



Evaluation of viscometric properties of carboxymethylcellulose and gellan

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ABSTRACT

Viscometry is an inexpensive characterization method to obtain important information about the hydrodynamic volume and conformation of polymers in diluted solutions, in a determined solvent and specific temperature. The viscometric parameters can be mathematically calculated by graphical extrapolation or single-point determination. This article reports a viscometric study of two polysaccharides, carboxymethylcellulose (CMC) (degree of substitution = 2.23) and gellan (GL), with the use of two calculation methods, employing a series of six equations: Huggins, Kraemer and Schulz-Blaschke, by graphical extrapolation; and Schulz-Blaschke, Solomon-Ciuta and Deb-Chanterjee, by single-point determination. It is also used Wolf equations for a different way to determine the intrinsic viscosity. The solution for CMC analyses was NaCl 0.2 mol/L, and for gellan determination, the solvent applied was KCl 0.1 mol/L. For both polymers, the test temperature was 30 ± 0.1 °C. The average molar mass was also determined by the viscometry analysis. The values of intrinsic viscosity of some constants indicated that the solvents systems used for CMC and for gellan, the solvents used are classified as a good system ($k_h + k_k < 0.5$). It was also observed that the method of calculation by a single-point determination was valid for both polyelectrolytes analyzed.

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1. Introduction

The development of sustainable materials, which pollute the environment less, is important both for environmental protection and industrial development. With this view, natural polymers are excellent alternatives for engineering materials, especially polysaccharides, due to properties such as biocompatibility, biodegradability, abundance in nature and versatility of applications in engineering, biotechnology and medicine. Additionally, they are usually nontoxic, inexpensive and obtained from renewable sources. The polysaccharides often have an ionic character and belong to the class of polyelectrolytes [1–6].

Carboxymethylcellulose is an anionic polymer derived from cellulose that is very soluble in water, both cold and hot. It is sensitive to pH variation and ionic strength, the only polyelectrolyte derived from cellulose with this characteristic. It is usually sold as sodium salt, since its acid form has low solubility in water [7, 8]. The structure of carboxymethylcellulose is based on the β -(1,4)-D-glucopyranose cellulose polymer. Different preparations can have different degrees of substitution, referring to the number of substitutions that occur in their radicals [9].

Gellan gum is a linear anionic polysaccharide produced by fermentation of a pure culture of *Sphingomonas elodea* (formerly *Pseudomonas elodea*). The molecular structure is based on repeated units (β -1,3-D-glucose, β -1,4-D-glucuronic acid, β -1,3-D-glucose, α -1,4-L-rhamnose) and two acetyl groups, acetate and glycerate, linked to residual glucose adjacent to the glucuronic acid. Gellan gum is obtained commercially in two forms, with low and high acyl content. In the high acyl content form, approximately half of the glucose rings have an acyl group on carbon C6 and an L-glycerate on carbon C2 or are deacetylated. In aqueous solution, gellan forms a very loose gel. It was shown to adopt a double helix conformation at room temperature, formed by two chains [5, 10–18].

Polyelectrolytes, including carboxymethylcellulose and gellan, have an overall net negative charge. A decrease in ionic strength causes polymeric chain reorientation [18].

Viscosity measurement is a simple and appropriate method to provide information about macromolecular chains in solution. By the use of viscosity analysis of a dilute polymer solution, it is possible to obtain parameters related to the behavior of the chain isolated in the solvent, at a given temperature. The dilute solution viscometry method provides information about both the polymer-polymer interactions and polymer-solvent interactions in solution. Capillary viscometry is easily executed, which makes the technique useful both in academia and industry.

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However, the viscometric method, although simple, is laborious. Thus, there is strong interest in methods (experimental and mathematical) that can concomitantly reduce the time for determination and provide results with reduced margin of error [19–23].

Intrinsic viscosity $[\eta]$ is the parameter that enables characterization of the dimension and configuration of a polymer in solution, so this property is related to the hydrodynamic properties of the chain. The values of various mathematical constants indicate the quality of the solvent, *i.e.*, the solvent-polymer affinity [24, 25]. The intrinsic viscosity can be described by Eq. (1):

$$[\eta] = \lim_{c \rightarrow 0} [\eta_{sp}/c] \quad (1)$$

where η_{sp} is the specific viscosity, which is defined by Eq. (2). The specific viscosity determines the contribution of solute (polymer) on the solution viscosity [25].

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 \quad (2)$$

where η is the polymer solution's viscosity and η_0 is the pure solvent's viscosity.

In the literature, it is possible to find some mathematical equations to determine the intrinsic viscosity $[\eta]$ of a polymeric material when in solution, by graphical extrapolation. In this case, the most commonly employed equations are those of Huggins (h), Kraemer (k) and Schulz-Blaschke (sb) (Eqs. (3) to (5), respectively) [19, 22, 26–29].

$$\eta_{sp}/c = [\eta]_h + k_h [\eta]_h^2 c \quad (3)$$

$$\ln \eta_r/c = [\eta]_k - k_k [\eta]_k^2 c \quad (4)$$

$$\eta_{sp}/c = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

where: $\eta_r = \eta/\eta_0$ = relative viscosity, η_{sp} = specific viscosity; $\eta_{sp}/c = \eta_{red}$ = reduced viscosity; and k_h , k_k and k_{sb} = coefficients of Huggins, Kraemer and Schulz-Blaschke respectively.

By combining Eqs. (3) and (4), and assuming that $k_h + k_k = 0.5$, Solomon and Ciuta [30] determined Eq. (6) to calculate the intrinsic viscosity by the single-point method.

$$[\eta]_{sc} = \left[2 \left(\eta_{sp} - \ln \eta_r \right) \right]^{1/2} / c \quad (6)$$

Eq. (7) was proposed by Deb and Chatterjee [31] as an expression of the intrinsic viscosity, also determined by the single-point method.

$$[\eta]_{dc} = \left(3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp} \right)^{1/3} / c \quad (7)$$

In graphical extrapolation method, practical determinations using different concentrations of polymer solutions are carried out by counting the efflux time of these solutions through a capillary. On the other hand, the single point determination has the advantage of being more rapid and adequate when a large number of samples have to be analyzed in short periods of time. Moreover, this method has the advantage of being independent of a constant value [19, 26–28], in contrast to graphical extrapolation determinations. So, the use of single-point equations is very useful to simplify the technique and reduce the time to obtain the results.

The Schulz-Blaschke equation can also be used for single-point determination. In this case, it is necessary to consider $k_{sb} = 0.28$, which according to the literature, is appropriate for many polymer-solvent-temperature systems [19, 21, 26–28, 32, 33].

From the Mark-Houwink-Sakurada equation, the intrinsic viscosity value depends on the molar mass of the polymer (\bar{M}_v) (Eq. (8)) [34].

$$[\eta] = K (\bar{M}_v)^a \quad (8)$$

where K and a are related to the viscometric constants, which change as a function of solvent, temperature and chemical structure or molar mass of the polymer [22, 35].

The addition of a salt in the aqueous solution of polyelectrolytes, such as the polysaccharides, reduces the electrostatic repulsion, leading to conformation that is neither excessively extended nor overly entangled, resulting in reduced viscosity [20, 36]. Based on this, a lower viscosity can be achieved by adding a salt, like NaCl or KCl that provides a weak electrostatic repulsive force, hence reducing intrinsic viscosity values [22, 37].

Until now, it was not found in the literature a work that has evaluated the single point determination method and the method proposed by Wolf [37, 42] to calculate the viscosimetric parameters of carboxymethylcellulose and gellan. Thus, the principal goal of this study was to determine the best equation to calculate the intrinsic viscosity and viscometric average molar mass of carboxymethylcellulose with high degree of substitution, and gellan, using an inorganic salt in the solution (NaCl for CMC, and KCl for gellan). For this purpose, different equations were applied: Huggins, Kraemer and Schulz-Blaschke (extrapolation method), Schulz-Blaschke, Solomon-Ciuta, Deb-Chatterjee (single-point method), and Wolf equations. The validity of the single point determination method for these polyelectrolytes, in the investigated conditions, was also evaluated.

2. Materials and methods

Carboxymethylcellulose (CMC) was manufactured by Denver Especialidades Químicas and is sold under the trade name CMC Induskol t-9000-2. This material was donated by Teadit Indústria e Comércio Ltda. The product was used as received. The degree of substitution (DS) was determined by ¹H NMR spectra according to a method previously described [38] and defined as follows: (one half of the integral of the carboxymethyl signals in the region between 4.0 and 4.5 ppm)/(one-sixth of the total integral of the major C-H signals at a higher field between 3 and 4 ppm). The DS was 2.23.

Gellan (GL) Kelcogel F (deacetylate) was manufactured by CPKelco Brasil S.A. and the material was also used as received.

To realize the analyses, specific solutions were prepared according to the literature. For CMC, 0.1% (w/v) solution was prepared with 0.2 M of NaCl (Proquímica Ltda.) [39]. In the case of GL, the solution prepared was 0.1% (w/v) with 0.1 M of KCl (Vetec Química Fina Ltda.) [40]. The CMC and GL dispersions were kept under magnetic stirring for 24 h at room temperature.

The viscometric parameters were determined at 30 ± 0.1 °C using an Ubbelohde C529 viscometer with capillary diameter of 0.63 mm, in a ThermoHaake DC30 thermostatic bath.

The experimental determination was made by timing the flow time of the solvents, the initial stock polymeric solution and six dilutions of it (for each dilution 2 mL of distilled water was added). The variation of the determinations was lower than 0.08%. In the determinations by a single point, the solution with lowest concentration was chosen for the calculations [19, 21, 22, 27]. It is important to note that the flow time of the polymer solution should not be too low, since this increases the likelihood of reading errors. In addition, very high flow times mean that the polymer solution has high concentration, a characteristic that does not satisfy the concept of the Newtonian regime.

For viscosity average molar mass (\bar{M}_v) determination, the constants $k = 4.30 \times 10^{-3} \text{ cm}^3/\text{g}$ and $a = 0.74$ were used for the CMC sample [40, 42]. For GL, the constants $k = 7.48 \times 10^{-3} \text{ cm}^3/\text{g}$ and $a = 0.91$ were employed [41].

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