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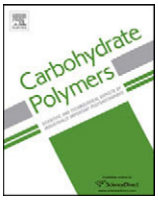

Hydrodynamic properties of some cationic amphiphilic polysaccharides in dilute and semi-dilute aqueous solutions

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ABSTRACT

The dynamic properties of aqueous solutions of amphiphilic cationic polyelectrolytes based on polysaccharides with N,N-dimetyl-N-alkyl-N-(2-hydroxypropyl)ammonium chloride pendant groups were studied by capillary viscometry over a large concentration range (0.01–10 g/dL), as a function of the degree of substitution with pendant groups, length of the alkyl substituent (C_8, C_{12}, C_{16}), molar mass and nature of polysaccharide backbone. Intrinsic viscosity determined in dilute solution using Rao or Heller equations provided information on the conformation of individual polymer chains. Comparison of the specific viscosity–concentration relationships with scaling theories allowed the delimitation of concentration domains and calculation of overlap and entanglement concentrations. Semi-empirical equations (Fedors, Martin) could describe the viscosity variation with concentration only for polymers with low degree of substitution (<10 mol%). All these studies help to identify the predominant characteristic for each amphiphilic polyelectrolyte (neutral, charged or associative polymer), determined by its chemical structure, as a result of the balance between electrostatic repulsion and intra- or/and intermolecular associations. The obtained information could be very useful to tailor the cationic amphiphilic polysaccharide's chemical structure to the viscometric properties suitable to different application as flocculants, thickeners or drug delivery systems.

1. Introduction

Polyelectrolytes and their hydrophobically modified derivatives (amphiphilic or hydrophobically modified polyelectrolytes) are extensively used in both nature and industry. This large applicability is the result of their unique viscometric behavior in aqueous solutions, therefore the study of solution dynamics of polyelectrolytes is necessary to gain insight into many biological and industrial processes, and allows a fine tuning and control of the flow properties of fluids, which has a great importance in various areas such as the petrochemical, cosmetics, pharmaceutical, food and paint industries (Glass, 1989, 2000; Molyneaux, 1984). Cationic polyelectrolytes based on quaternary ammonium group containing polysaccharides are more suitable for many of these applications due to their biocompatibility and biodegradability, which are characteristic to the polysaccharide backbone.

Theoretical description of polyelectrolyte solutions' viscosity has been for decades a challenge for scientists due to the complicated behavior both in dilute and semi-dilute domains, as a result of combined action of electrostatic and hydrodynamic interactions. Scaling theories have been formulated to help in predicting the viscosity–concentration dependence and for identification of concentration regimes (Dobrynin, Colby, & Rubinstein, 1995; de Gennes, Pincus, Velasco, & Brochard, 1976; Muthukumar, 1997; Odijk, 1979). Prediction of viscometric behavior for amphiphilic polyelectrolyte solutions is complicated by occurrence, besides electrostatic interactions, of associations between hydrophobic moieties which can take place inside the same polymer chain (intra-molecular interactions) or between different chains (intermolecular interactions). The viscosity of the solutions is the macroscopic result of the interplay of these interactions, and it depends on a variety of factors including the nature of polymer backbone (hydrophilicity, flexibility, molar mass), the chemical structure of ionic groups (strong/weak acid or base) and hydrophobic entities (alkylic, cyclic or aromatic), degree of substitution, the place of hydrophobic groups along polymer backbone (blocky, randomly) and the distance between them, polymer concentration. At the extremes, two distinct types of polymer behavior are observed based on intrapolymer or interpolymer associations. Polymers with a high concentration of amphiphilic molecules incorporated as side chain on a linear molecule are called "polysoaps" (Strauss & Gershfeld, 1954) and are characterized by predominance of intra-molecular hydrophobic interactions even in very dilute solutions and by a low viscosity at high concentrations. The polymers

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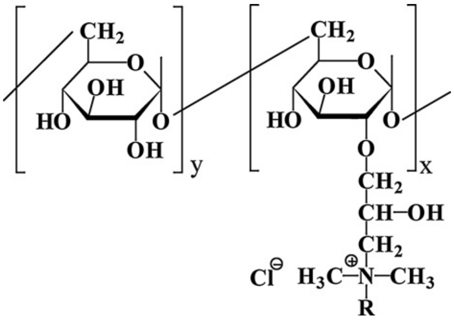

Scheme 1. Chemical Structure of cationic amphiphilic polyelectrolytes obtained by chemical modification of dextran. R = Octyl (C_8), Dodecyl (C_{12}) or Cetyl (C_{16}); DS = $100x/(x+y)$.

with a low content in hydrophobic moieties are characterized by high viscosity due to the occurrence of inter-molecular associations; therefore, they are often named associative thickeners (Kotz, Kosmella, & Beitz, 2001).

Theoretical treatments have been proposed for describing the phase behavior of polysoaps (Dobrynin & Rubinstein, 2000; Turner & Joanny, 1993), or the dynamics of associating polymers in unentangled (Rubinstein & Semenov, 1998) and entangled (Rubinstein & Semenov, 2001) forms. Some of these theoretical approaches have been applied to the viscometric behavior of several amphiphilic polyelectrolytes (Di Cola et al., 2004; Di Cola, Waigh, & Colby, 2007; Jianping, Yonggang, Quiang, & Quiang, 2009; Kujawa, Audibert-Hayet, Selb, & Candeau, 2006; Paillet et al., 2009; Souguir, Roudesli, About-Jaudet, Picton, & Le Cerf, 2010) and helped to identify the concentration regimes.

The aim of the present study is to investigate the viscometric behavior of hydrophobically modified cationic polymers based on different polysaccharides (dextran, pullulan), carrying pendant N-alkyl-N,N-dimethyl-N-(2-hydroxypropyl) ammonium chloride groups, where alkyl is an octyl, dodecyl, or cetyl group. These pendant groups are randomly distributed along the polysaccharide backbone. Capillary viscometry, in dilute and semi-dilute domain, was employed for measurement of the low shear rate polymer solution viscosity. In the dilute regime, intrinsic viscosity values, $[\eta]$, were determined to obtain information about the individual chain conformation. The scaling behavior over a large polymer concentration (0.01–10 g/dl) was compared with those predicted for neutral, charged and/or associative polymers. Finally, the application of some semi-empirical equation for describing the viscosity–concentration relationship was examined. All these aspects were related to the physico-chemical properties of the polymers, namely the degree of substitution with pendant groups, hydrophobicity (length of the alkyl substituent), molar mass (M_w) and polysaccharide flexibility. The results may be useful for the proper choice of the most appropriate chemical structure for a specific application of these cationic amphiphilic polysaccharides.

2. Experimental

2.1. Materials

Two dextran samples were supplied by Sicomed S.A. Bucharest: D40 with $M_w = 40$ kDa and $M_w/M_n = 1.12$, and D200 with $M_w = 210$ kDa and $M_w/M_n = 1.45$. The pullulan sample P200 with $M_w = 200$ kDa and $M_w/M_n = 1.40$ was obtained from Hayashibara, Okayama, Japan. Deionized water, with a conductance <10^{-6} mho/cm, was obtained with a Millipore purification system.

Cationic polymers with pendant quaternary ammonium groups, with chemical structure depicted in Scheme 1, were synthesized by chemical modification of polysaccharides, after a procedure described in detail elsewhere (Nichifor, Stanciu, & Simionescu, 2010a). The polysaccharide, having different M_w, was dissolved in deionized water and a mixture of epichlorohydrin and N,N-dimethyl-N-alkylamine (both from Aldrich) was added, then the resulting solution was stirred for 6 h at 70 °C. The polymer was recovered from the reaction mixture by precipitation in acetone, then purified by repeated precipitation and finally by sequential dialysis against 0.1 N HCl and water. Dialysis tubing with a cut-off of 12,000 from Sigma was used for this purpose. Liofilization of the diluted water solution obtained after dialysis provided the final polymer as a white powder. Chemical structure was proved by ^{1}H NMR and elemental analysis. The content in amino groups (degree of substitution—DS) was determined from the nitrogen content (elemental analysis) and chloride ion content (potentiometric titration with $AgNO_3$). The cationic polysaccharides have a general code PsM-RX, where Ps defines the polysaccharide (D for dextran and P for pullulan), M is the molar mass of the polysaccharide (in kDa), and R is the substituent at amino group, according to Scheme 1 (R = Oct (C8), Dod (C12), Cet (C_{16})), and X = DS = $100x/(x+y)$.

2.2. Measurements

Capillary viscometry was performed with Ubbelhode viscometers, immersed in a thermostated bath at 25.0 ± 0.1 °C. Two viscometers were used: size 0a, capillary diameter of 0.53 mm for liquid with viscosity up to 0.03 Pa s, and size Ia, capillary diameter 0.95 mm, for liquids with viscosity in the range 0.03–0.1 Pa s. The shear rate in capillary viscometer is not precisely defined, but it is low enough to allow the measurement of low-shear rate viscosity. Aqueous solutions of known polymer concentrations (C_P = 0.01–10 g/dl) were prepared and let to equilibrate for 48 h prior viscosity measurements. No corrections were applied, as flow times were proportional to kinematic viscosities. The data are average of at least two experiments and the reliability of the data was within ±3%.

3. Results and discussion

Viscosity studies provide a reasonable evaluation of the bulk macroscopic solution behavior. Several viscometric studies made with aqueous solutions of amphiphilic polyelectrolytes revealed the balance between the forces acting in a solution for dilute and semi-dilute concentrated regimes (Bataille, Huguet, Muller, Mocanu, & Carpov, 1997; Knudsen, Lauten, Kjøniksen, & Nyström, 2004; Mocanu, Carpov, Chapelle, Merle, & Muller, 1995; Nichifor, Stanciu, & Zhu, 2004). The increase in viscosity is due to electrostatic repulsions between charges and/or intermolecular hydrophobic associations, and the decrease in viscosity is a result of intramolecular hydrophobic associations. The polysaccharides under study have the charge and the hydrophobes located on the same side chain (head attached surfactant) therefore the molar ratio charge/hydrophobe is always 1/1, and variation of DS leads to simultaneous variation of electrostatic and hydrophobic interactions. Previous fluorescence studies (Nichifor, Lopes, Bastos, & Lopes, 2004; Nichifor, Stanciu, & Simionescu, 2010b) performed on these polymers revealed the occurrence of intra- and inter-molecular hydrophobic association at very low C_P. By means of free fluorescence probes (pyrene or *N*-phenylnaphthylamine) we could identify the minimum concentration at which hydrophobic microdomains start to form by hydrophobic associations (about 0.001 g/dl for most of polymers with R = cetyl or dodecyl, and about 0.1–0.3 g/dl for octyl derivatives) (Nichifor, Lopes, et al., 2004). Using fluorescently labeled polymers we also showed that