\eta]^*$ are two system-specific constants. The values of the parameters $[\eta]$, B and $[\eta]^*$ can be easily determined on a personal computer from a sufficiently large number of viscosity measurements at different polymer concentrations by any non-linear least-squares fitting program.

Principal features of the connection between the intrinsic viscosity and the coil dimension of *random flight* polymer chains are well established.[19] Thus when the coil dimensions are described in terms of the unperturbed root-mean-square separation of the chain ends $\langle r^2 \rangle_\theta^{1/2}$, the intrinsic viscosity in Flory θ solvent media is given by

$$[\eta]_\theta = \Phi_0 \left[\frac{\langle r^2 \rangle_\theta}{M} \right]^{3/2} M^{1/2} \tag{3}$$

where Φ_0 is a universal Flory constant[20] and for linear flexible chain molecules under theta conditions is equal to 2.87 x 10^{23} when intrinsic viscosities are expressed in cm^3/g.

The root-mean-square radius of gyration under theta conditions $\langle S^2 \rangle_\theta^{1/2}$ can be obtained from the following relationship:

$$[\eta]_\theta = 6^{3/2} \Phi_0 \left[\frac{\langle S^2 \rangle_\theta}{M} \right]^{3/2} M^{1/2} \tag{4}$$

To connect chain dimensions and intrinsic viscosities in good solvents the uniform expansion approximation of Flory and Fox[21] is frequently employed whereby it is assumed

that the intrinsic viscosity increases in proportion to the cube of the expansion factor α_η for the intrinsic viscosity defined by Reed *et al.*,[22]

$$[\eta] = [\eta]_\theta \alpha_\eta^3 \tag{5}$$

The expansion factor α_η for the intrinsic viscosity is a complex function of the expansion factor for the root-mean-square radius of gyration α_S. Weill and Cloizeaux[23] derived a the following semiempirical relation between α_η and α_S:

$$\alpha_\eta^3 = \alpha_S^{2.43} \tag{6}$$

A knowledge of the expansion factor for the root-mean-square radius of gyration α_S in conjunction with the information on the root-mean-square radius of gyration under theta conditions $\langle S^2 \rangle_\theta^{1/2}$ would help ascertain the root-mean-square radius of gyration values under non-θ conditions according to the following relationship:

$$\langle S^2 \rangle^{1/2} = \alpha_S \langle S^2 \rangle_\theta^{1/2} \tag{7}$$

The $\langle S^2 \rangle^{1/2}$ values provide a measure of the actual state of coiling of the polyion chains in experimental solutions.

Experimental

Materials

Methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance of less than 10^{-6} S/cm at 308.15 K was used for the preparation of the solvent mixtures. Sodium carboxymethylcellulose, a negatively charged polyelectrolyte, employed in this investigation was purchased from Aldrich Chemical Company, Inc. Three samples with average molecular

weights (M) of 90,000, 250,000, and 700,000 were used; the first sample had a degree of substitution of 0.70, whereas the later two samples had a degree of substitution of 0.90. These were characterized as described earlier by us.[24]

Viscosity Measurements

The viscosity measurements were performed at the experimental temperature using a Schultz-Immergut-type viscometer[25] with a sintered disc fitted to the widest arm to filter the solution/solvent from dust particles, if any. The flow time measurements were carried out in a water 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.[26,27] Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosity values depend on the shear rate within the concentration range investigated, measurements with capillaries of different inner diameters were made. This did not lead to different values of the reduced viscosity.
The reduced viscosity is obtained from

$$\frac{\eta_{sp}}{c} = \frac{t - t_0}{t_0}\frac{1}{c} \tag{8}$$

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 representative plots (Figs. 1a – 1c) show the concentration dependence of η_{sp}/c for the sodium carboxymethylcellulose samples investigated in methanol-water mixture containing 30 volume percent of methanol at 308.15 K. For the sample with a molecular weight of 90,000 no maxima in the η_{sp}/c vs. c profiles were detected even in salt-free and

the lowest-salt solutions (Fig. 1a); rather appreciable increase in the η_{sp}/c values as the polyelectrolyte concentration decreases was noticed. The 250,000 sample, on the other hand, exhibits maxima in salt-free and the lowest-salt solutions (Fig. 1b). For the sample with the highest molecular weight (700,000) the η_{sp}/c values decrease with the decrease in the polyelectrolyte concentration without manifesting any maxima in salt-free and the lowest-salt solutions (Fig. 1c). It is, thus, apparent that for the 700,000 sample the maxima may be located at the higher concentration region, and we are on the lower concentration side of these maxima. For the 90,000 sample, we are yet to reach the maxima which are expected to appear at even lower polyelectrolyte concentrations. The investigated concentration range is, however, appropriate to manifest the maxima for the 250,000 sample. Thus the position of the maximum in our experiments significantly depends on the molecular weight and is shifted towards smaller polyelectrolyte concentration for smaller polyelectrolyte chains. We also observed similar behavior in the other media investigated. These observations are in good agreement with earlier observations for other aqueous polyelectrolyte systems.[28,29]

The non-linear dependence of η_{sp}/c on polymer concentration - especially in salt-free and low-salt solutions - renders the determination of the intrinsic viscosities for the systems described above using the Huggins relation [Eq. (1)] impossible. Similar difficulties were also encountered with the other systems investigated.

We, therefore, analyzed the primary viscosity data on the basis of the Wolf[15] phenomenological approach [Eq. (2)]. The values of the parameters $[\eta]$, B and $[\eta]^*$ obtained from non-linear least-squares fit of the experimentally determined $\ln\eta_r$ *vs.* c values have been listed in Table 1. Figs. 2a - 2c show the fits in accordance with Eq. (2) by means of the parameters listed in Table 1 along with the experimental results for the sodium carboxymethylcellulose samples investigated in methanol-water mixture containing 30 volume percent of methanol at 308.15 K. An excellent agreement between the experimental and the fitted values demonstrates clearly the efficacy of the Wolf approach for the determination of the intrinsic viscosities.

The experimental $[\eta]$ values show a linear dependence on $c_s^{-1/2}$ (where c_s is the concentration of the added salt) for $c_s \geq 0.001$ mol.L^{-1} for all the systems under investigation (Fig. 3). This kind of linearity of the $[\eta]$ *vs.* $c_s^{-1/2}$ profiles above a certain system-dependent critical salt concentration was also reported earlier for solutions of other polyelectrolytes.[30-33]

We extrapolated the linear plots obtained in the present study to infinite salt concentration in order to determine the limiting values of the intrinsic viscosities. It is interesting to note that these limiting intrinsic viscosity values correspond to the unperturbed conditions (or θ conditions) in an appropriate mixed solvent medium for sodium carboxymethylcellulose samples. These $[\eta]_\theta$ values have, then, been converted into the unperturbed root-mean-square radii of gyration $\langle S^2 \rangle_\theta^{1/2}$ using Eq. (4). Under this condition, the expansion factor α_s will be equal to unity. The $\langle S^2 \rangle_\theta^{1/2}$ values thus obtained are listed in Table 2. These values are also shown graphically in Fig. 4. It is interesting to note that $\langle S^2 \rangle_\theta^{1/2}$ values decreases linearly with the percentage of methanol in the methanol-water media for the three polyelectrolyte samples investigated.

Under non-θ conditions, the polyion chains will expand from their unperturbed values $\langle S^2 \rangle_\theta^{1/2}$. The values of the expansion factors for the radiii of gyration α_s have been estimated from the experimental $[\eta]$ values, and the $[\eta]_\theta$ values (see above) using Eqs. (5) and (6).

We then obtained the radii of gyration values of the polyion chains in salt-free solutions as well as in solutions with finite amount of salt with the aid of Eq. (7). These are recorded in Table 3.

From Table 3, it is apparent that the root-mean-square radii of gyration for the polyelectrolyte systems under investigation vary with the medium at a given ionic strength, and with the ionic strength in a given medium. The effect of added salt is, however, found to be more prominent compared to that of the medium for all the systems. This observation, thus, indicates that the polyelectrolyte sodium carboxymethylcellulose differs appreciably in its solvodynamic behaviour, in particular, when the medium ionic strength is altered. This observed behaviour is consistent with changes in coil dimension. The radius of gyration for the polyions increases with a decrease in the ionic strength. For example the polyion radii of gyration are found to be expanded in salt-free solutions by a factor of around 2.5-3 compared to their unperturbed state. The results are also shown graphically in representative Figs. 5 and 6. One common feature observed from these plots is that the polymer coils are expanded at low ionic strength and collapse drastically with increasing ionic strength. The onset of significant collapse of the coil is found to be around a salt concentration of 0.001 mol.L^{-1} for

the three polyelectrolyte samples in aqueous and in the three methanol-water mixtures investigated.

Conclusions

The present chapter reported precise measurements on the viscosities of solutions of three sodium carboxymethylcellulose samples with molecular weights of 90,000 (DS = 0.7), 250,000 (DS = 0.9), and 700,000 (DS = 0.9) in water and methanol-water mixtures in the absence as well as in the presence of varying concentrations of NaCl (c_s) at 35 ^{0}C. Analyses of the results on the basis of the phenomenological approach for the viscosity of polymers solutions put forward by Wolf[14] help determine the intrinsic viscosities of the investigated polyelectrolyte samples. This contribution proposed a new method for the determination of the unperturbed and the perturbed root-mean-square radii of gyration of the polyion chains from the intrinsic viscosity values obtained in solutions with varying ionic strengths in a very convenient manner. This newly proposed method has been applied to the intrinsic viscosity vs. added-salt concentration data from the system under investigation. One common feature observed from the $\langle S^2 \rangle^{1/2} = f(c_s^{-1/2})$ profiles is that the polymer coils are expanded at low ionic strength and collapse drastically with increasing ionic strength. The onset of significant collapse of the coil is found to be around a salt concentration of 0.001 mol.L^{-1} for the three polyelectrolyte samples in aqueous and in the three methanol-water mixtures investigated. The polyion radii of gyration are found to be expanded in salt-free solutions by a factor of 2.5-3 compared to their respective unperturbed states for the polyelectrolytes investigated. Thus, the method proposed here in this article for the determination of the unperturbed and perturbed root-mean-square radii of gyration of polyions simply from viscosity measurements and the information obtained for some selected carbohydrate polymers might be useful in various branches of nanoscience.

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Table 1. Parameters of Eq. (2) Describing the Composition Dependence of Viscosity of Solutions of Sodium Carboxymethylcellulose in Water and Methanol-Water Mixtures at 308.15 K in the Absence and in Presence of a Salt (NaCl)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
Sodium Carboxymethylcellulose (M = 90,000; DS= 0.7)			
Water			
0	1615	165.99	1.67
0.0001	1492	139.07	1.47
0.001	652	61.33	0.74
0.01	306	41.34	0.31
0.1	179	39.12	0.11
10 vol. % methanol			
0	1478	159.19	1.68
0.0001	1370	135.91	1.53
0.001	602	56.82	0.74
0.01	271	39.72	0.32
0.1	148	37.09	0.13
20 vol. % methanol			
0	1416	158.02	1.72
0.0001	1225	130.79	1.58
0.001	574	53.704	0.75
0.01	248	36.38	0.32
0.1	123	35.96	0.16
30 vol. % methanol			
0	1335	130.75	1.74
0.0001	1107	126.35	1.67
0.001	546	51.07	0.77
0.01	217	36.10	0.34
0.1	112	35.55	0.16

Table 1. (contd..)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
Sodium Carboxymethylcellulose (M = 250,000; DS = 0.9)			
	Water		
0	8324	355.75	0.43
0.0001	7362	327.75	0.41
0.001	3851	267.33	0.34
0.01	1486	208.77	0.23
0.1	812	193.42	0.12
	10 vol. % methanol		
0	8104	348.57	0.43
0.0001	7209	324.03	0.41
0.001	3678	261.76	0.35
0.01	1409	202.74	0.23
0.1	778	189.66	0.12
	20 vol.% methanol		
0	7901	340.55	0.44
0.0001	7102	323.79	0.42
0.001	3492	254.29	0.35
0.01	1350	186.10	0.22
0.1	735	170.43	0.12
	30 vol.% methanol		
0	7532	325.41	0.42
0.0001	7027	317.80	0.42
0.001	3304	248.09	0.36
0.01	1294	165.78	0.20
0.1	702	153.13	0.12

Table 1. (contd..)

c_s (mol.L^{-1})	$[\eta]$(ml.g^{-1})	$[\eta]^*$(ml.g^{-1})	B
Sodium Carboxymethylcellulose (M = 700,000; DS = 0.9)			
	Water		
0	12700	619.72	0.28
0.0001	11400	497.81	0.26
0.001	6400	339.40	0.21
0.01	2950	260.11	0.19
0.1	1818	234.23	0.16
	10 vol.% methanol		
0	12400	593.12	0.28
0.0001	10800	487.72	0.26
0.001	6250	314.33	0.21
0.01	2812	256.17	0.19
0.1	1726	224.90	0.15
	20 vol.% methanol		
0	12100	553.44	0.28
0.0001	9980	476.37	0.26
0.001	5996	308.25	0.21
0.01	2680	243.19	0.19
0.1	1636	216.06	0.13
	30 vol.% methanol		
0	11900	499.85	0.28
0.0001	9832	463.60	0.27
0.001	5650	303.39	0.21
0.01	2517	234.47	0.20
0.1	1519	208.47	0.12

Table 2. Unperturbed Root-mean-square Radii of Gyration, $\langle S^2 \rangle_\theta^{1/2}$, of Sodium Carboxymethylcellulose in Water and Methanol-Water Mixtures at 308.15 K

M	DS	$\langle S^2 \rangle_\theta^{1/2}$ (nm)			
		water	10 vol.% methanol	20 vol.% Methanol	30 vol.% methanol
90,000	0.7	14.16	13.09	12.01	11.10
250,000	0.9	29.72	29.26	28.85	28.63
700,000	0.9	60.36	58.77	57.57	56.08

Table 3. Root-mean-square Radii of Gyration, $\langle S^2 \rangle^{1/2}$ of Sodium Carboxymethylcellulose in Water and Methanol-water Mixtures in Salt-free and Salt Solutions at 308.15 K

c_s(mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)	c_s (mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)
Sodium Carboxymethylcellulose (M = 90,000; DS = 0.7)			
Water		10 vol.% methanol	
0	39.68	0	38.90
0.0001	38.40	0.0001	37.73
0.001	27.32	0.001	26.86
0.01	20.01	0.01	19.39
0.1	16.05	0.1	15.07
20 vol.% methanol		30 vol.% methanol	
0	38.88	0	38.72
0.0001	36.66	0.0001	35.85
0.001	26.84	0.001	26.80
0.01	18.96	0.01	18.33
0.1	14.16	0.1	13.97
Sodium Carboxymethylcellulose (M = 250,000; DS = 0.9)			
water		10 vol.% methanol	
0	99.2	0	98.74
0.0001	94.4	0.0001	94.12
0.001	72.5	0.001	71.35
0.01	48.7	0.01	48.08
0.1	38.11	0.1	37.65
20 vol.% methanol		30 vol.% methanol	
0	97.80	0	96.12
0.0001	93.60	0.0001	93.41
0.001	69.89	0.001	68.47
0.01	47.27	0.01	46.62

Table 3. (contd..)

c_s (mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)	c_s (mol.L^{-1})	$\langle S^2 \rangle^{1/2}$ (nm)
Sodium Carboxymethylcellulose (M = 250,000; DS = 0.9)			
20 vol.% methanol		30 vol.% methanol	
0.1	36.81	0.1	36.20
Sodium Carboxymethylcellulose (M = 700,000; DS = 0.9)			
water		10 vol.% methanol	
0	153.10	0	152.53
0.0001	146.45	0.0001	144.11
0.001	115.36	0.001	115.06
0.01	83.96	0.01	82.91
0.1	68.80	0.1	67.62
20 vol.% methanol		30 vol.% methanol	
0	151.72	0	151.58
0.0001	140.15	0.0001	140.13
0.001	113.64	0.001	111.57
0.01	81.59	0.01	79.99
0.1	66.59	0.1	64.98

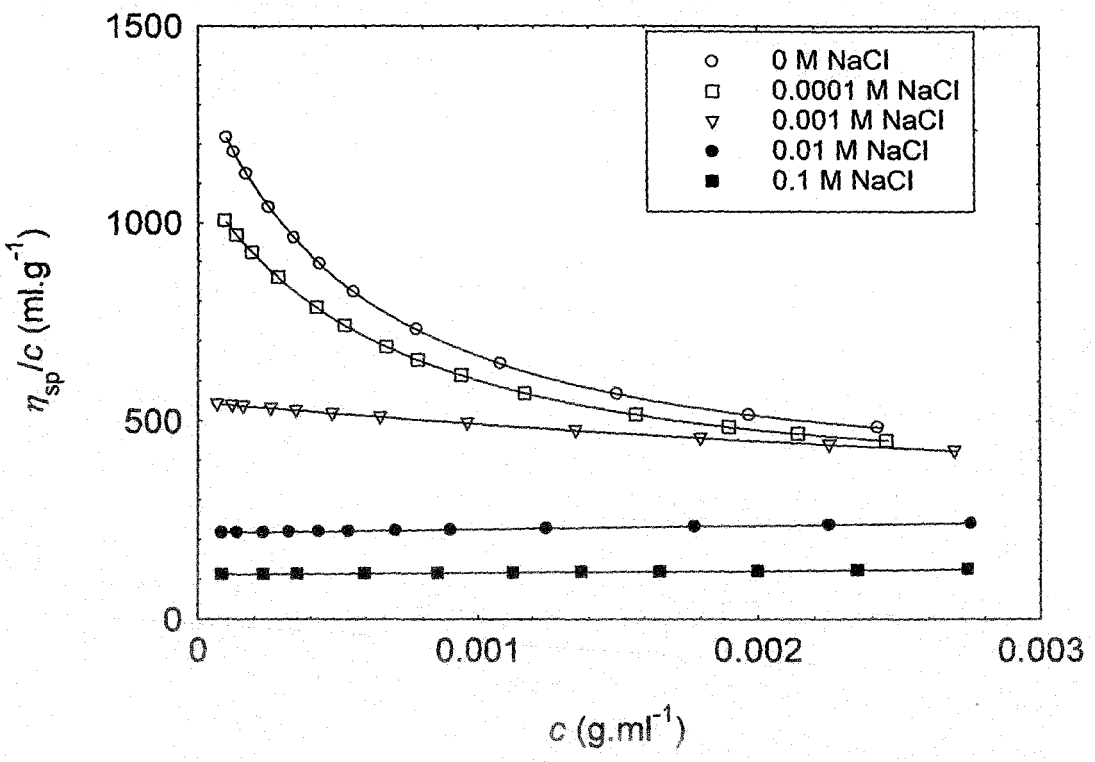

Fig. 1a. Huggins plot for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

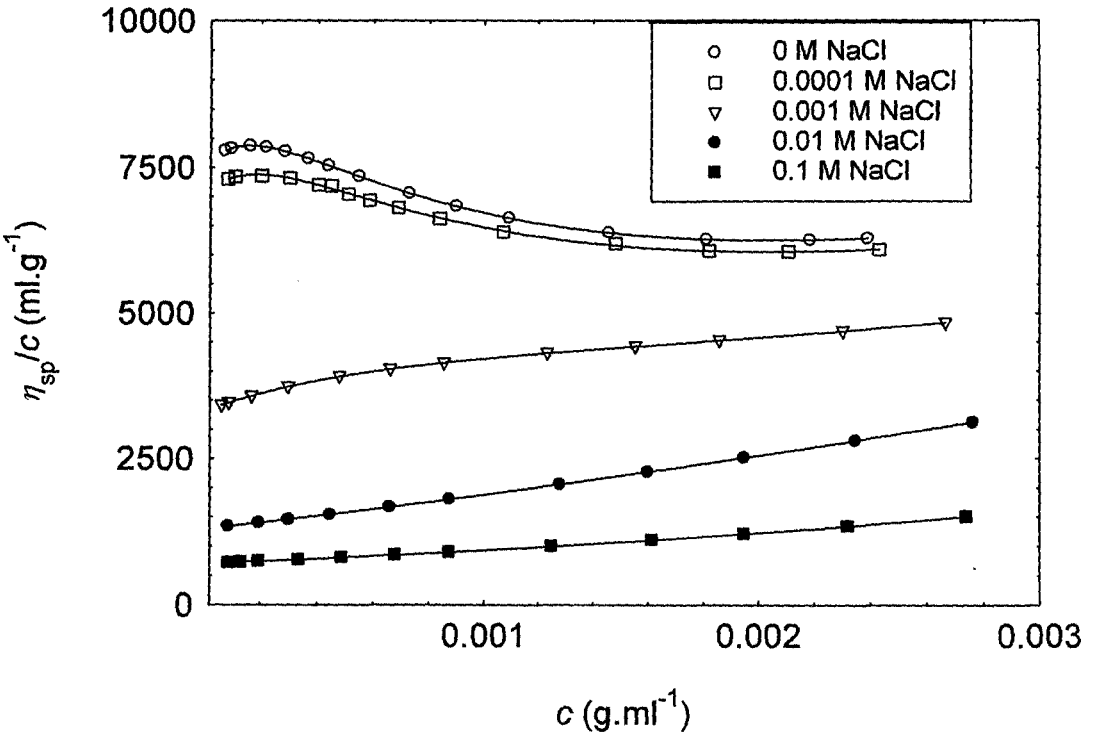

Fig. 1b. Huggins plot for solutions of sodium carboxymethylcellulose (M = 250,000 and DS = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

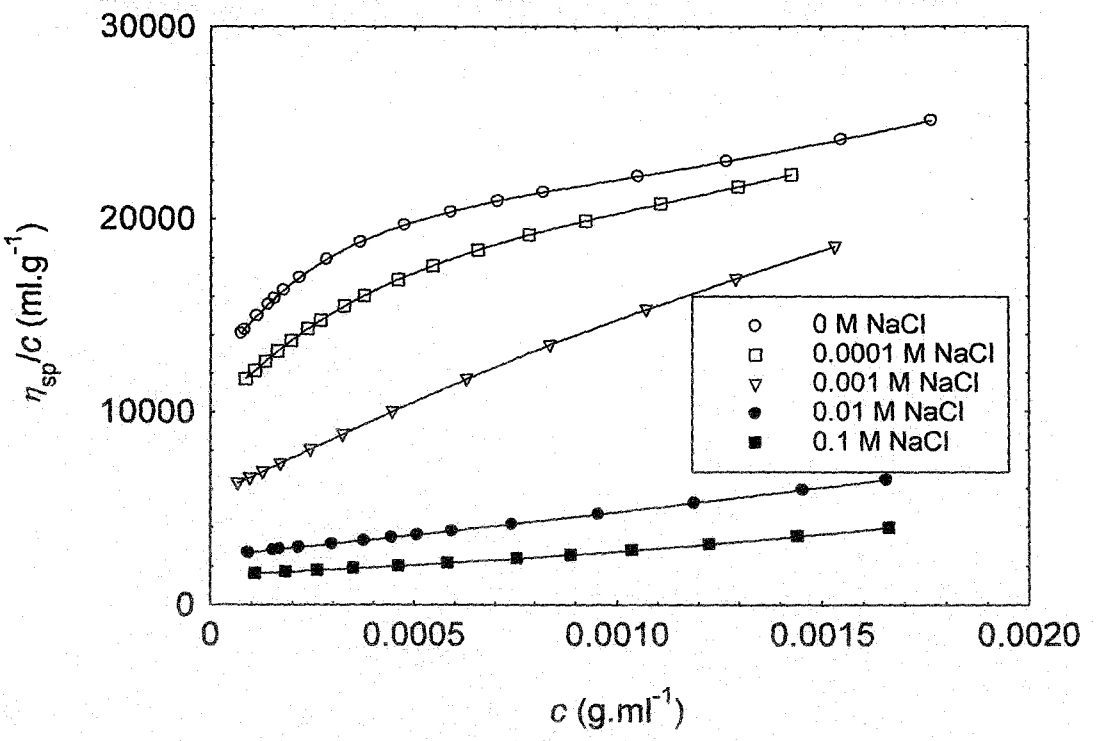

Fig. 1c. Huggins plot for solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 308.15 K. The lines are meant to guide the eye.

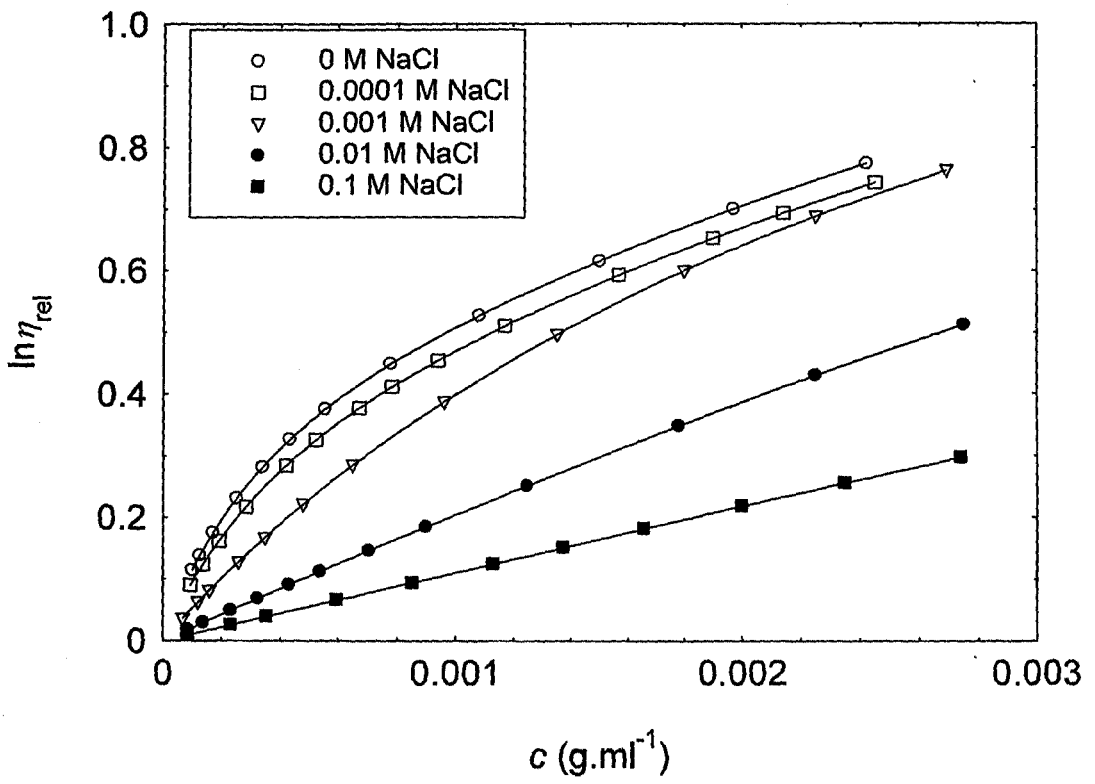

Fig. 2a. Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

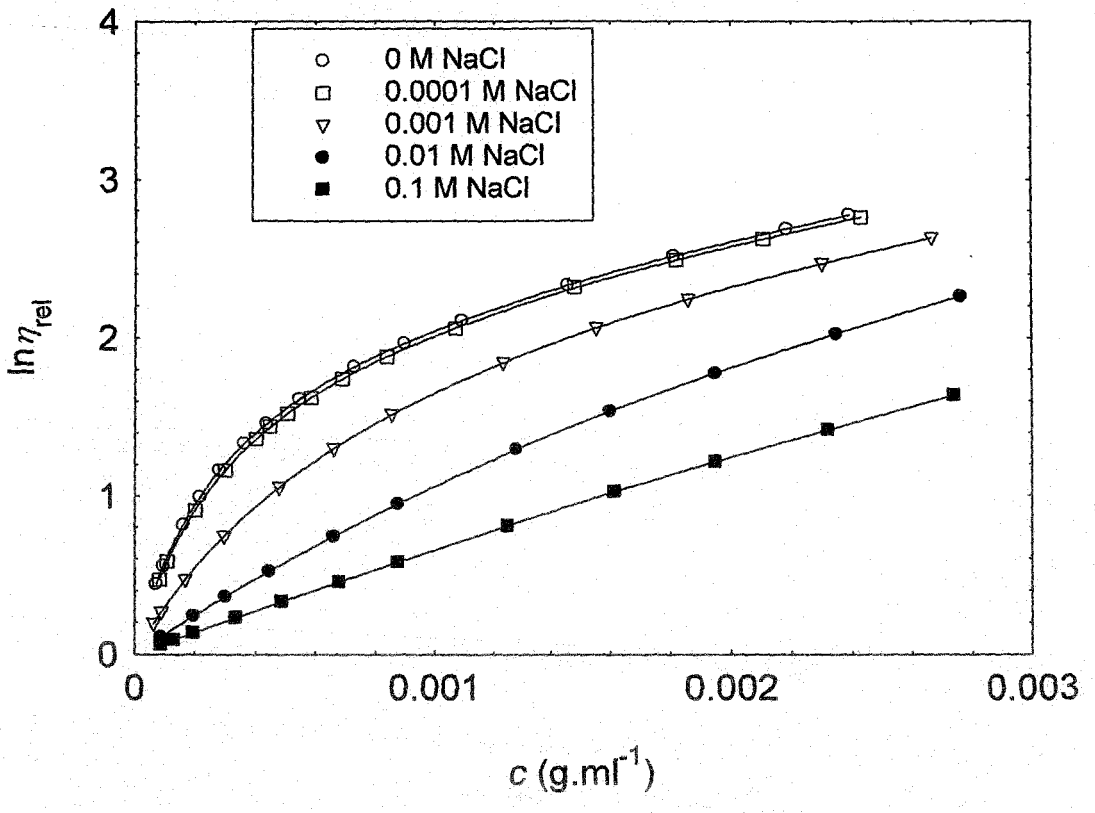

Fig. 2b. Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 250,000 and DS = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

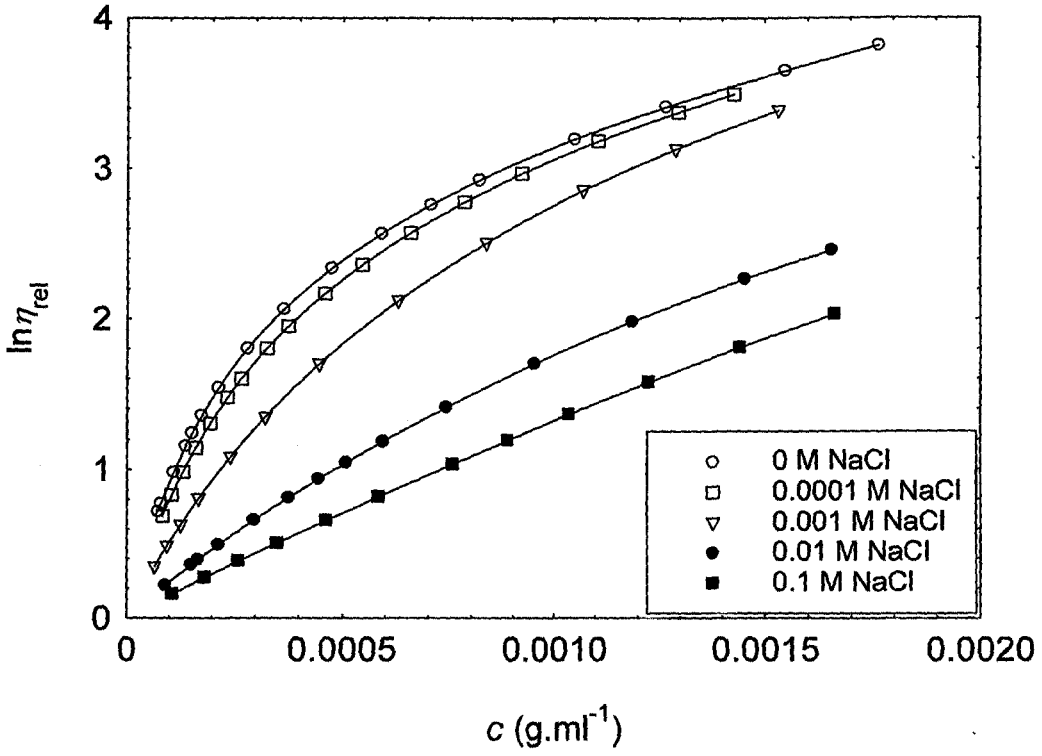

Fig. 2c. Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in methanol-water mixture containing 30 vol. % methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 308.15 K. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

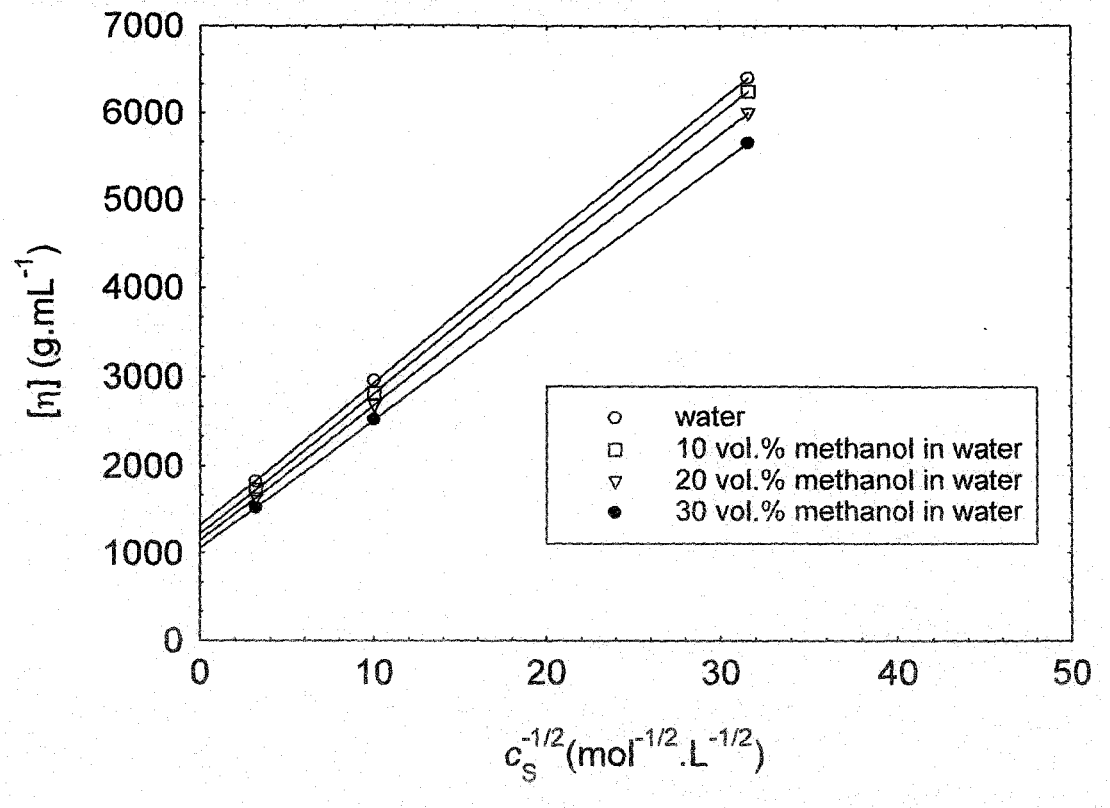

Fig. 3. Dependence of the intrinsic viscosity $[\eta]$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in different solvent media at 308.15 K.

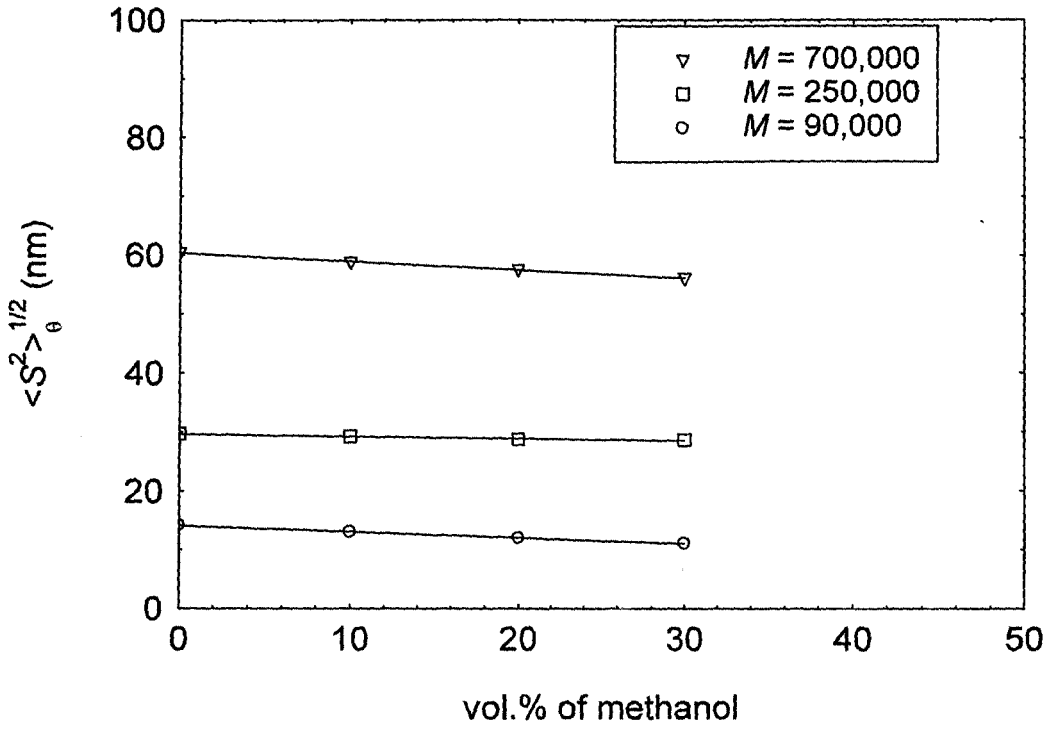

Fig. 4. Variation of the unperturbed radius of gyration for solutions of sodium carboxymethylcellulose with the solvent composition at 308.15 K.

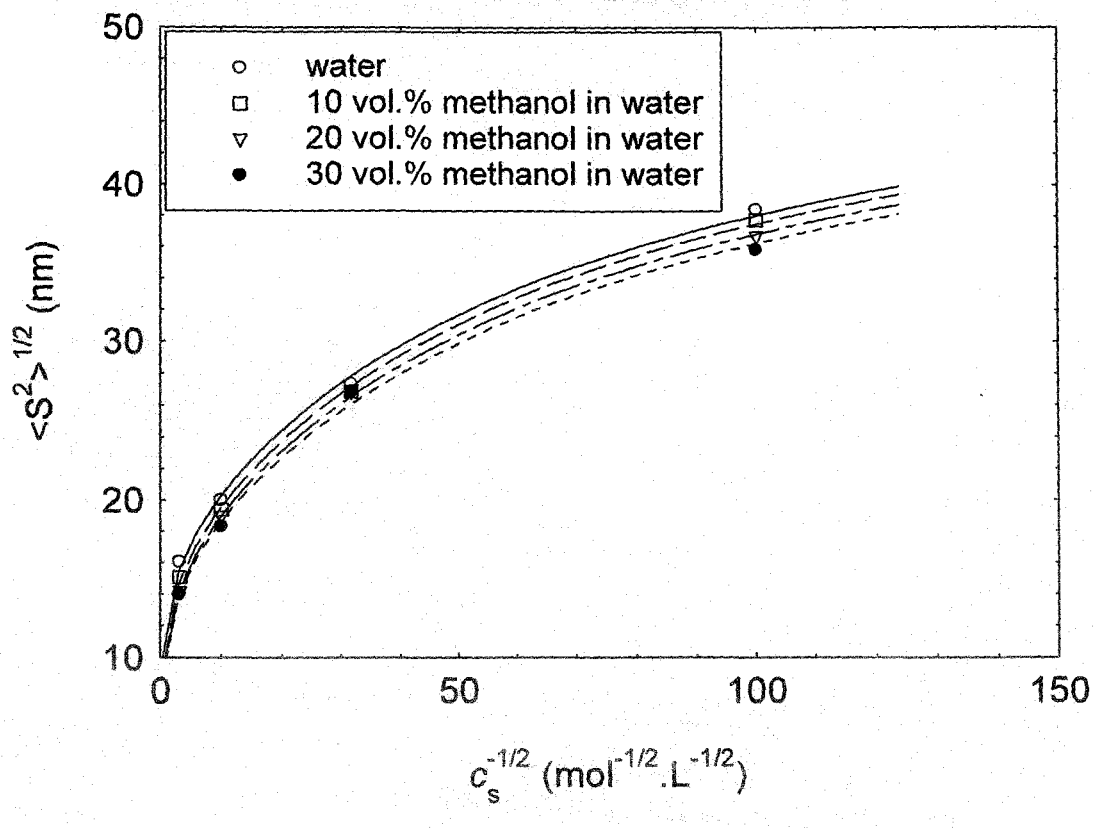

Fig. 5. Dependence of the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in different solvent media at 308.15 K.

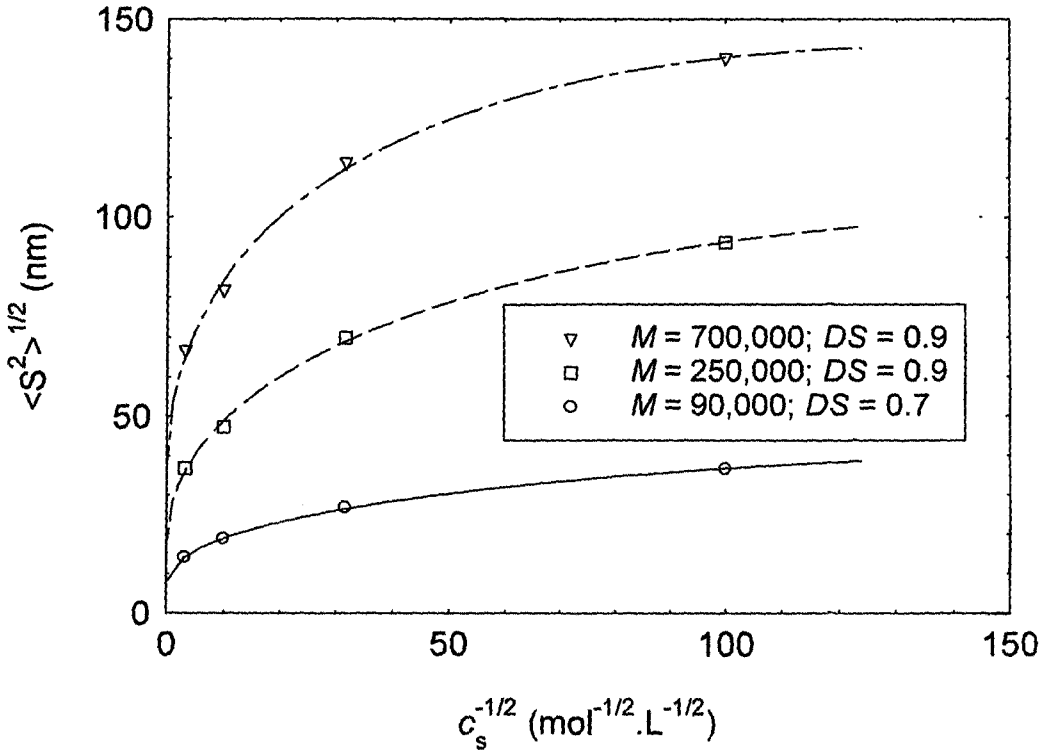

Fig. 6. Effect of the molecular weight on the dependence of the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose in methanol-water mixture containing 20 vol. % of methanol at 308.15 K.