Carbohydrate Polymers 133 (2015) 245–250

Carbohydrate Polymers

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

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

Cristiane N. Costa[a], Viviane G. Teixeira[b], Marcia C. Delpech[a], Josefa Virginia S. Souza[a], Marcos A.S. Costa[a,*]

[a] Universidade do Estado do Rio de Janeiro, Instituto de Química, R. São Francisco Xavier, 524, Maracanã, 20550-900 Rio de Janeiro, RJ, Brazil
[b] Universidade Federal do Rio de Janeiro, Instituto de Química, Av. Athos da Silveira Ramos, 149, 21941-909, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form 29 June 2015
Accepted 30 June 2015
Available online 13 July 2015

Keywords:
Chitosan
Single-point determination
Solvent quality
Molecular weight determination

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 [η] 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 [η] and $-\bar{M}_v$ and the Schulz–Blachke constant (k_{SB}), equal to 0.28, already utilized for various systems, can also be employed to analyze chitosan solutions under the conditions studied.

1. Introduction

Chitosan is a linear polysaccharide obtained by alkaline deacetylation of chitin. Chitin is a linear homopolymer composed poly-[→4)-*N*-acetyl-β-*D*-glucosamine-(1→] (Rinaudo, 2006). Chitosan is a cationic linear polysaccharide composed essentially of (1→4)-linked β-*D*-glucosamine units together with some proportion of *N*-acetyl-β-*D*-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 [η] 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 [η], 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 (M.A.S. Costa).

http://dx.doi.org/10.1016/j.carbpol.2015.06.094
0144-8617/

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

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

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

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

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

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

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) (Shulz–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):

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

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 (Matusinoviíi, 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 in 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 (Canela & 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 (Canela & Garcia, 2001).

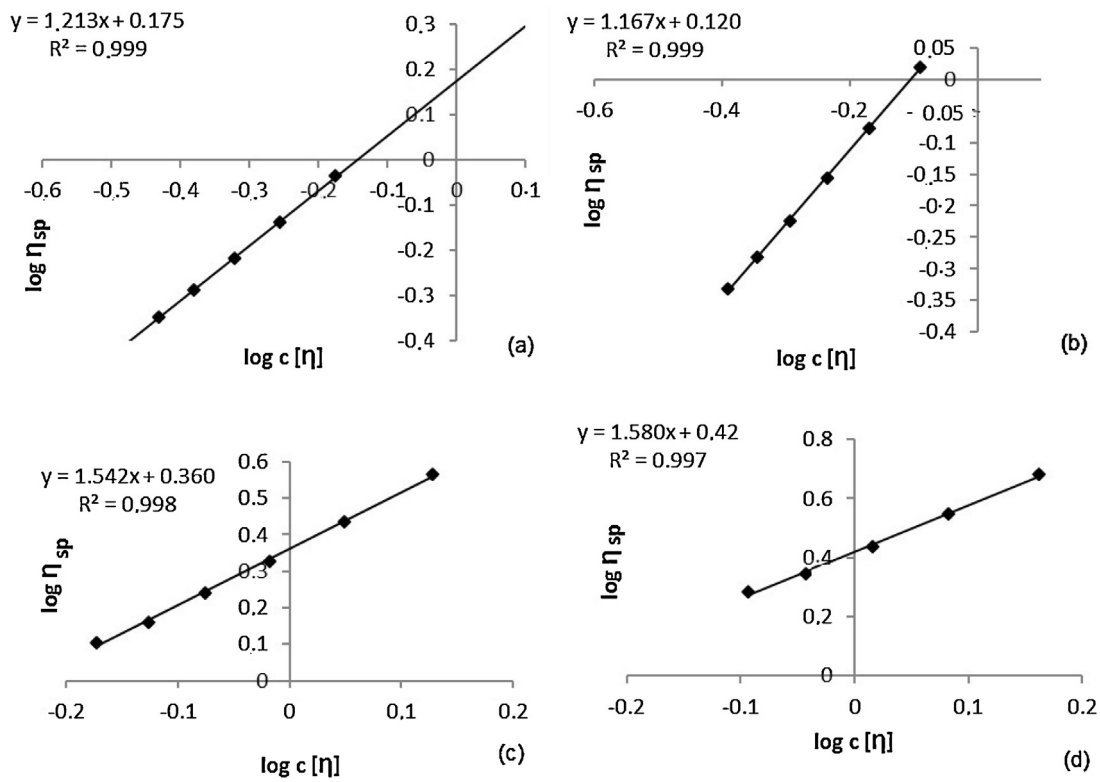

Fig. 1. Log η_{sp} versus log $c[\eta]$ for chitosan C1 in (a) CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L and (b) CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L. Log η_{sp} versus log $c[\eta]$ for chitosan C2 in (c) CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L and (d) CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L.

2.2. Determination of viscosity and molar mass

To determine the intrinsic viscosity, $[\eta]$, the chitosan samples, identified as C1 and C2, were dissolved in an aqueous medium (medium 1) of acetic acid and sodium acetate (Vetec Química Fina Ltda.) (CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L) or another aqueous solution (medium 2) of acetic acid and sodium chloride (Merck S.A.) (CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L), to obtain a chitosan concentration of 0.003 g/mL. While preparing the solution, the polymer was kept under stirring for approximately 18 hours to assure complete solubilization of the macromolecules in the medium employed. The solvents were then filtered through a cellulose acetate membrane with pore size of 0.45 μm and the chitosan solution was filtered through Whatman no. 40 filter paper (8 μm) and then a cellulose acetate membrane with the same pore size.

The viscometric parameters were measured at 25 ± 0.05 °C using a Ubbelohde C529 capillary viscometer with capillary diameter of 0.63 mm, in a ThermoHaake DC30 temperature controlled bath apparatus. The experimental determination of the intrinsic viscosity, by extrapolation, was performed by timing the flow of the solvents (t_o), and the flow of the initial stock solution and of five dilutions from it. The flow time values, employed to determine intrinsic viscosities values employing Eqs. (1)–(3), corresponded to the average of at least five time measurements with variation lower than 0.09%. In the single-point determinations (Eqs. (3)–(5)), the solution with lowest concentration was chosen (Delpech et al., 2002a, 2002b).

3. Results and discussion

Fig. 1 presents the ratio between log η_{sp} and log $c[\eta]$ obtained for chitosan samples C1 and C2, respectively, in the two media studied, at 25 °C, applying the intrinsic viscosity value provided by Huggins' equation. The parameter $c[\eta]$ (dimension with the lowest coil overlap parameter, where c is the concentration) can be defined as the total volume occupied by novel polymers, i.e., $c[\eta]$ is the fraction, by volume, of the polymer present in the solution. This parameter is independent of the polymer's type and molar mass. We observed a linear relation for all the samples analyzed, indicating that all determinations were obtained in a Newtonian regime, a range in which the viscosimetry data are valid (Mello et al., 2006, 2005; Silva et al., 2013).

Table 1 reports the intrinsic viscosity values related to all the equations and Table 2 shows the viscometric constants obtained for the two chitosan samples (C1 and C2).

The values of k_h for chitosan C1 in both media fit in the range of good solvents. In counterpart, the values of k_h for chitosan C2 indicate stronger polymer–polymer interaction and weaker polymer–solvent interaction. Unlike flexible polymers, polysaccharides have more rigid structures, so the values of k_h are normally higher (Wang & Xu, 1994). This difference in the Huggins' constant values can be explained by the structural differences between the chitosan samples (C1 and C2). Chitosan C2 has a deacetylation degree (DD) of 93% while the degreed of chitosan C1 is 85%. Chitosan is a cationic electrolyte, and in an acidic solution the charge density along the main chain increases with rising DD, resulting in a more expanded conformation of the chain with a smaller number of entanglements, making it stiffer. The movement of the individual chains is restricted with the increase in the number of entanglements. As the polymer's concentration increases, the disentangled chains cannot form new entanglements due to their lack of mobility. The reduction of viscosity in the presence of NaCl can be explained by the fact that sodium acetate already greatly diminishes the electrostatic repulsion (Brant, 2008).

The values found for the constant k_k were negative for the two chitosan samples, indicating there was good solubilization of the polymer chains. However, the values of $k_h + k_k$ for chitosan C2 tended to be higher than 0.5 for the two media studied,

Table 1
Intrinsic viscosity values for chitosan samples C1 and C2 in the systems CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L (medium 1) and CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L (medium 2).

Medium	μ[d] (mol/L)	Intrinsic viscosity [η] (mL/g)					
		H[a]	K[a]	SB[a]	SB[b]	SC[c]	DC[c]
Chitosan C1							
1	0.2	44.97	44.69	46.23	45.26	44.85	46.44
2	0.2	20.53	21.16	21.58	21.99	21.80	22.46
Chitosan C2							
1	0.2	101.29	131.31	157.56	140.31	146.37	161.71
2	0.2	34.84	40.34	46.62	42.89	43.76	47.46

[a] H = Huggins; K = Kraemer; M = Martin; SB = Schulz–Blascke-calculated by graphical extrapolation.
[b] SB = Schulz–Blascke (k_{SB} = 0.28)-calculated by single-point determination.
[c] SC = Solomon–Ciuta; DC = Deb–Chanterjee-calculated by single-point determination.
[d] μ = Ionic force (Kassai, 2007).

Table 2
Viscometric constants calculated for chitosan samples C1 and C2 in the systems CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L (medium 1) and CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L (medium 2).

Medium	Viscometric constants			
	k_h	k_k	k_{sb}	$k_h + k_k$
Chitosan C1				
1	0.33	−0.15	0.23	0.48
2	0.59	−0.07	0.35	0.65
Chitosan C2				
1	1.21	−0.08	0.19	1.28
2	1.19	−0.09	0.21	1.28

k_h—Huggins' constant; k_k—Kraemer's constant; k_{SB}—Shulz–Blaschke constant.

providing evidence of poor solubilization and that the media used did not have sufficiently high polarity to overcome the effects of interaction among the chains of this polymer.

For single-point determination we used the equations of Solomon–Ciuta (SC) and Deb–Chanterjee (DC) (Eqs. (4) and (5), respectively). We also performed a test using Eq. (3), from Shulz–Blasche (SB), in this case attributing the value of 0.28 to the respective constant (k_{SB}) (Abdel-Azim et al., 1998; Delpech & Oliveira, 2005; Delpech et al., 2002a, 2002b; Khan et al., 1983; Schoff, 1999).

The SC and DC equations have been used based on the premise that $k_h + k_k = 0.5$ (Abdel-Azim et al., 1998). However, as shown in Table 2, in this work $k_h + k_k$ varied from 0.2 to 1.28. Nevertheless, the values found for $[\eta]_{SC}$ were near those obtained by graphical extrapolation ($[\eta]_h$, $[\eta]_k$ and $[\eta]_{SB}$) (Table 1).

Table 3 presents the percentage differences (Δ%) calculated for the intrinsic viscosity values obtained from the equations of Kraemer, Schulz–Blascke, Solomon–Ciuta and Deb–Chanterjee, when compared with those produced by the equation of Huggins, i.e., how much these former values deviated from the base value, chosen from Huggins' equation, most often used for these calculations (Abdel-Azim et al., 1998; Delpech et al., 2007, 2002a, 2002b; Delpech & Oliveira, 2005; Mello et al., 2006, 2005; Khan et al., 1983; Schoff, 1999).

$$\Delta\% = \left[100\left(\frac{[\eta]}{[\eta]_h}\right)\right] - 100$$

For the values obtained in medium 1 (CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L) and medium 2 (CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L), comparison of the intrinsic viscosity values obtained from the equations of Schulz–Blascke (SB) and Solomon–Ciuta (SC), employed in the single-point determination method, showed a tendency to lower percentage differences in relation to the values obtained from the Schulz–Blascke (SB) equation by graphical extrapolation, although the employment of the SB equation is connected to the value of a constant (k_{SB} = 0.28). It can be seen in Table 3 that the SB equation in general produced the smallest deviations from the values obtained by extrapolation with Huggins' equation, producing a better result and making its application more advisable for the systems studied, in both solvent systems, a finding that also validates the use of the constant 0.28.

It is also important to observe that the sum $k_h + k_k = 0.5$ did not occur for either of the samples analyzed (Table 3), principally for chitosan C2. Nevertheless, both $[\eta]_{SC}$ and $[\eta]_{DC}$ presented values near $[\eta]_h$, $[\eta]_k$ and $[\eta]_{SB}$, which were obtained by graphical extrapolation, with the lowest percentage differences being for sample C1. Therefore, the application of the SC and DC equations for this chitosan in the two solvents systems analyzed is not restricted to this

Table 3
Percentage differences (Δ%) obtained for the intrinsic viscosity values calculated by graphical extrapolation: equations of Kraemer (K) and Schulz–Blaschke (SB); and by single-point determination with the equations of Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC), employing as reference the intrinsic viscosity of Huggins $[\eta]_h$.

Medium	Graphical extrapolation		Single-point determination		
	K	SB	SB	SC	DC
Chitosan C1					
1	−0.62	2.80	0.64	−0.27	3.27
2	3.07	5.11	7.11	6.19	9.40
Chitosan C2					
1	29.23	55.55	38.52	44.51	59.65
2	15.79	33.81	23.11	25.60	36.22

Table 4
Values of K and α found in the literature for the solvent systems CH_3COOH 0.3 mol/L/CH_3COONa0.2 mol/L (medium 1) and CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L (medium 2) (Canella & Garcia, 2001; Campana-Filho et al., 2007; Kassai, 2007; Moura et al., 2011; Mutalik et al., 2006; Qun & Ajun, 2006; Santos et al., 2003).

Solvent	K (mL/g)	α
Medium 1	0.93	0.76
Medium 2	1.81×10^{-3}	0.74

Temperature: 25 °C.

Table 5
Mean viscometric molar mass for chitosan samples C1 and C2 in CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L (medium 1) and CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L (medium 2).

Medium	μ (mol/L)	pH	Molar mass (g/mol)
	Chitosan C1		
1	0.2	4.7	1.6×10^2
2	0.2	2.9	3.0×10^5
	Chitosan C2		
1	0.2	4.7	4.8×10^2
2	0.2	2.9	6.1×10^5

Table 6
Intrinsic viscosity of Huggins $[\eta]_h$ and molar mass (expressed in g/mol) of chitosan obtained by viscometry.

Medium	$[\eta_h]$ (mL/g)	Mean viscometric molar mass (g/mol)					
		$\bar{M}_{v_h}$	$\bar{M}_{v_k}$	$\bar{M}_{v_{SB}}$	$\bar{M}_{v_{SB}}$	$\bar{M}_{v_{SC}}$	$\bar{M}_{v_{DC}}$
Chitosan C1							
1	44.97	1.6×10^2	1.6×10^2	1.7×10^2	1.7×10^2	1.6×10^2	1.6×10^2
2	20.53	3.0×10^5	3.1×10^5	3.2×10^5	3.3×10^5	3.2×10^5	3.4×10^5
Chitosan C2							
1	101.29	4.8×10^2	6.7×10^2	8.9×10^2	7.4×10^2	7.8×10^2	8.9×10^2
2	34.84	6.1×10^5	7.5×10^5	9.3×10^5	8.2×10^5	8.3×10^5	9.3×10^5

sum. However, all the percentage differences for chitosan C2 were very high, suggesting that the viscosity and flow properties of the solutions differ with the deacetylation degree (DD) of chitosan. The deacetylation degree of chitosan is an important molecular structure parameter, because the viscometric constants in the equations can change when the DD changes. The viscosity of chitosan C2, with DD of 93%, is higher than that of chitosan C1, with DD of 85%.

The mean viscometric molar mass of chitosan samples C1 and C2 in media 1 and 2 were calculated from the Mark–Houwink–Sakurada equation (Eq. (6)). The values of the constants K and α found in the literature for the solvents used here, at 25 °C, are presented in Table 4 (Campana-Filho et al., 2007; Canella & Garcia, 2001; Kassai, 2007; Moura, Moura, Soares, & Pinto, 2011; Mutalik et al., 2006; Qun & Ajun, 2006; Rinaudo & Domard, 1989; Rinaudo, Milas, & Dung, 1993; Santos, Soares, Dockal, Campana Filho, & Cavalheiro, 2003).

The mean viscometric molar mass values determined for chitosan samples C1 and C2 in media 1 and 2 are reported in Table 5.

The results found suggest that the two solvent systems have different solubilization power. The mean molar masses are higher for the solvent system CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L (medium 2), suggesting stronger polymer–polymer interaction and weaker polymer–solvent interaction in CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L (medium 1). The higher molar mass values in medium 2 suggest that the secondary forces between chitosan samples C1 and C2 and the molecules of this medium are strong. In other words, it is a better solvent. This can be explained by the variation of pH, because the ionic forces of the two solvents are equal. Comparison of the viscosity in function of pH (pH of 2.9 for CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L and pH of 4.7 for CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L) shows that in increase in pH of the medium reduces the polymer's molar mass. Chitosan contains a primary amino group and two free hydroxyl groups for each C6 unit. Due to the easy availability of free amino groups in chitosan, this polymer is positively charged at acidic pH values. At low pH, these amino groups are protonated and become positively charged, making chitosan a water-soluble cationic polyelectrolyte. The increase in pH diminishes the cationic characteristic, leaving chitosan less protonated and consequently with smaller hydrodynamic volume. When the pH increases above 6, chitosan's amino groups are deprotonated and the polymer loses its charge, becoming insoluble. The soluble-insoluble transition occurs at pH values near the its pKa value, around 6 or 6.5 (Dash, Chiellini, Ottenbrite, & Chiellini, 2011). The number of positive charges ($-NH_3^+$) in chitosan will be higher in a medium with lower pH, because the chains are more extended, increasing the hydrodynamic volume and hence the molar mass.

Table 6 presents a comparison between the molecular weight values for chitosan obtained by viscometry using the intrinsic viscosity values obtained from the equations of Huggins (H), Kraemer (K) and Schulz–Blaschke (SB) and by single-point determination employing the equations of Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC). The mean molar masses are higher when using medium 2 (CH_3COOH 0.1 mol/L/NaCl 0.2 mol/L), suggesting stronger polymer–polymer interaction and weaker polymer–solvent interaction in medium 1 (CH_3COOH 0.3 mol/L/CH_3COONa 0.2 mol/L).

Table 7
Percentage differences (Δ%) obtained for viscometric molar mass values calculated by graphical extrapolation: equations of Kraemer (K) and Schulz–Blaschke (SB); and by single-point determination: equations of Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC), employing as reference the intrinsic viscosity of Huggins ($\bar{M}_{v_h}$).

Medium	Graphical extrapolation		Single-point determination		
	K	SB	SB	SC	DC
Chitosan C1					
1	4.06	6.8	9.5	8.2	12.6
2	0.84	3.80	0.87	0.36	4.44
Chitosan C2					
1	21.3	46.7	31.5	35.0	50.2
2	42.0	82.0	55.3	64.5	88.2

The percentage differences (Δ%)obtained for the viscometric-molecular weights are presented in Table 7. These values were calculated with $\bar{M}_v$ determined by using Huggins' equation as reference. A decreasing trend of the Δ% values can be noted for chitosan C1, for which the viscometric molar mass is lower. Among the molar mass values obtained from a single point, the three equations applied (SB, SC and DC) presented results are not very different from those obtained by graphical extrapolation. The Schulz–Blaschke equation (SB) by a single point again presented the lowest percentage differences, making that equation more suitable for rapid determination in the systems analyzed.

4. Conclusion

The $k_h + k_k$ values of medium 1 (acetic acid 0.3 mol/L and sodium acetate 0.2 mol/L) were higher than 0.5 for the two samples studied, providing evidence of poor solubilization of the samples and that this solvent system does not have sufficiently high polarity to overcome the effects of the interaction among the polymer chains. The results suggest stronger polymer–polymer interaction and weaker polymer–solvent interaction in medium 1. In turn, the higher molar mass values in medium 1 (acetic acid 0.3 mol/L and sodium acetate 0.2 mol/L) suggests that the secondary forces between chitosan samples C1 and C2 and the molecules of this medium are strong, meaning it is a better solvent. The results indicate that the viscosity and flow properties of the solutions differ with the deacetylation degree (DD) of chitosan.

For media 1 and 2 (acetic acid 0.3 mol/L/sodium acetate 0.2 mol/L and acetic acid 0.1 mol/L/sodium chloride 0.2 mol/L, respectively), comparison of the values obtained from the equations of Schulz–Blascke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC), employed in the single-point determination method, showed a tendency for lower percentage differences of the intrinsic viscosity values obtained by the SB equation than those obtained by graphical extrapolation, validating the use of the

constant 0.28 for both systems. The SC equation also presented small percentage differences, so it is also suitable for the calculation.

Acknowledgments

We gratefully acknowledge CAPES for a scholarship to C.N. Costa and FAPERJ (E-26/010.002630/2014) for financial support.

References

Abdel-Azim, A. A-A., Atta, A. M., Farahat, M. S., & Boutros, W. Y. (1998). Determination of intrinsic viscosity of polymeric compounds through a single specific viscosity measurement. *Polymer*, *39*(26), 6827–6833.

Brant, A. J. C. (2008). *Preparo e caracterização de hidrogéis a partir de misturas de soluções de quitosana e poli (N-vinil-2-pirrolidona)*. Brazil: Instituto de Química. Universidade de São Paulo (Doctoral thesis in organic chemistry).

Campana-Filho, S. P., Brito, D., Curti, E., Abreu, F. R., Cardoso, M. B., Battisti, M. V., et al. (2007). Extração, estruturas e propriedades de α e β-quitina. *Química Nova*, *30*, 644–650.

Canella, K. M. N. C., & Garcia, R. B. (2001). Caracterização de quitosana por cromatografia de permeação de gel–influência do método de preparação e do solvente. *Química Nova*, *24*, 13–17.

Chen, A. H., Liu, S. C., Chen, C. Y., & Chen, C. Y. (2008). Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Journal of Hazardous Materials*, *154*, 184–191.

Cho, J., Heuzey, M. C., Bégin, A., & Carreau, P. J. (2006). Viscoelastic properties of chitosan solutions: Effect of concentration and ionic strength. *Journal of food Engineering*, *74*, 500–515.

Dash, M., Chiellini, F., Ottenbrite, R. M., & Chiellini, E. (2011). Chitosan—A versatile semi-synthetic polymer in biomedical applications. *Progress in Polymer Science*, *36*, 981–1014.

Deb, P. C., & Chatterjee, S. R. (1968). Unperturbed dimension of polymer molecules from viscosity measurements. *Die Makromolekulare Chemie*, *120*, 49–57.

Delpech, M. C., Coutinho, F. M. B., & Habibe, M. E. S. (2002). Viscometry study of ethylene–cyclic olefin copolymers. *Polymer Testing*, *21*, 411–415.

Delpech, M. C., Coutinho, F. M. B., & Garcia, M. E. F. (2002). Evaluation of gas permeability of membranes obtained from poly(urethane-urea)s aqueous dispersions based on hydroxyl-terminated polybutadiene. *Polymer Testing*, *21*, 719–723.

Delpech, M. C., Coutinho, F. M. B., Souza, K. G. M., & Cruz, R. C. (2007). Estudo viscosimétrico de pré polímeros uretânicos. *Polímeros*, *17*, 294–298.

Delpech, M., & Oliveira, C. M. F. (2005). Viscometric study of poly(methyl methacrylate-*g*-propylene oxide) and respective homopolymers. *Polymer Testing*, *24*, 381–386.

Desbrières, J., Martinez, C., & Rinaudo, M. (1996). Hydrophobic derivatives of chitosan: Characterization and rheological behavior. *International Journal of Biological Macromolecules*, *19*, 21–28.

Huggins, M. L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence of concentration. *Journal of the American Chemical Society*, *64*, 2716–2718.

Khan, H. U., Gupta, V. K., & Bhargava, G. S. (1983). Determination of intrinsic viscosity of high polymers through a single specific viscosity measurement. *Polymer Communication Journal*, *24*, 191–193.

Kassai, M. R. (2007). Calculation of Mark–Houwink–Sakurada (MHS) equation viscometric constants for chitosan in any solvent–temperature system using experimental reported viscometric constants data. *Carbohydrate Polymers*, *68*, 477–488.

Kraemer, E. O. (1938). Molecular weights of cellulose and cellulose derivatives. *Industrial and Engineering Chemistry*, *30*, 1200–1203.

Matusinovií, Z., Rogošić, M., & Mencer, H. J. (2005). A correlation of the limiting viscosity number, molecular mass and composition of statistical linear styrene–methyl methacrylate copolymers. *European Polymer Journal*, *41*, 2934–2944.

Mello, I. L., Delpech, M. C., Fernanda, M. B., & Albino, F. F. M. (2005). Viscometric study of high-cispolybutadiene in cyclohexane solution at 30 °C. *Polymer Bulletin*, *55*, 115–122.

Mello, I. L., Delpech, M. C., Fernanda, M. B., & Albino, F. F. M. (2006). Viscometric study of high-cispolybutadiene in toluene solution. *Journal of the Brazilian Chemical Society*, *17*(1), 194–199.

Moreira, J. C., Silva, I. F., Wang, S. H., & Balogh, D. T. (2004). Determinação das Constantes K e α da Equação de Mark-Houwink de poli(p-acetóxiestireno). *Polímeros: Ciência e Tecnologia*, *14*(2), 80–82.

Moura, C. M., Moura, J. M., Soares, N. M., & Pinto, L. A. A. (2011). Evaluation of molar weight and deacetylation degree of chitosan during chitin deacetylation reaction: Used to produce biofilm. *Chemical Engineering and Processing*, *50*, 351–355.

Mutalik, V., Manjeshwar, L. S., Wali, A., Sairam, M., Raju, K. V. S. N., & Aminabhavi, T. M. (2006). Thermodynamics/hydrodynamics of aqueous polymer solutions and dynamic mechanical characterization of solid films of chitosan, sodium alginate, guar gum, hydroxy ethyl cellulose and hydroxypropyl methylcellulose at different temperatures. *Carbohydrate Polymers*, *65*, 9–21.

Peniche, C., Arguelles-Monal, W., Peniche, H., & Acosta, N. (2003). Chitosan: An attractive biocompatible polymer for microencapsulation. *Macromolecular Bioscience*, *3*, 511–520.

Qun, G., & Ajun, W. (2006). Effects of molecular weight, degree of acetylation and ionic strength on surface tension of chitosan in dilute solution. *Carbohydrate Polymers*, *64*, 29–36.

Rinaudo, M., & Domard, A. (1989). Solution properties of chitosan. Chitin and Chitosan. *Applied Sciences*, 71–79.

Rinaudo, M., Milas, M., & Dung, P. L. (1993). Characterization of chitosan. Influence of ionic strength and degree of acetylation on chain expansion. *International Journal of Biological Macromolecules*, *15*, 281–285.

Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. *Progress in Polymer Science*, *31*, 603–632.

Robinson, J. P., Holladay, L. A., Hash, J. H., & Puettl, D. (1982). Conformational and molecular weight studies of tetanus toxin and its major peptides. *Journal of Biological Chemistry*, *257*, 407–411.

Santos, J. E., Soares, J. P., Dockal, E. R., Campana Filho, S. P., & Cavalheiro, E. T. G. (2003). Caracterização de quitosanas comerciais de diferentes origens. *Polímeros: Ciência e Tecnologia*, *13*(4), 242–249.

Schoff, C. K. (1999). Concentration dependence of the viscosity of dilute polymer solutions: Huggins and Schultz–Blaschke constants. In J. Brandrup, E. H. Immergut, & E. A. Grulke (Eds.), *Polymer handbook*. New York: Wiley-Interscience, pp. VII/265–289.

Schulz, G. V., & Blaschke, F. (1941). Eine Gleichung zur Berechnung der Viscositätszahl für sehr kleine Konzentrationen, Molekulargewichtsbestimmungen an makromolekularen Stoffen, IX. *Journal für Praktische Chemie*, *158*, 130–135.

Silva, G. M., Mello, I. L., Delpech, M. C., & Costa, M. A. S. (2013). Estudo viscosimétrico de copolímeros à base de 1,3-butadieno e 1-octeno em tolueno e hexano. *Polímeros*, *23*, 758–763.

Simionescu, C. I., Loan, S., & Simionescu, B. C. (1987). Solution properties of ultra-high molecular weight polymers—13. Viscosity–molecular weight relationships and unperturbed dimensions of poly(butyl methacrylate) in various solvents. *European Polymer Journal*, *23*(1), 69–72.

Solomon, O. F., & Ciută, I. Z. (1962). Détermination de la viscosité intrinsèque de solutions de polymères par une simple détermination de la viscosité. *Journal of Applied Polymer Science*, *6*, 683–686.

Wang, W., & Xu, D. (1994). Viscosity and flow properties of concentrated solutions of chitosan with different degrees of deacetylation. *International Journal Biology Macromolecules*, *16*, 149–152.

Yomota, C., Miyazaki, T., & Okada, S. (1993). Determination of the viscometric constants for chitosan and the application of universal calibration procedure in its gel permeation chromatography. *Colloid and Polymer Science*, *271*, 76–82.