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

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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 $[\eta]$ 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 $[\eta]$ 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 $[\eta]$ 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 $[\eta]$ 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_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):

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

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 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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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 $\eta_{\mathrm{rel}}(=\eta_{\mathrm{sp}}+1)$ 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

$$\ln\eta_{\mathrm{rel}}=\frac{c_{\mathrm{p}}[\eta]+Bc_{\mathrm{p}}^{2}[\eta][\eta]^{*}}{1+Bc_{\mathrm{p}}[\eta]} \tag{2}$$

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

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

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 $\mathrm{cm^3\,g^{-1}}$, 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:

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

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}:

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