



## Viscometric study of chitosan solutions in acetic acid/sodium acetate and acetic acid/sodium chloride



Cristiane N. Costa<sup>a</sup>, Viviane G. Teixeira<sup>b</sup>, Marcia C. Delpech<sup>a</sup>, Josefa Virginia S. Souza<sup>a</sup>, Marcos A.S. Costa<sup>a,\*</sup>

<sup>a</sup> Universidade do Estado do Rio de Janeiro, Instituto de Química, R. São Francisco Xavier, 524, Maracanã, 20550-900 Rio de Janeiro, RJ, Brazil

<sup>b</sup> Universidade Federal do Rio de Janeiro, Instituto de Química, Av. Athos da Silveira Ramos, 149, 21941-909, Rio de Janeiro, RJ, Brazil

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### ABSTRACT

A viscometric study was carried out at 25 °C to assess the physical–chemical behavior in solution and the mean viscometric molar mass ( $\bar{M}_v$ ) of chitosan solutions with different deacetylation degrees, in two solvent mixtures: medium 1—acetic acid 0.3 mol/L and sodium acetate 0.2 mol/L; and medium 2—acetic acid 0.1 mol/L and sodium chloride 0.2 mol/L. Different equations were employed, by graphical extrapolation, to calculate the intrinsic viscosities  $[\eta]$  and the viscometric constants, to reveal the solvent's quality: Huggins ( $H$ ), Kraemer ( $K$ ) and Schulz–Blaschke ( $SB$ ). For single-point determination, the equations used were  $SB$ , Solomon–Ciuta ( $SC$ ) and Deb–Chanterjee ( $DC$ ), resulting in a faster form of analysis. The values of  $-\bar{M}_v$  were calculated by applying the equation of Mark–Houwink–Sakurada. The  $SB$  and  $SC$  equations were most suitable for single-point determination of  $[\eta]$  and  $-\bar{M}_v$ , and the Schulz–Blaschke constant ( $k_{SB}$ ), equal to 0.28, already utilized for various systems, can also be employed to analyze chitosan solutions under the conditions studied.

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### 1. Introduction

Chitosan is a linear polysaccharide obtained by alkaline deacetylation of chitin. Chitin is a linear homopolymer composed poly- $[\rightarrow 4\text{-}N\text{-acetyl-}\beta\text{-}D\text{-glucosamine-}(1\rightarrow)]$  (Rinaudo, 2006). Chitosan is a cationic linear polysaccharide composed essentially of  $(1\rightarrow 4)$ -linked  $\beta\text{-}D\text{-glucosamine}$  units together with some proportion of  $N\text{-acetyl-}\beta\text{-}D\text{-glucosamine}$  units (Peniche, Arguelles-Monal, Peniche, & Acosta, 2003), i.e. chitosan is derived from chitin by (partial) deacetylation. The two biopolymers are distinguished from each other mainly by their solubility in acidic aqueous solutions. An important parameter of the molecular structure of these materials is the deacetylation degree, or the percentage of glucosamine units in the chitosan molecule. The copolymer is generally accepted as being chitosan when the deacetylation degree is greater than 50% (Rinaudo, 2006).

The efficacy of chitosan depends on its molar mass and polydispersion. If the molar mass is known and there is good understanding of the conformation of the polymer in the solvent medium, the

rheological and mechanical properties can be estimated (Kassai, 2007).

In infinitely diluted solutions, the polymer–solvent interactions can provide information on the hydrodynamic volume of the chain in the solvent and the dimensions of the macromolecule. Capillary viscometry is an easily executed but laborious experimental method that supplies this information. Hence, there is strong interest in developing experimental and mathematical methods that can simultaneously reduce the time of experimental determination of these parameters and provide results with small error margin (Delpech, Coutinho, Souza, & Cruz, 2007; Delpech & Oliveira, 2005; Delpech, Coutinho, & Habibe, 2002a; Delpech, Coutinho, & Garcia, 2002b; Mello, Delpech, Fernanda, & Albino, 2006, 2005; Silva, Mello, Delpech, & Costa, 2013).

The intrinsic viscosity  $[\eta]$  is considered a measure of the volume of a single polymer molecule in an ideal condition. Therefore, the mean viscometric molar mass ( $-\bar{M}_v$ ) is determined from the intrinsic viscosity  $[\eta]$ , which in turn can be obtained by graphical extrapolation, in an infinite dilution model, by applying various mathematical equations, like those developed by Huggins ( $H$ ), Kraemer ( $K$ ) and Schulz–Blaschke ( $SB$ ) (Eqs. (1)–(3), respectively). (Huggins, 1942; Kraemer, 1938; Schulz & Blaschke, 1941).

$$\frac{\eta_{sp}}{c} = [\eta]_h + k_h[\eta]_h^2 c \quad (1)$$

\* Corresponding author. Tel.: +55 21 2334 0563.

E-mail address: [marcos.costa@uerj.br](mailto:marcos.costa@uerj.br) (M.A.S. Costa).

$$\frac{\ln \eta_r}{c} = [\eta]_k - k_k [\eta]_k^2 c \quad (2)$$

$$\frac{\eta_{sp}}{c} = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (3)$$

where  $\eta_r$  = relative viscosity or viscosity ratio ( $\eta_r = t/t_0$ , being  $t_0$  the efflux time of the solvent and  $t$  the efflux time of the solution in a given concentration),  $\eta_r - 1 = \eta_{sp}$  ( $\eta_{sp}$  = specific viscosity),  $\eta_{sp}/c = \eta_{red}$  = reduced viscosity or viscosity number,  $c$  = concentration,  $[\eta]_h = \lim_{c \rightarrow 0} \eta_{sp}/c$  = intrinsic viscosity or limiting viscosity number of Huggins,  $[\eta]_k = \lim_{c \rightarrow 0} \ln \eta_r/c$  = intrinsic viscosity or limiting viscosity number of Kraemer,  $[\eta]_{SB} = \lim_{\eta_{sp} \rightarrow 0} \eta_{sp}/c$  = intrinsic viscosity or limiting viscosity number of Schulz–Blaschke, and  $k_h$ ,  $k_k$  and  $k_{SB}$  = coefficients of Huggins, Kraemer and Schulz–Blaschke, respectively.

Experimental results show that  $k_h < 0.50$  and  $k_k < 0$  indicate good solvents, while  $k_h > 0.50$  and  $k_k > 0$  indicate poor solvents (Delpech et al., 2007, 2002a, 2002b; Delpech & Oliveira, 2005; Mello et al., 2006, 2005; Silva et al., 2013).

Combining Eqs. (1) and (2) and starting from the premise that  $k_h + k_k = 0.5$ , Solomon and Ciută (1962) obtained Eq. (4) to determine the intrinsic viscosity by a single point, using a single concentration value.

$$[\eta]_{sc} = \frac{[2(\eta_{sp} - \ln \eta_r)]^{1/2}}{c} \quad (4)$$

Eq. (5) was proposed by Deb and Chanterjee (1968) as an expression of intrinsic viscosity, also determined from a single point.

$$[\eta]_{dc} = \frac{((3 \ln \eta_r + 3) / (2 \eta_{sp}^2 - 3 \eta_{sp}))^{1/3}}{c} \quad (5)$$

Eqs. (4) and (5) are therefore independent of constants, unlike Eqs. (1)–(3), allowing direct calculation without the need for various concentration values for extrapolation. Eq. (3) (Schulz–Blaschke) also is widely used for single-point determination, using the fixed value of 0.28 for  $k_{SB}$ , which according to the literature is adequate for many polymer–solvent–temperature systems (Abdel-Azim, Atta, Farahat, & Boutros, 1998; Delpech et al., 2007, 2002a, 2002b; Delpech & Oliveira, 2005; Khan, Gupta, & Bhargava, 1983; Mello et al., 2005, 2006; Schoff, 1999; Silva et al., 2013).

Using a single concentration value substantially reduces the time necessary to conduct the experiment, making the application of these equations very attractive both among researchers and industrial technicians, for quality control. However, for the results of intrinsic viscosity measurements using equations with a single point to be validated, the polymer–solvent–temperature system first needs to be studied by graphical extrapolation. The single-point equations are then employed, choosing the lowest concentration value, i.e., the one nearest zero concentration. An error analysis based on the percentage difference between the values obtained by graphical extrapolation and by single-point determination is then carried out to choose the best equation. The equation of Huggins is generally employed as the base for the calculations (Delpech et al., 2007, 2002a, 2002b; Delpech & Oliveira, 2005; Mello et al., 2006, 2005; Silva et al., 2013).

The intrinsic viscosity of a polymer in a given solvent increases with the polymer's molar mass. This relation is the base for the viscometric method to assess the molar mass of a polymer from the equation of Mark–Houwink–Sakurada (MHS):

$$[\eta] = K(\bar{M}_v)^a \quad (6)$$

Here  $-\bar{M}_v$  is the mean viscometric molar mass while  $K$  and  $a$  are the viscometric constants, which vary in function of the nature of the solvent, temperature and chemical structure of the polymer (Matusinović, Rogošić, & Mencer, 2005; Moreira, Silva, Wang, &

Balogh, 2004; Robinson, Holladay, Hash, & Puettl, 1982; Simionescu, Loan, & Simionescu, 1987).

Various parameters affect the intrinsic viscosity of chitosan, such as concentration, molar mass, solvent, temperature, shear rate, chemical structure of the polymer and deacetylation degree of the chitosan. In the case of polyelectrolytes, as is the case of chitosan in acidic media, the degree of dissociation of the ionic groups also is an important factor that must be considered. For chitosan in solution and polyelectrolytes in general, the presence of ionic groups in their structures leads to expansion of the polymer chains due to the electrostatic repulsions, causing an increase in viscosity. However, the addition of a salt to the aqueous solution of polyelectrolytes triggers a reduction of the electrostatic repulsion, leading to a conformation that is neither excessively extended nor excessively entangled, diminishing the viscosity (Cho, Heuzey, Bégin, & Carreau, 2006; Desbrières, Martinez, & Rinaudo, 1996).

The literature describes the use of different dilution media and the importance of determining the molar mass to estimate the rheological and mechanical properties of chitosan. Kassai (2007) calculated the viscometric constants  $K$  and  $a$  of the MHS equation for chitosan samples in different solvents and at varied temperatures, while Canella and Garcia (2001), Chen, Liu, Chen, and Chen (2008) and Yomota, Miyazaki, and Okada (1993) determined the intrinsic viscosity of chitosan by extrapolation of data on viscosity at infinite dilution, according to the equation of Huggins and the mean viscometric molar mass ( $-\bar{M}_v$ ), through the Mark–Houwink–Sakurada equation.

Physical–chemical studies of the solvent quality and determination of the best equation to calculate the intrinsic viscosity and molar mass from a single point have been described for various polymer–solvent–temperature systems (Delpech et al., 2007, 2002a; 2002b; Delpech & Oliveira, 2005; Mello et al., 2006, 2005; Silva et al., 2013). To the best of our knowledge, there are no reports in the literature of this type of study of polymers based on chitosan. Therefore, the aim of this work was to investigate the viscosimetry, at 25 °C, of chitosan samples with different acetylation degrees to verify the quality of the solvent medium and to ascertain the best equation to calculate the both the intrinsic viscosity and mean viscometric molar mass from a single point. We used two aqueous media as solvents. These aqueous media were selected because they are most commonly found in the literature. Medium 1 was composed of a mixture of acetic acid 0.3 mol/L and sodium acetate 0.2 mol/L while medium 2 consisted of acetic acid 0.1 mol/L and sodium chloride 0.2 mol/L (Canella & Garcia, 2001).

## 2. Experimental

### 2.1. Purification of the chitosan

Approximately 1 g of commercial chitosan sample (acquired either from Polymar, deacetylation degree 85%—sample C1, or from Aldrich, deacetylation degree 93%—sample C2) was dispersed in 300 mL of an aqueous solution of acetic acid (Vetec Química Fina Ltda.) at 0.5 mol/L and the system was kept under stirring for 24 h. The resulting solution was filtered through Whatman no. 40 filter paper (8 μm) and then through a cellulose acetate membrane with 0.45 μm pores (Millipore), under low pressure. An aqueous solution of 10% sodium hydroxide (Vetec Química Fina Ltda.) was then added to the filtered solution until precipitation of the chitosan. The precipitated polymer was separated by centrifugation and was washed repeatedly with distilled water until neutral pH. Then it was washed with mixtures of water and ethanol (Vetec Química Fina Ltda.) in proportions of 3:1, 1:1, 1:3 and also in absolute ethanol (Vetec Química Fina Ltda.). The product obtained was dried in an oven at 60 °C for 48 h (Canella & Garcia, 2001).

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