Carbohydrate Polymers 98 (2013) 1297–1303

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Radii of gyration of sodium carboxymethylcellulose in aqueous and mixed solvent media from viscosity measurement

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ARTICLE INFO

Article history:
Received 21 March 2013
Received in revised form 12 August 2013
Accepted 12 August 2013
Available online 14 August 2013

Keywords:
Sodium carboxymethylcellulose
Methanol–water mixed solvent media
Intrinsic viscosity
Root-mean-square radius of gyration
Expansion factor

ABSTRACT

The viscosities of three sodium carboxymethylcellulose samples with molecular weights of 90,000 [degree of substitution (*DS*): 0.7], 250,000 (*DS*: 0.9), and 700,000 (*DS*: 0.9) have been reported in water and methanol–water mixtures in salt-free and salt-containing solutions at 35 °C. The results were analyzed in terms of a phenomenological approach for the viscosity of polymer solutions to determine the intrinsic viscosities [η] of the polyelectrolyte samples. This contribution presents a new and convenient method for the determination of the root-mean-square radii of gyration of the polyion chains using the [η] values obtained as a function of the added salt concentration. The polyion coils are found to expand at low ionic strength and these collapse drastically with increasing ionic strength. Addition of methanol to the medium in which these samples are dissolved causes a contraction of the polyion chains, although this influence is less pronounced than that of the added salt.

1. Introduction

A fundamental aspect in understanding the physical properties of polymers is the determination of their single chain parameters in solution. In this context, an accurate determination of the intrinsic viscosity [η] and the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ of the polymeric samples is of great importance.

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 this distinct polyelectrolyte behavior is characterized by complex interactions, conformations, structures and dynamics (Cohen & Priel, 1994; Dautzenberg et al., 1994a; Oosawa, 1993; Schmitz, 1994). It is thus not surprising that although the experimental determination of the intrinsic viscosity [η] 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_p; η_{sp} = specific viscosity and c_p = polymer concentration) varies linearly with concentration c_p in dilute solutions which led Huggins to propose the following equation (Huggins, 1938; Schmitz, 1994):

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

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

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 (Fuoss, 1948, 1949). In these studies, which have been summarized in the pioneering work of Fuoss (1948, 1949), a straight line is obtained when the reciprocals of the reduced viscosity values are plotted as a function of the square root of the polyelectrolyte concentration. The underlying assumption in these analyses was 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 behavior revealed that the apparent unbounded rise in the reduced viscosity is invariably followed by a maximum (Cohen, Priel, & Rabin, 1988; Cohen, Priel, & Rabin, 1989; Eisenberg, 1976; Pals & Hermans, 1952) and normal polymer behavior is recovered as the polyelectrolyte concentration approaches zero. The method of Fuoss (1948, 1949) could, thus, not be employed to obtain the intrinsic viscosity of polyelectrolytes and, in fact, this is now known to be one of the capital errors in the history of polyelectrolyte research. It has been argued that the maximum in the η_{sp}/c_p vs. c_p profiles results from a competition between screening of

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http://dx.doi.org/10.1016/j.carbpol.2013.08.019

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 works 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 usually 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 (Fedors, 1979; Juan, Dougherty, & Stivala, 1972; Lovell, 1989; Rao, 1993; Yang, 2004). Tobitani and Ross-Murphy (1997) revisited several models for predicting the polyelectrolyte intrinsic viscosities, and examined their validity by means of 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 relative viscosity of polymer solutions $\eta_{rel}(=\eta_{sp}+1)$ 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 (Wolf, 2007). This model has been shown to be equally applicable for charged and uncharged, linear and non-linear macromolecules in salt-free solutions as well as in solutions containing an external low-molar mass electrolyte (Eckelt, Knopf, & Wolf, 2008; Ghimici, Nichifor, & Wolf, 2009; Samadai, Wolf, Guo, Zhang, & Schlüter, 2008; Wolf, 2007).

Static light scattering measurements are widely used to determine the root-mean-square radii of gyration of polyelectrolytes in solution (Dautzenberg et al., 1994a). The principal aim of this study is to show how the root-mean-square radii of gyration of a polyelectrolyte dissolved in a solution could be obtained using simple viscosity measurements in a convenient manner. In particular, we have determined the 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 behavior 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 behavior 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. (Dautzenberg et al., 1994b). Thus, an accurate information on their radii of gyration could help predict their solution properties (for example their rheological behavior) and their efficacies in various applications.

Although the method has been developed to obtain the root-mean-square radii of gyration of a polyion with reference to sodium carboxymethylcellulose solutions, it is quite general, and can be employed to other polyelectrolyte solutions.

2. Theory

In accordance with Wolf (2007), the concentration dependence of the relative viscosity of a polyelectrolyte in solution can be conveniently expressed as

$$\ln \eta_{rel} = \frac{c_p[\eta] + Bc_p^2[\eta][\eta]^*}{1 + Bc_p[\eta]} \tag{2}$$

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.

Here we propose a convenient method for the determination of the $\langle S^2\rangle^{1/2}$ values for polyelectrolytes in solution using viscometric measurements.

Principal features of the connection between the intrinsic viscosity and the coil dimension of *random flight* polymer chains are well established (Berry, 1967).

The root-mean-square separation of the chain ends ($\langle R^2\rangle^{1/2}$) in good solvent media is given by

$$\langle R^2\rangle^{1/2} = \alpha_R \left(\frac{M[\eta]_\theta}{\Phi_0}\right)^{1/3} \tag{3}$$

where Φ_0 is a universal Flory constant (Flory, 1953) and for linear flexible chain molecules under theta conditions is equal to 2.87×10^{23} when intrinsic viscosities are expressed in $cm^3\,g^{-1}$, α_R is the expansion factor for the root-mean-square separation of the chain ends, and $[\eta]_\theta$ is the intrinsic viscosity value under theta condition.

The root-mean-square radii of gyration in good solvent media can be obtained from the following relationship:

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

where α_S is the expansion factor for the root-mean-square radius of gyration.

Therefore, the evaluation of $\langle S^2\rangle^{1/2}$ requires a knowledge on the values of $[\eta]_\theta$ and α_S. The value of $[\eta]_\theta$ can be obtained from a measurement of the intrinsic viscosity values as a function of the ionic strength; the limiting value of $[\eta]$ as the salt concentration becomes infinitely high provides a measure of $[\eta]_\theta$ since this situation corresponds to the theta condition.

In order to relate chain dimensions and intrinsic viscosities in good solvents the uniform expansion approximation of Flory and Fox (1951) is frequently employed whereby it is assumed that the intrinsic viscosity increases proportionately with the cube of the expansion factor α_η for the intrinsic viscosity defined by (Reed, Ghosh, Medjahdi, & Francois, 1991):

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

The expansion factor for the intrinsic viscosity (α_η) is a complex function of the expansion factor for the root-mean-square radius of gyration (α_S). Weill and des Cloizeaux (1979) derived 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-$\boldsymbol{\theta}$ conditions according to the following relationship:

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

The proposed method relies upon the evaluation of the intrinsic viscosity in Flory $\boldsymbol{\theta}$ solvent media. This will be discussed in detail in Section 4.

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

3. Experimental

3.1. Materials

The solvent methanol (Acros Organics, 99.9% pure) was distilled twice. The middle fraction was collected and redistilled. Triply distilled water with a specific conductance of $\leq 10^{-6}$ S cm^{-1} at 35 °C 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 polyelectrolyte samples with average molar masses (M) of 90,000, 250,000, and 700,000 g mol^{-1} were used; the first sample had a degree of substitution of 0.70, whereas each of the later two samples had a degree of substitution of 0.90. These samples were characterized as described earlier by one of us (Sharma, Das, Nandi, & Das, 2010).

3.2. Viscosity measurements

The viscosity measurements were performed at the experimental temperature using a Schultz-Immergut-type viscometer (Schulz & Immergut, 1952) with a sintered disk fitted to the widest arm to filter the dust particles, if any, from the solution/solvent. The flow time measurements were carried out in a water thermostat maintained within ±0.01 °C 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 (Das & Hazra, 1992, 1995). Several independent solutions were prepared, and viscosity 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. These did not lead to different values of the reduced viscosity.

The reduced viscosity is readily obtained from

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

where t and t_0 are the measured times of flow 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.

4. Results and discussion

The representative plots (Figs. 1a–c) show the concentration dependence of η_{sp}/c_p for the sodium carboxymethylcellulose samples investigated in methanol–water mixture containing 30 volume percent of methanol at 35 °C. For the sample with a molecular weight of 90,000 no maxima in the η_{sp}/c_p vs. c_p profiles were detected even in the salt-free and the lowest-salt-containing solutions (Fig. 1a); rather, appreciable increase in the η_{sp}/c_p values

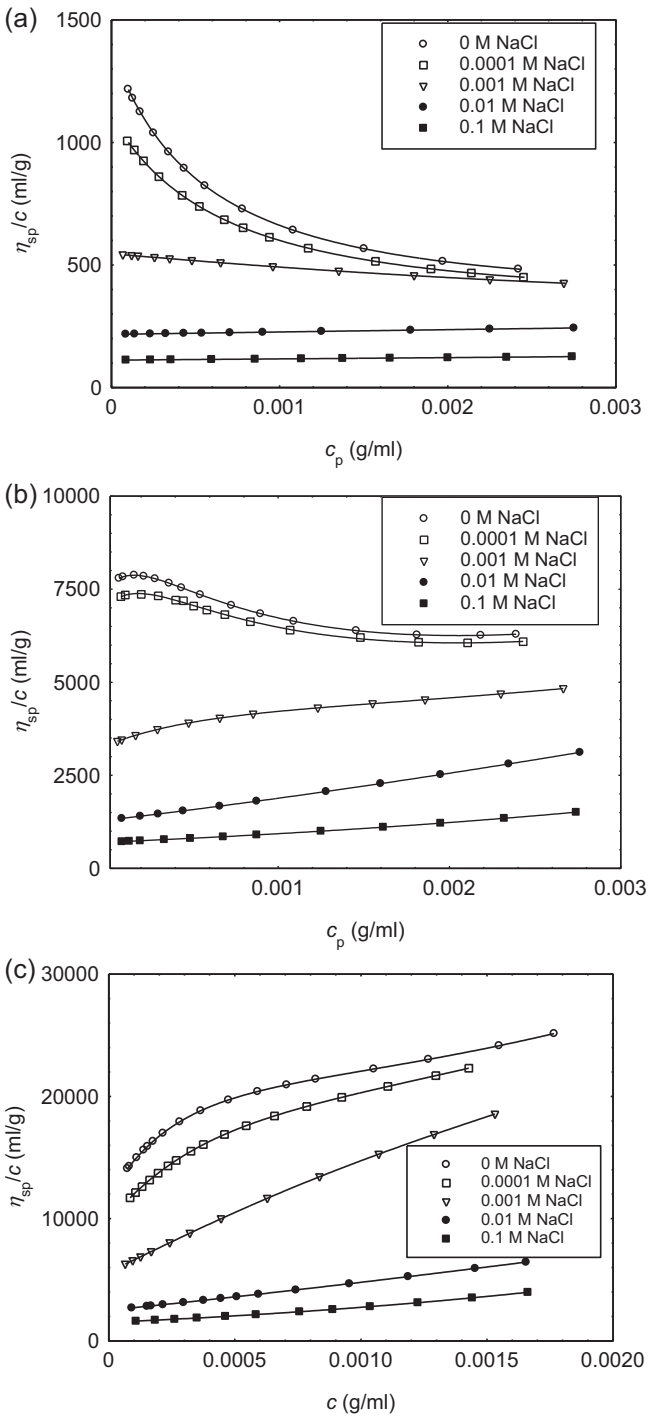

Fig. 1. (a) Huggins plot for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 35 °C. The lines are meant to guide the eye. (b) Huggins plot for solutions of sodium carboxymethylcellulose (M = 250,000 and DS = 0.9) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 35 °C. The lines are meant to guide the eye. (c) Huggins plot for solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) at 35 °C. The lines are meant to guide the eye.

as the polyelectrolyte concentration decreases was noticed. The 250,000 sample, on the other hand, exhibits maxima in the salt-free and the lowest-salt-containing solutions (Fig. 1b). For the sample with the highest molecular weight (700,000) the η_{sp}/c_p values decrease with the decrease in the polyelectrolyte concentration without manifesting any maxima in the salt-free and the lowest-salt-containing 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 toward smaller polyelectrolyte concentration for smaller-sized polyelectrolyte chains. We also observed similar behavior in the other media investigated here. These observations are in good agreement with earlier observations for other aqueous polyelectrolyte systems (Antonietti, Briel, & Forster, 1996; Cohen & Priel, 1990).

The non-linear dependence of η_{sp}/c_p on polymer concentration – especially in salt-free and low-salt-containing 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 here.

We, therefore, analyzed the primary viscosity data on the basis of the Wolf phenomenological approach [Eq. (2)]. The values of the parameters $[\eta]$, B and $[\eta]^*$ obtained from non-linear least-squares fit of the experimentally determined $\ln\eta_{rel}$ vs. c_p values have been listed in Table 1. Fig. 2a–c shows 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 35 °C. 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 $c_s \geq 0.01$ 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 (Fisher, Sochor, & Tan, 1977; Fujita & Homma, 1955; Nishida, Kaji, Kanaya, & Fanjat, 2002; Pals & Hermans, 1952). We extrapolated the straight lines obtained in the present study to *infinite salt concentration* in order to determine the limiting values of the intrinsic viscosities. It is worth noting that these limiting intrinsic viscosity values correspond to the theta conditions in an appropriate mixed solvent medium for sodium carboxymethylcellulose samples.

Under non-theta 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 radii 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 the added salt with the aid of Eq. (7).

A convenient expression for the radius of gyration can be obtained by combining Eqs. (4)–(7) and is given below

$$\langle S^2\rangle^{1/2} = \left(\frac{[\eta]}{[\eta]_\theta}\right)^{1/2.43} \frac{M^{1/3}[\eta]_\theta^{1/3}}{6^{1/2}\Phi_0^{1/3}} \quad (9)$$

Table 1
Parameters of Eq. (2) describing the composition dependence of viscosity of solutions of sodium carboxymethylcellulose in water and methanol–water mixtures at 35 °C 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	158.03	1.72
0.0001	1225	130.79	1.58
0.001	574	53.70	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
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
Sodium carboxymethylcellulose (M = 700,000; DS = 0.9)			
Water			
0	12,700	619.72	0.28
0.0001	11,400	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	12,400	593.12	0.28
0.0001	10,800	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	12,100	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	11,900	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

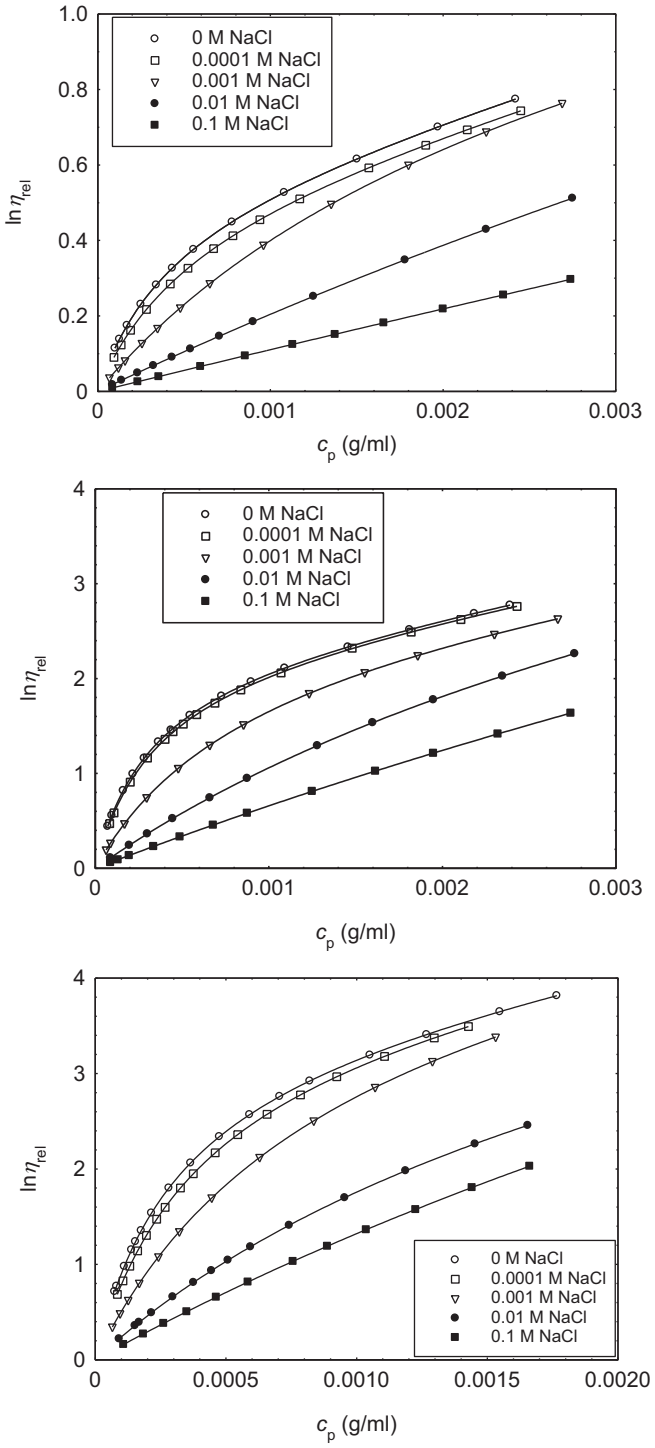

Fig. 2. (a) Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 35 °C. The lines are calculated according to Eq. (2) by means of the parameters of Table 1. (b) Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 250,000 and DS = 0.9) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 35 °C. The lines are calculated according to Eq. (2) by means of the parameters of Table 1. (c) Relative viscosities of the solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in methanol–water mixture containing 30 volume percent methanol in the absence and in presence of varying concentration of an added salt (NaCl) as a function of the polymer concentration at 35 °C. The lines are calculated according to Eq. (2) by means of the parameters of Table 1.

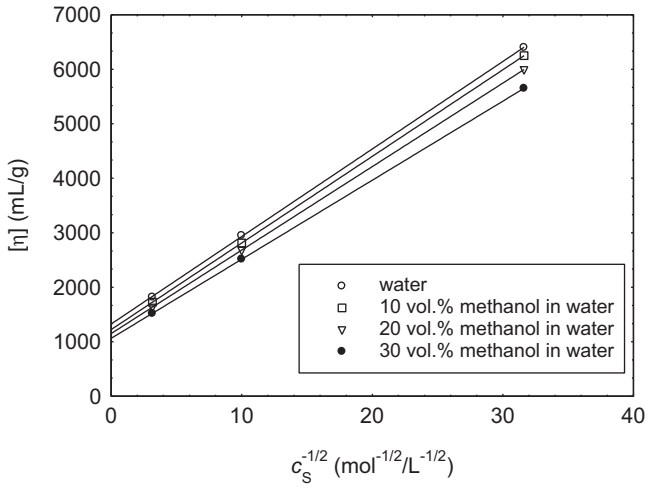

Fig. 3. Dependence of the intrinsic viscosity [η] with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (M = 700,000 and DS = 0.9) in different solvent media at 35 °C.

Table 2 lists the values of the radii of gyration of sodium carboxymethylcellulose in water and in methanol–water mixtures. It is apparent from this table that the root-mean-square radii of gyration for the polyelectrolyte system under investigation vary with the medium at a given ionic strength, and with the ionic strength

Table 2
Root-mean-square radii of gyration, $\langle S^2 \rangle^{1/2}$ of sodium carboxymethylcellu-lose in water and methanol–water mixtures in salt-free and salt solutions at 35 °C.

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
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

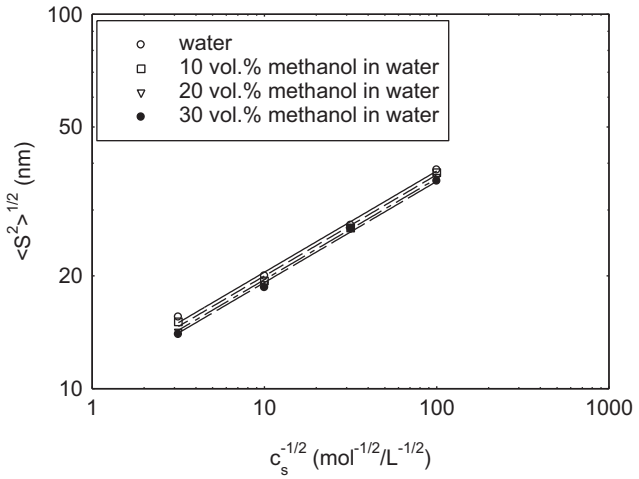

Fig. 4. Log–log plot showing the dependence of the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ with $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose (M = 90,000 and DS = 0.7) in different solvent media at 35 °C.

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 behavior, in particular, when the medium ionic strength is altered. This observed behavior provides an important insight into the changes in coil dimensions as discussed below.

The radii of gyration of the polyion are found to decrease as the medium becomes richer in methanol (*cf.* Table 2 and Fig. 4). Such a variation could be ascribed to a changed counterion condensation onto the polyion chains in solution. The relative permittivity of the medium decreases upon addition of methanol to water which results in a stronger electrostatic interactions between the polyion and the counterions. This brings about more counterion condensation. Consequently, the intramolecular Coulombic repulsive interactions would decrease which reduces the electrostatic persistence length, thus allowing the chain to coil more tightly.

The radius of gyration for the polyions decreases with an increase in the ionic strength of the medium (*cf.* Table 2, and Figs. 4 and 5). Greater screening of the chain charges with increasing ionic strength causes reduced intramolecular electrostatic repulsion thus promoting chain contraction as the ionic strength of the solution increases. One common feature observed from Table 2 is that the polymer coils are expanded at low ionic strength and collapse drastically with increasing ionic strength. Various properties of polyelectrolyte solutions exhibit power law behavior as described by de Gennes (1979). The representative double logarithmic plots (Figs. 4 and 5) depicting the variation of the root-mean-square-radius of gyration of the polyions as a function of the inverse square root of the added salt concentration demonstrate clearly that a power law behavior is found to be observed for the system under investigation and that the slope is the same (≈0.3) for each molecular weight.

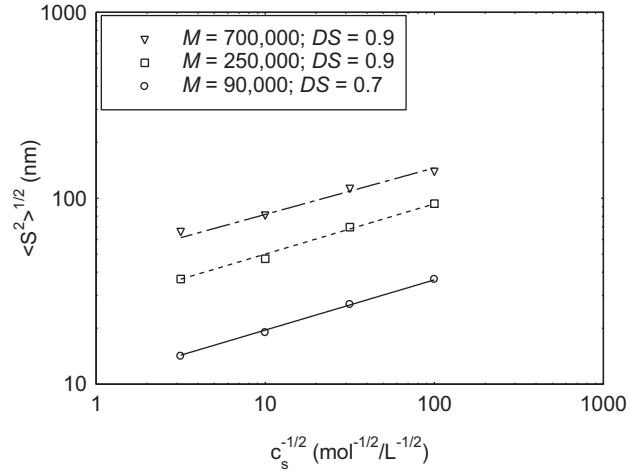

Fig. 5. Effect of the molecular weight on the log–log plot of the root-mean-square radius of gyration $\langle S^2\rangle^{1/2}$ vs. $c_s^{-1/2}$ for solutions of sodium carboxymethylcellulose in methanol–water mixture containing 20 vol.% of methanol at 35 °C.

5. Conclusions

The present article 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 °C. Analyses of the results on the basis of the phenomenological approach for the viscosity of polymers solutions put forward by Wolf (2007) help determine the intrinsic viscosities of the investigated polyelectrolyte samples. This contribution proposed a new method for the determination of the 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 of 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. Thus, the method proposed here in this article for the determination of the 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.

Acknowledgements

This work is supported by the Department of Science and Technology, New Delhi, Government of India [SR/S1/PC-67/2010]. The Department of Chemistry, North Bengal University is also gratefully acknowledged for its support while carrying out this work there.

References

Antonietti, M., Briel, A., & Forster, S. (1996). Intrinsic viscosity of small spherical polyelectrolytes: Proof for the intermolecular origin of the polyelectrolyte effect. *Journal of Chemical Physics*, *105*, 7795–7807.

Berry, G. C. (1967). Thermodynamic and conformational properties of polystyrene. II. Intrinsic viscosity studies on dilute solutions of linear polystyrenes. *Journal of Chemical Physics*, *46*, 1338–1352.

Cohen, J., Priel, Z., & Rabin, Y. (1988). Viscosity of dilute polyelectrolytes solutions. *Journal of Chemical Physics*, *88*, 7111–7116.

Cohen, J., Priel, Z., & Rabin, Y. (1989). Molecular weight dependence of the viscosity in dilute polyelectrolyte solutions. *Polymer Communications*, *29*, 235–239.

Cohen, J., & Priel, Z. (1990). Viscosity of dilute polyelectrolytes solutions: Temperature dependence. *Journal of Chemical Physics*, *93*, 9062–9068.

Cohen, J., & Priel, Z. (1994). Behavior of polyelectrolytes in extremely dilute and semidilute solutions. *Trends in Macromolecular Research*, *1*, 201–203.

Das, B., & Hazra, D. K. (1992). Studies on the viscosities, conductances and adiabatic compressibilities of some tetraalkylammonium perchlorates in 2-methoxyethanol. *Bulletin of the Chemical Society of Japan*, *65*, 3470–3473.

Das, B., & Hazra, D. K. (1995). Conductometric, viscometric, and spectroscopic investigations on the solvation phenomena of Alkali-metal ions and ion pairs in 2-methoxyethanol. *Journal of Physical Chemistry*, *99*, 269–273.Dautzenberg, H., Jager, W., Koetz, J., Philipp, B., Seidel, C., & Stscherbina, D. (1994a). *Polyelectrolytes: Formation characterization and application*. Munich: Hanser Publishers (Chapter 5).

Dautzenberg, H., Jager, W., Koetz, J., Philipp, B., Seidel, C., & Stscherbina, D. (1994b). *Polyelectrolytes: Formation characterization and application*. Munich: Hanser Publishers (Chapter 7).

de Gennes, P.-G. (1979). *Scaling concepts in polymer physics*. Ithaca, NY: Cornell University Press.
Eckelt, J., Knopf, A., & Wolf, B. A. (2008). Polyelectrolytes: Intrinsic viscosities in the absence and in the presence of salt. *Macromolecules*, *41*, 912–918.
Eisenberg, H. (1976). *Biological macromolecules and polyelectrolytes in solution*. London: Oxford University.
Fedors, R. F. (1979). An equation suitable for describing the viscosity of dilute to moderately concentrated polymer solutions. *Polymer*, *20*, 225–228.
Fisher, L. W., Sochor, A. R., & Tan, J. S. (1977). Chain characteristics of poly(2-acrylamido-2-methylpropanesulfonate) polymers. 1. Light-scattering and intrinsic viscosity studies. *Macromolecules*, *10*, 949–954.
Flory, P. J., & Fox, T. G. (1951). Treatment of intrinsic viscosities. *Journal of the American Chemical Society*, *73*, 1904–1908.
Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca, NY: Cornell University Press (Chapter XIV).
Fujita, H., & Homma, T. (1955). Non-Newtonian viscosities in dilute aqueous solutions of sodium carboxymethylcellulose. *Journal of Polymer Science*, *15*, 277–295.
Fuoss, R. M. (1948). Viscosity function for polyelectrolytes. *Journal of Polymer Science*, *3*, 603–604.
Fuoss, R. M. (1949). Viscosity function for polyelectrolytes. *Journal of Polymer Science*, *4*, 96.
Ghimici, L., Nichifor, M., & Wolf, B. (2009). Ionic polymers based on dextran: Hydrodynamic properties in aqueous solution and solvent mixtures. *Journal of Physical Chemistry B*, *113*, 8020–8025.
Huggins, H. L. (1938). *Journal of Physical Chemistry*, *42*, 911–920.
Juan, L., Dougherty, T. J., & Stivala, S. (1972). A semi-empirical approach to the viscosities of polyelectrolyte solutions. *Journal of Polymer Science, Part A-2*, *10*, 171–189.
Lovell, A. (1989). Dilute solution viscometry. In C. Booth, & C. Price (Eds.), *Comprehensive polymer science: The synthesis, characterization, reactions, and applications of polymers* (pp. 173–200). London and New York: Pergamon Press.
Nishida, K., Kaji, K., Kanaya, T., & Fanjat, N. (2002). Determination of intrinsic viscosity of polyelectrolyte solutions. *Polymer*, *43*, 1295–1300.
Oosawa, F. (1993). *Polyelectrolytes*. New York: Marcel Dekker.
Pals, D. T. F., & Hermans, J. J. (1952). Sodium salts of pectin and carboxy methyl cellulose in aqueous sodium chloride. I. Viscosities. *Recueil des Travaux Chimiques des Pays-Bas*, *71*, 433–457.
Rao, M. V. S. (1993). Viscosity of dilute to moderately concentrated polymer solutions. *Polymer*, *34*, 592–596.
Reed, W. F., Ghosh, S., Medjahdi, G., & Francois, J. (1991). Dependence of polyelectrolyte apparent persistence lengths, viscosity, and diffusion on ionic strength and linear charge density. *Macromolecules*, *24*, 6189–6198.
Samadai, F., Wolf, B. A., Guo, Y., Zhang, A., & Schlüter, A. D. (2008). Branched versus linear polyelectrolytes: Intrinsic viscosities of peripherally charged dendronized poly(methyl methacrylate)s and of their uncharged analogues. *Macromolecules*, *41*, 8173–8180.
Sharma, R., Das, B., Nandi, P., & Das, C. (2010). *Journal of Polymer Science: Part B*, *48*, 1196–1202.
Schmitz, K. S. (1994). Macro-ion characterization. From dilute solutions to complex fluids. In *ACS symposium series 548*. Washington, DC: American Chemical Society.
Schulz, J., & Immergut, E. H. (1952). Instrument for determining Shear dependence of intrinsic viscosity of high polymer solutions. *Journal of Polymer Science*, *9*, 279–281.
Tobitani, A., & Ross-Murphy, S. B. (1997). The intrinsic viscosity of polyelectrolytes revisited. *Polymer International*, *44*, 338–347.
Weill, G., & des Cloizeaux, J. (1979). Dynamics of polymers in dilute solutions: An explanation of anomalous indices by cross-over effects. *Le Journal de Physique (Orsay, France)*, *40*, 99–105.
Wolf, B. A. (2007). Polyelectrolytes revisited: Reliable determination of intrinsic viscosities. *Macromolecular Rapid Communications*, *28*, 164–170.
Yang, Y. (2004). Interpretation of viscosity behavior of a polyelectrolyte in a salt-free polar solvent by ion-association. *Journal of Macromolecular Physics Part B: Physics*, *43*, 845–858.