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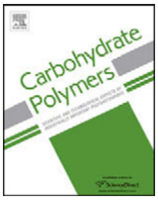

Hydrodynamic properties of some cationic amphiphilic polysaccharides in dilute and semi-dilute aqueous solutions

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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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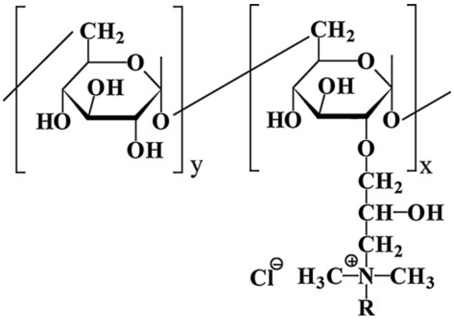

Scheme 1. Chemical Structure of cationic amphiphilic polyelectrolytes obtained by chemical modification of dextran. R = Octyl (C_8), Dodecyl (C_{12}) or Cetyl (C_{16}); DS = $100x/(x+y)$.

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

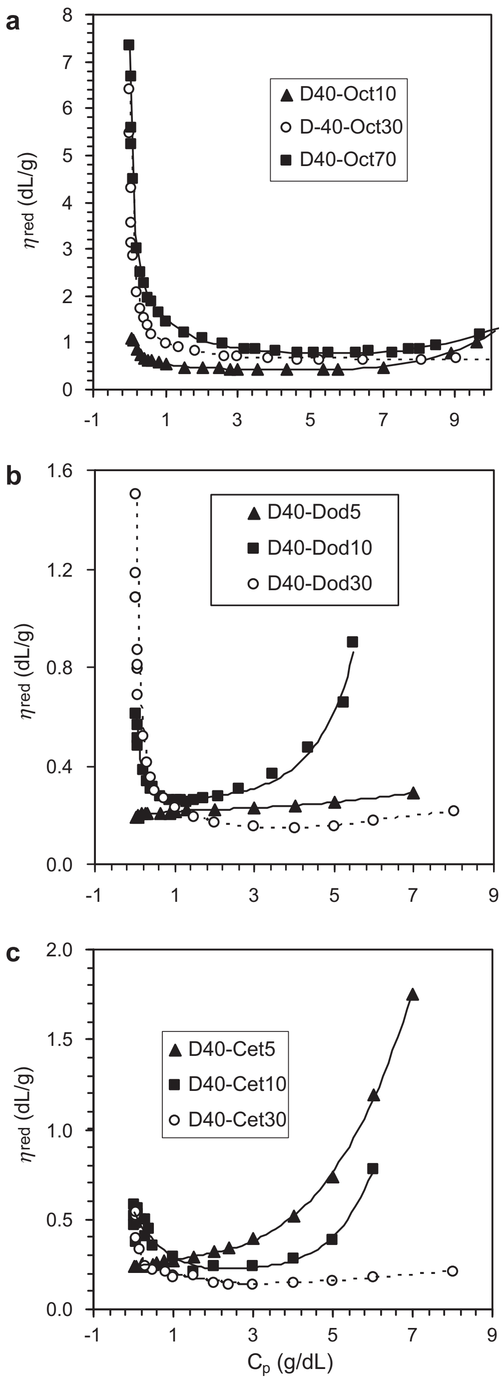

Fig. 1. Huggins plots for amphiphilic polyelectrolytes in dilute and semi-dilute aqueous solutions.

the intermolecular hydrophobic interactions occur at very low polymer concentrations (as low as 0.008 g/dl) for polymers with 5–10 mol% side groups with R = cetyl or dodecyl, but for polymers with 30 mol% dodecyl containing groups no intermolecular interaction was observed on a large C_P domain (0.02–2 g/dL) (Nichifor et al., 2010b). Now we used viscometry to investigate the polymer hydrodynamics over a much larger C_P range, and studied the influence of different polymer characteristics such as DS, hydrophobicity (i.e. R length), M_w, and type of polysaccharide, on macroscopic hydrodynamic properties of salt free aqueous polymer solutions.

Fig. 1 presents the Huggins plots (reduced viscosity, $\eta_{red} = \eta_{sp}/C_P$, versus C_P) for cationic amphiphilic polymers solutions over a large polymer concentration range ($0.01\ \mathrm{g\,dL^{-1}} < C_P < 10\ \mathrm{g/dL}$) which may include different concentration regimes. Polyion concentration modifies the flexibility of the chain, giving rise to different conformational aspects.

As it is obvious form these plots, all the polymers with DS ≥ 10 mol% show clear polyelectrolyte behavior, since in dilute solutions they present a clear up-turn of reduced viscosity. Only polymers with DS = 5 mol% do not show this behavior, indicating the lack of polyelectrolyte character at this very low DS. At higher polymer concentrations, a leveling of the reduced viscosity at low values is observed, and the width of the low viscosity region depends on DS and R length, being very large for high DS and shorter R (as in Fig. 1a). In some cases (D40-Dod10, D40-Cet5 and PsM-Cet5, Fig. 1b and c) a sharp increase of reduced viscosity at $C_P \geq 2$ g/dL indicates the behavior of these polymers as associative thickeners (with pronounced inter-molecular hydrophobic interactions).

In order to better describe the hydrodynamic properties of these polymers, we will discuss in the following the determination of intrinsic viscosities of the polymers from the experimental data in dilute solutions, the scaling behavior over the entire concentration domain studied, and finally an attempt to fit some known semi-empiric equations to the viscosity data for the whole concentration domain.

3.1. Intrinsic viscosities in dilute regime

Intrinsic viscosity is a measure of hydrodynamic volume of macromolecules in dilute solution (at concentration lower than the overlap concentration, C^*) where the polymer chains are separated and the intrinsic viscosity depends only on the dimensions of the individual polymer chains. Therefore, the magnitude of $[\eta]$ should reflect the size and conformation of a single polymer chain but, in the case of amphiphilic polymers, the occurrence of intermolecular aggregates cannot be neglected even in dilute domain (Nichifor et al., 2010b; Simon, Dugast, Le Cerf, Picton, & Muller, 2003).

In order to define the dilute regime one should know C^*, and several definitions were proposed to express the overlap concentration, which can differ up to a factor of 10 (Ioan, Aberle, & Burchard, 2001). The main criterion for its determination is the magnitude of the volume occupied by a random coil at C^*, therefore $C^* \sim 1/[\eta]$ (Qicong & Chu, 1987), but many times it is assumed that $C^* \approx 1/[\eta]$ (Candeau, Regalado, & Selb, 1998; Frish & Simha, 1956; Litmanovich, Zakharchenko, & Stoichev, 2007). Sometimes, C^* value is arbitrarily determined as the concentration corresponding to a viscosity twice that of the solvent (i.e. for $\eta_r = 2$ or $\eta_{sp} = 1$, where η_r and η_{sp} are relative and specific viscosity, respectively) (Di Cola et al., 2004; Rubinstein, Colby, & Dobrynin, 1994; Bromberg, 1998). The C^* values calculated according to the last definition are given in Table 1 (column 4), and these values seem to indicate that, when $C_P < 0.5$ g/dL, all the polymers are in dilute domain, consequently, all the viscosity data used for the calculation of the intrinsic viscosity were in this range.

Usually, $[\eta]$ of neutral polymer solution can be obtained by means of the Huggins Eq. (1), after extrapolation of the linear plots $\eta_{sp}/C_P - C_P$ to $C_P = 0$.

$$\frac{\eta_{sp}}{c} = [\eta](1 + k_H c[\eta] + \ldots) \tag{1}$$

where k_H = Huggins coefficient, which quantifies the specific hydrodynamic interactions between polymer and solvent. For the unmodified D40 sample the extrapolation of η_{sp}/C_P to zero concentration gives $[\eta] = 0.18$ dL/g.

Due to the non-linear shape of the $\eta_{sp}/C_p - C_p$ curves for cationic dextran samples (Fig. 1), extrapolation to zero concentration was not possible. This problem can be solved either by addition of low-molar- mass electrolyte or by means of semi-empirical equa-

Table 1
Experimental parameters for the viscometric behavior of cationic amphiphilic polymers and their parent polysaccharides. All concentrations are expressed in g/dL, and $[\eta]$ in dL/g; n.d. – not determined value because it was out of the studied concentration range; n.a. – equation not appropriate to fit the experimental data.

Polymer code	C^*, determined as			From log–log plots η_{sp} versus C_p						From fitting equations			
										Fedors		Martin	
	$[\eta]_{Rao}$	$1/[\eta]_{Rao}$	C_P for $\eta_{sp} = 1$	n_1	n_2	n_3	n_4	C^*	C_e	$[\eta]$	C_{max}	$[\eta]$	k_M
D40	0.19	5.26	4.00	1.00	1.58	n.d.	n.d	3.16	n.d.	0.19	45	0.19	0.43
D200	0.47	2.13	1.65	1.00	1.44	1.85	n.d	1.67	6.00	0.43	30	0.43	0.33
P200	0.53	1.88	1.50	1.10	1.53	2.66	n.d	1.40	5.73	0.51	19	0.49	0.40
D40-Oct10	1.38	0.72	2.15	0.75	1.30	n.d.	n.d	3.64	n.d.	n.a	n.a	n.a	n.a
D40-Oct30	6.89	0.14	1.05	0.71	0.55	1.30	n.d.	0.04	4.30	n.a.	n.a.	n.a.	n.a.
D40-Oct70	8.21	0.12	0.52	0.75	0.53	1.30	2.50	0.06	4.75	n.a.	n.a.	n.a.	n.a.
D40-Dod5	0.19	5.26	4.14	1.05	n.d.	n.d.	n.d	n.d.	n.d	0.18	60	0.14	0.40
D40-Dod10	0.68	1.47	3.00	0.71	1.41	3.50	n.d	1.46	3.80	0.20	10	0.18	1.24
D40-Dod30	1.34	0.75	5.85	0.70	0.52	1.70	n.d.	0.10	3.54	n.a.	n.a.	n.a.	n.a.
D40-Cet5	0.24	4.16	2.80	1.03	1.50	3.60	n.d	1.42	4.20	0.23	10	0.2	1.25
D40-Cet10	0.49	2.00	3.70	1.20	0.61	1.50	4.80	0.13	2.30	n.a.	n.a.	n.a.	n.a.
D40-Cet30	0.60	1.66	5.80	0.68	1.70	n.d.	n.d	3.42	n.d.	n.a.	n.a.	n.a.	n.a.
D200-Dod10	4.03	0.25	0.56	0.50	1.20	4.80	n.d	1.30	2.20	0.60	5.5	0.50	1.10
P200-Dod10	4.48	0.22	0.62	0.54	1.30	6.00	n.d	1.00	2.10	0.6	4.3	0.55	1.20
D200-Cet5	1.32	0.76	0.72	0.93	1.60	5.00	n.d	1.01	2.00	0.65	3.8	1.0	0.30

tions, like Fuoss and Strauss (1948), Yang (2004), Rushing and Hester (2004), or Wolf (Eckelt, Knopf, & Wolf, 2008). Fedors' equation (Fedors, 1979) modified by Rao (Rao, 1993) and verified for neutral polymer, has been successfully extended to some polyelectrolytes in both water (Ghimici & Popescu, 1998; Ghimici & Nichifor, 2006, 2009) and water/organic solvent mixtures (Dragan & Ghimici, 2001; Ghimici & Avram, 2003; Ghimici & Nichifor, 2006, 2009). In the case of amphiphilic polymers, the meaning of the intrinsic viscosity can sometimes be doubtful since macromolecules can form aggregate (inter- or/and intramolecular), as we have already shown for these polymers using fluorescence techniques based on fluorescence probe or fluorescently labeled polymers (Nichifor, Lopes, et al., 2004). We have checked the applicability of most of these equations, but only Rao (2) and Heller (3) (Durand, 2007) equations lead to linear plots (Fig. 2 gives an example for the polymers D40-OctX) which allowed the calculation of intrinsic viscosity for all the amphiphilic cationic polyelectrolytes and their parent polysaccharides.

$$\frac{1}{2(\eta_r^{1/2}-1)} = \frac{1}{[\eta]C} - \frac{a-1}{2.5} \tag{2}$$

$$\frac{1}{2}\left(\frac{1}{\eta_{sp}} + \frac{1}{\ln(1+\eta_{sp})}\right) = \frac{1}{C[\eta]} - K_{He} \tag{3}$$

"a" and K_{He} are constants describing the interactions in the solution.

The values of intrinsic viscosities obtained by application of the two equations were identical, therefore in Table 1 only the values obtained by Rao equation were included. The calculated $[\eta]$ values can serve as a semi-quantitative comparison of polymer conformation and dimension in dilute solution, as a function of DS, R length and M_w. All $[\eta]$ values are higher than those of the parent polysaccharide, except for D40-Dod5, the $[\eta]$ of which is identical with that of D40. For the same R, $[\eta]$ increases with DS, and, for the same DS it decreases significantly with increasing R length. These findings suggest that the main forces influencing the polymer hydrodynamics in the dilute aqueous solutions are the electrostatic and intra-molecular hydrophobic interactions, and the electrostatic repulsions seem to overcome hydrophobic intra-molecular hydrophobic attractions, even for a very hydrophobic polyelectrolyte such as D40-Cet30 (the up-turn of viscosity with dilution is weak, but still present). The occurrence of intermolecular hydrophobic interactions was certainly assessed in this concentration domain for polymers with DS = 5–10mol%, by means of non-radiative energy transfer experiments performed on mixtures of single fluorescently labeled cationic polymers (Nichifor et al., 2010b). However, these type of interactions is not clearly indicated by viscometric behavior (they would give an increase of reduced viscosity with C_P). The difference can arise from the conditions under which the two measurements were performed: fluorescence measurements were carried out under static (equilib-

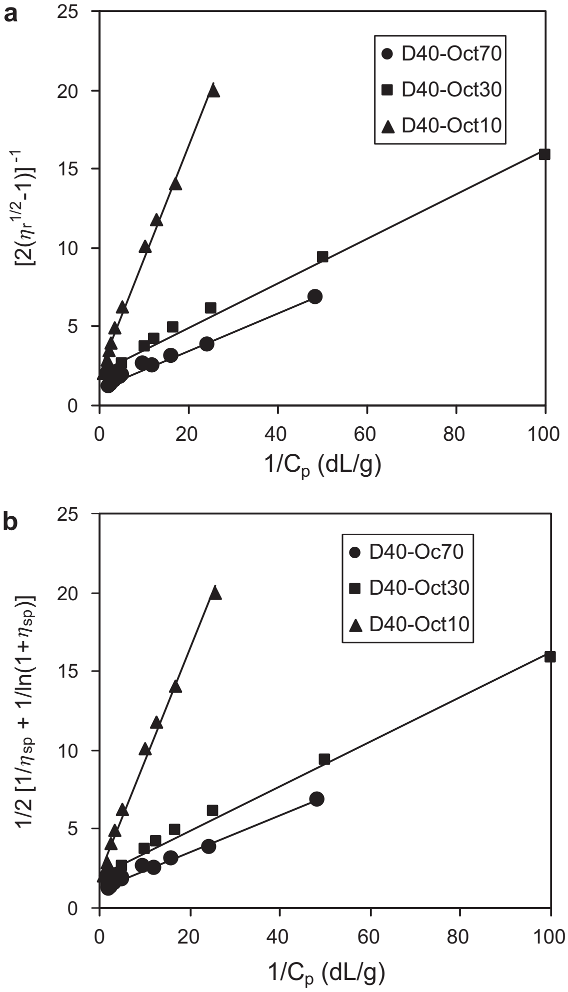

Fig. 2. Plots of viscosity data for D40-OctX in terms of Rao (a) and Heller (b) equations.

rium) conditions, but viscosity is a dynamic process, during which the weak hydrophobic associations can be destroyed, even at the low shear rates of the viscosity experiments. Thus, the $[\eta]$ values of most cationic polymers indicate the conformation of single polymer chains in the dilute regime, which assume the form of extended coils, but the extension is controlled by X and R. However, the polymers DM-Cet5 with no polyelectrolyte behavior, have $[\eta]$ values higher than those of the parent dextrans, what can support the presence of intermolecular hydrophobic interactions which are strong enough to overcome shear thinning.

The C^* values calculated as $1/[\eta]$ are included in Table 1, and their comparison with those found for C_P corresponding to $\eta_{sp} = 1$ show a relatively good agreement only for unmodified polysaccharides and their cationic derivatives with DS = 5 mol%, for all the other samples $1/[\eta] < C_P$ (for $\eta_{sp} = 1$), and the difference increases with DS. The difference might be assigned to different conformation of amphiphilic single chains at infinite and finite dilution, mainly to the greater influence of intramolecular hydrophobic associations (leading to a more compact structure) at finite concentration, in comparison with a relatively stretched coil conformation at infinite dilution due to the stronger electrostatic repulsions.

3.2. Scaling behavior of amphiphilic polyelectrolytes

The viscosity variation over a larger concentration domain can be better evaluated in double-logarithmic plots of η_{sp} versus C_P. The plots included in Fig. 3 provide a qualitative evaluation of polymer structure influence on viscosity–C_P relationships. Fig. 3a presents the influence of DS for polymers D40-DodX viscosity, in comparison to that of the D40. When $X = 5$, the viscosity is very close to that of the unmodified dextran. Raising X to 10 leads to a different behavior, with viscosity higher than that of native dextran over the whole concentration domain, and when $X = 30$ the viscosity is higher in dilute regime and lower in semi-dilute one. As for the length of R, Fig. 3b testifies its influence on polymer conformation, which is more extended in case of D40-Oct30 (the difference in viscosity is almost one order of magnitude comparing with D40-Dod30) and the viscosity values of the octyl derivative are higher than those of D40 over the entire concentration domain. D40-Cet30 behaves similarly to D40-Dod30 in semi-dilute regime, but its viscosity in dilute domain is lower.

For a more quantitative evaluation of the interplay between electrostatic and hydrophobic interactions over the entire concentration range investigated, we try to apply the scaling theories developed for polyelectrolytes and neutral polymers. According to these theories, the variation of η_{sp} with C_P is described by power-law functions, $\eta_{sp} \sim C_P^n$, where the exponent n depends on the mechanism of mass transfer in the flow process (Muthukumar, 1997), and its value can discriminate among several concentration regimes (Dobrynin et al., 1995; Dou & Colby, 2006): dilute, at $C_P < C^*$ (with $n \sim 1$ for both neutral and ionic polymers), semi-dilute unentangled, when $C^* < C_P < C_e$ ($n \sim 5/4$ for neutral polymers, $n \sim 1/2$ for polyelectrolytes), semi-dilute entangled for $C_P > C_e$ ($n \sim 3/2$ for polyelectrolytes and 15/4 for neutral polymers) and semidilute overlapped electrostatic blobs ($n \sim 15/4$) characteristic only for polyelectrolytes, and defined by a critical concentration, C^{**}, above which the electrostatic interactions no longer perturb the chain conformation. Usually, the curves η_{sp} versus C_P are smooth lines (Fig. 3), but different regimes can be approximated by straight lines with different slopes ($n_1 - n_4$), which can be compared with those predicted by scaling theories. The crossovers of these lines allow the calculation of different critical concentrations (C^*, C_e—the entanglement concentration, C^{**}) and discrimination between concentration regimes, as Fig. 4 illustrates for several polymers: D40-Oct70 with a predominant polyelectrolyte character, D40-Cet5 with significant associative properties, and D40-Cet10 with a mixed behavior. The scaling exponents $n_1 - n_4$, C^* and C_e values obtained for all investigated polymers are collected in Table 1. Analysis of the data included in Table 1 and Figs. 3 and 4 highlights some general behaviors but also some exceptions:

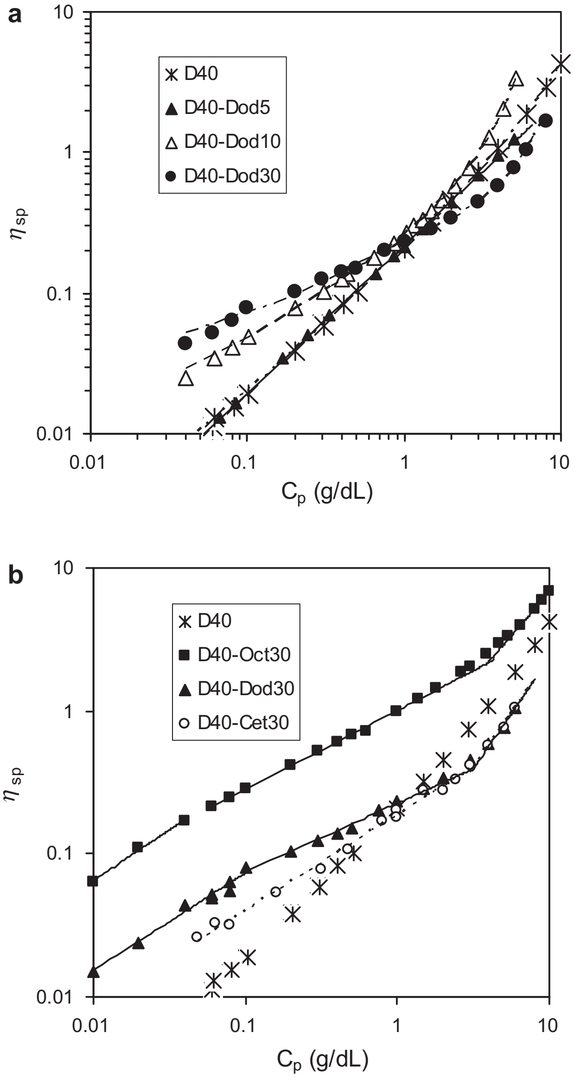

Fig. 3. Influence of the degree of substitution (a) and length of alkyl substituent (b) on the specific viscosity variation with polymer concentration.

(a) C^* values obtained from these graphs deviate from those calculated by other assumptions, and there is no general rule for the deviation (columns 3, 4 and 9 in Table 1). Nevertheless, the variation of all C^* values with R length and DS follows the same tendency as shown for $[\eta]$.

(b) Native polysaccharides and amphiphilic polymers with DS = 5 mol% display a typical behavior for the neutral polymers with scaling exponents $n_1 \approx 1.0$ (dilute regime) and $n_2 \approx 1.5$ (1.3–1.6) in unentangled semi-dilute regime. However, D40-Dod5 has a single linear domain over the whole concentration range investigated, therefore no value for C^* and C_e could be determined. At $C_P > 3$ g/dL, its viscosity becomes lower than that of D40 (see Fig. 3a), meaning that intra-molecular hydrophobic interactions are still active at this rather high concentration.

(c) Viscosity of all amphiphilic polymers with DS ≥ 10 mol% follow an atypical power law ($n_1 \approx 0.7$) in dilute regime, what could be a proof for intra-molecular hydrophobic interactions effectively

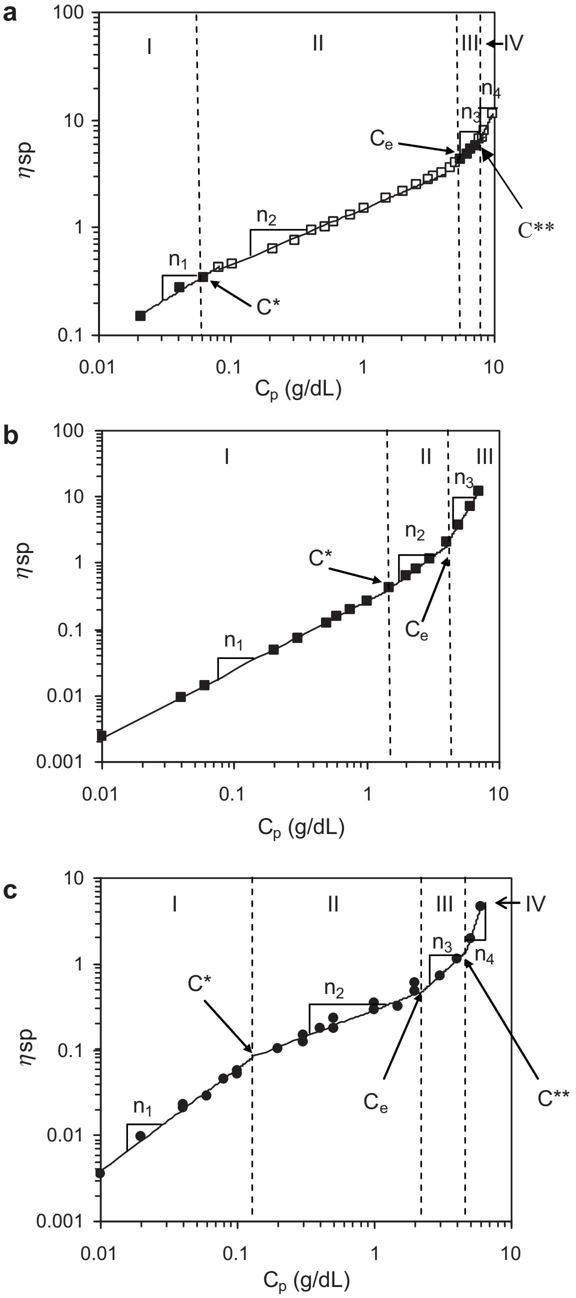

Fig. 4. Dependence of specific viscosity on concentration of amphiphilic polymers with a predominant polyelectrolyte (D40-Oct70) (a), predominant neutral (D40-Cet5) (b), and combined (D40-Cet10) (c) behavior. The solid lines are the best linear fits to the experimental data, with the slopes $n_1 - n_4$. Dashed vertical lines separates the concentration regimes: I – dilute, II – unentangled semi-dilute, III – entangled semi-dilute and IV – overlapped electrostatic blobs.

acting in this domain. The somewhat lower values (about 0.6) obtained for higher molecular mass polymers D200-Dod10 and P200-Dod10 suggest a small enhancement of intra-molecular hydrophobic attractions by M_w increase.

(d) Only the amphiphilic polymers with high charge content (DS ≥ 30 mol%) assume power laws of viscosity–C_P relationship which are specific to polyelectrolytes in the unentangled ($n_2 \approx 0.5$) and entangled semi-dilute regime ($n_3 \approx 1.5$), but the width of the unentangled regime is narrower than that usually reported for hydrophilic polyelectrolytes ($C_e/C^* \approx 1000$, Dou & Colby, 2006), and it becomes narrower with increasing *R* length, stretching over about 2 orders of concentration magnitude for D40-Oct30, about 1 order of magnitude for D40-Dod30, and being almost absent for D40-Cet30 (Fig. 3b) (actually, in the semi-dilute unentangled regime D40-Cet30 viscosity follows a power law characteristic to non-charged polymers, i.e. $n_2 \approx 1.5$). This finding is obviously the result of increasing preponderance of hydrophobic intra-molecular associations over electrostatic interactions with increasing the length of alkyl substituent *R*, leading to higher values of C^*. Further, most of the highly substituted polymers do not show an entangled semi-dilute regime in the studied concentration range (meaning a $C^{**} > 10$ g/dl), as a result of the combined effect of electrostatic autoscreening and intramolecular hydrophobic interactions, which decrease the coil size and delay chain entanglement. A narrow entangled regime could be defined only for D40-Oct70 (Fig. 4a). This highly substituted polymer with less hydrophobic substituents has a more stretched conformation which favors the chain entanglements.

(e) Amphiphilic polymers with DS = 5–10 mol% behave like neutral polymers ($n_2 \approx 1.5$) and display a narrow unentangled semi-dilute domain ($C_e/C^* \approx 2$–3), which, in case of D200-Cet5 is rather a transition domain than a well defined concentration regime. The power law in the entangled regime (n_3) overcomes in some cases the value of 3.75 predicted by theory for both neutral and charged polymers (Dobrynin et al., 1995). This strong concentration dependence of η_{sp}, characteristic to associative polymers and consistent with the sticky reptation model developed by Rubinstein and Semenov (2001), was experimentally observed for other hydrophobically modified polyelectrolytes (Di Cola et al., 2004; Kujawa et al., 2006). This shows that the presence of a few long hydrophobic chains determines a more rapid entanglement of the polymer chains, which favors the inter-molecular hydrophobic interactions (or vice-versa: the intermolecular hydrophobic associations favor the chain entanglement). The value of scaling exponent n_3 increases with increasing *R* length and M_w, and is higher for more flexible pullulan than for dextran derivatives of the same molar mass (Table 1, columns 7 and 8), suggesting the possibility to tailor the associative properties by changing these parameters.

D40-Cet10 displays a very complex viscosity–concentration relationship, which was not found for the other cationic polymers with DS = 10 mol%. In this case, four concentration regimes could be detected (Fig. 4c): regimes I and IV are characteristic to associative polymers, and regime II and III, with $n_2 \approx 0.5$ and $n_3 \approx 1.5$, respectively, would classify this polymer among polyelectrolytes. The high values for n_1 (1.2) and n_4 (4.8) are indicative for the presence of strong intermolecular hydrophobic interactions both in dilute and in semi-dilute entangled regimes. Apparently, at $C_P > C^*$, the autoscreening of electrostatic charges on the overlapped chains hampers a further increase in the number of junctions between the hydrophobic stickers, and this process occurs again only at $C_P > C^{**}$.

The values of concentrations C^*, C_e and C^{**}, as well as the those of exponents $n_1 - n_2$ are not absolute numbers, but they can indicate, in a semi-quantitative manner, the critical points for changes in the balance between electrostatic repulsions and intra/inter-molecular hydrophobic attractions with increasing C_P, as a function of polymer structural characteristics.

3.3. Application of semi-empirical equations

Prediction of viscosity of aqueous polymer solutions as a function of polymer concentration and chemical structure is very useful in application of amphiphilic polymers as viscosity modifiers. Recently, Durand (Durand, 2007; Rotureau, Dellacherie,

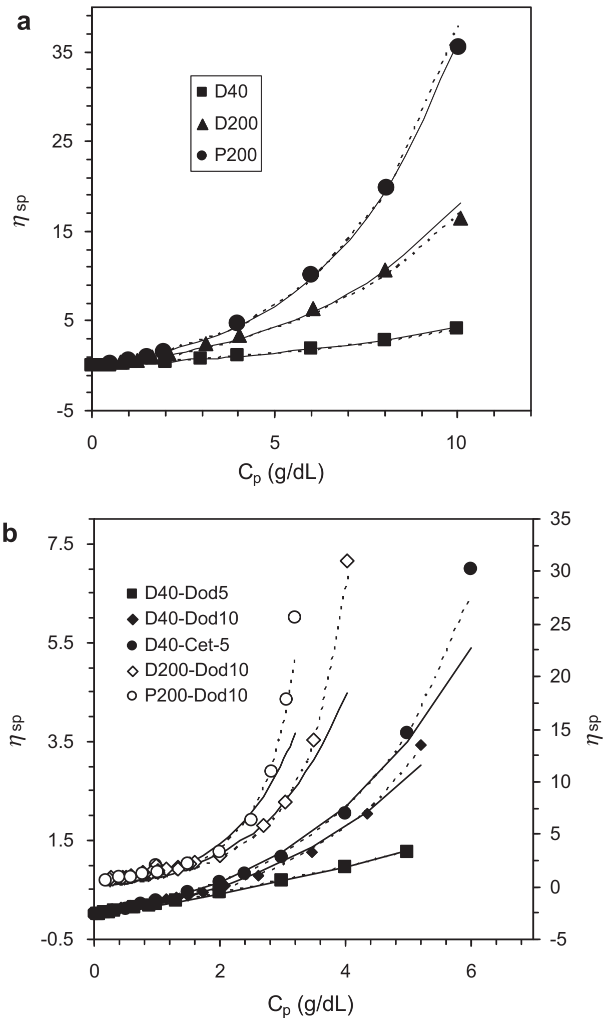

Fig. 5. Application of semi-empirical equations to specific viscosity variation with concentration of polysaccharides (a) and their low substituted cationic derivatives (b). The curves are the best fitting by Fedors (dotted lines) and Martin (solid lines) equations. In graph (b) the right Y axis corresponds to plots for D200-Dod10 and P200-Dod10.

& Durand, 2006) examined the applicability of several semi-empirical equations for describing the viscosity–concentration relationship of some neutral amphiphilic dextran derivatives over a large concentration domain (dilute and semi-dilute regimes). We checked the applicability of Fedors (1979), Martin (Durand, 2007), Matsuoka–Cowman (Kwei, Nakazawa, Matsuoka, Cowman, & Okamoto, 2000), and Heller (Durand, 2007) equations and obtained good fittings of experimental data only with Fedors Eq. (4) and partial fittings with Martin Eq. (5), both for the unmodified polysaccharides (Fig. 5a) and the cationic amphiphilic polyelectrolytes with low degree of substitution (5–10 mol%) and long alkyl substituents (Fig. 5b), i.e. only for amphiphilic polymers with a predominant neutral behavior. Polymers with clear polyelectrolyte behavior could not be described by any of the mentioned equations. The best fittings obtained by taking $[\eta]$ and C_{max} (Fedors) or K_M (Martin) as variable parameters allowed the calculation of these parameters (Table 1, the last 4 columns). The $[\eta]$ values so obtained for unmodified polysaccharides and cationic polymers with DS = 5 mol% are close to $[\eta]_{Rao}$ values, but deviate from them in case of polymers with DS > 5 mol%. The evaluation of C_{max}, which is defined as the concentration above which the polymer solution do not flow anymore (Fedors, 1979), is important for the prediction of rheological behavior and the obtained values are low enough for these polymers to be taken into account as associative thickeners.

$$\frac{1}{2(\eta_r^{1/2}-1)} = \frac{1}{C[\eta]} - \frac{1}{C_{max}[\eta]} \tag{4}$$

$$\eta_{sp} = C[\eta]\exp(K_M C[\eta]) \tag{5}$$

where K_M is a constant with a similar meaning as k_H and K_{He}.

4. Conclusions

An extensive viscometric study was performed with aqueous solutions of a series of cationic amphiphilic polyelectrolytes based on polysaccharides (dextran, pullulan) with N,N-dimetyl-N-alkyl-N-(2-hydroxypropyl)ammonium chloride pendant groups, over a large polymer concentration range, which included dilute and semi-dilute domains. The experimental data were worked up using either different semi-empirical equation to calculate intrinsic viscosity and to fit these data over the whole concentration range, or scaling theories to identify concentration domains and calculate overlap and entanglement concentrations. All the results were analyzed in relationship with chemical structure of the polymers (DS, the length of the alkyl substituent R, the nature of the polysaccharide and its molar mass), which determines the balance between electrostatic repulsions and inter- or/and intramolecular association. The following conclusions 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.

In dilute domain, all the polymers with a DS ≥ 10 mol% behave as polyelectrolytes, since the reduced viscosity increases with dilution. Intrinsic viscosity values, calculated using Rao or Heller equations, indicate the influence of both electrostatic and intramolecular interactions on the conformation of individual chains, with a predominance of electrostatic repulsion which diminishes with decreasing DS an increasing R length. The presence of intermolecular hydrophobic interactions in this domain was clearly observed only from viscosity behavior of polymer containing 5–10 mol% pendant groups with R = cetyl.

In semi-dilute unentangled domain, only the polymers with a degree of substitution ≥30 mol% show a power law dependence of specific viscosity, $\eta_{sp} \sim C^{1/2}$, which is characteristic to polyelectrolyetes, and the width of this domain becomes narrower with decreasing DS and increasing R length, due to the increased effect of intramolecular hydrophobic associations.

In semi-dilute entangled domain, some derivatives with low DS (5–10 mol%) behave like associative polymers (a sharp concentration dependence of specific viscosity), due to inter-molecular hydrophobic interactions, which are enhanced by increasing R length, polysaccharide molar mass and its flexibility. Fitting the viscometric data for these polymers with Fedors equation allowed an estimation of C_{max} value, which is very useful to evaluate the application of the polymers as thickeners.

References

Bataille, I., Huguet, J., Muller, G., Mocanu, G., & Carpov, A. (1997). Associative behaviour of hydrophobically modified carboxymethylpullulan derivatives. *International Journal of Biological Macromolecules*, *20*, 179–191.

Bromberg, L. (1998). Self-assembly in aqueous solutions of polyether-modified poly(acrylic acid). *Langmuir*, *14*, 5806–5812.

Candeau, F., Regalado, E. J., & Selb, J. (1998). Scaling behavior of the zero shear viscosity of hydrophobically modified poly(acrylamide)s. *Macromolecules*, *31*, 5550–5552.

de Gennes, P. G., Pincus, P., Velasco, R. M., & Brochard, F. (1976). Remarks on polyelectrolyte conformation. *Journal de Physique, France*, *37*, 1461–1473.

Di Cola, E., Plucktaveesak, N., Waigh, T. A., Colby, R. H., Tan, J. S., Pyckhout-Hintzen, W., & Heenan, R. K. (2004). Structure and dynamics in aqueous solutions of amphiphilic sodium maleate-containing alternating copolymers. *Macromolecules*, *37*, 8457–8465.

Di Cola, E., Waigh, T. A., & Colby, R. H. (2007). Dynamic light scattering and rheology studies of aqueous solutions of amphiphilic sodium maleate containing copolymers. *Journal of Polymer Science Part B: Polymer Physics*, *45*, 774–785.

Dobrynin, A. V., Colby, R. H., & Rubinstein, M. (1995). Scaling theory of polyelectrolyte solutions. *Macromolecules*, *28*, 1859–1871.

Dobrynin, A. V., & Rubinstein, M. (2000). Hydrophobically modified polyelectrolytes in dilute salt-free solutions. *Macromolecules*, *33*, 8097–8105.

Dou, S., & Colby, R. H. (2006). Charge density effects in salt-free polyelectrolyte solution rheology. *Journal of Polymer Science Part B: Physics*, *44*, 2001–2013.

Dragan, S., & Ghimici, L. (2001). Viscometric behaviour of some hydrophobically modified cationic polyelectrolytes. *Polymer*, *42*, 2887–2891.

Durand, A. (2007). Semiempirical equations for the viscosity of amphiphilic polymer solutions: a critical examination. *Polymer Engineering and Science*, *47*, 481–488.

Eckelt, J., Knopf, A., & Wolf, B. A. (2008). Polyelectrolytes: intrinsic viscosities in the absence and in the presence of salt. *Macromolecules*, *41*, 912–918.

Fedors, R. F. (1979). An equation suitable for describing the viscosity of dilute to moderately concentrated polymer solutions. *Polymer*, *20*, 225–228.

Frish, H. L., & Simha, R. (1956). *The Viscosity of Colloidal Suspension and Macromolecular Solution*. New York: Academic Press.

Fuoss, R. M., & Strauss, U. P. (1948). Polyelectrolytes. II. Poly-4-vinylpyridonium chloride and poly-4-vinyl-**N**-**n**-butylpyridonium bromide. *Journal of Polymer Science*, *3*, 246–263.

Ghimici, L., & Avram, E. (2003). Viscometric behavior of quaternized polysulfones. *Journal of Applied Polymer Science*, *90*, 465–469.

Ghimici, L., & Popescu, F. (1998). Determination of intrinsic viscosity for some cationic polyelectrolytes by Fedors method. *European Polymer Journal*, *34*, 13–16.

Ghimici, L., & Nichifor, M. (2006). Transport properties of some cationic polysaccharides.2. Charge density effect. *Journal of Colloid and Interface Science*, *302*, 589–596.

Ghimici, L., & Nichifor, M. (2009). Transport properties of some cationic amphiphilic polysaccharides. Effects of side chain length and solvent polarity. *Journal of Applied Polymer Science*, *111*, 3031–3038.

Glass, J. E. (Ed.). (1989). *Polymers in aqueous media: performance through association*. Washington, DC: American Chemical Society.

Glass, J. E. (Ed.). (2000). *Associative polymers in aqueous solution*. Washington, DC: American Chemical Society.

Ioan, C. E., Aberle, T., & Burchard, W. (2001). Light scattering and viscosity behavior of dextran in semidilute solution. *Macromolecules*, *34*, 326–336.

Jianping, Z., Yonggang, S., Qiang, W., & Qiang, Z. (2009). Hydrophobically modified poly(sodium 2-acrylamido-2-methylpropanesulfonate):synthesis and viscosity of aqueous solution. *Polymer International*, *58*, 1275–1282.

Knudsen, D. K., Lauten, R. A., Kjøniksen, A.-L., & Nyström, B. (2004). Rheological and structural properties of aqueous solutions of a hydrophobically modified polyelectrolyte and its unmodified analogue. *European Polymer Journal*, *40*, 721–733.

Kotz, J., Kosmella, S., & Beitz, T. (2001). Self-assembled polyelectrolyte systems. *Progress in Polymer Science*, *26*, 1199–1232.

Kujawa, P., Audibert-Hayet, A., Selb, J., & Candau, F. (2006). Rheological properties of multisticker associative polyelectrolytes in semidilute aqueous solutions. *Macromolecules*, *39*, 384–392.

Kwei, T. K., Nakazawa, M., Matsuoka, S., Cowman, M. K., & Okamoto, Y. (2000). Concentration dependence of solution viscosities of rigid rod polymers. *Macromolecules*, *33*, 235–236.

Litmanovich, E. A., Zakharchenko, S. O., & Stoichev, G. V. (2007). Influence of chain charge and complexation on the overlap and entanglements formation in poly(acrylic acid) salt-containing aqueous solutions. *Journal of Physical Chemistry B*, *111*, 8567–8571.

Mocanu, G., Carpov, A., Chapelle, S., Merle, L., & Muller, G. (1995). Chemically modified pullulans. 2. New hydrophobically substituted derivatives. *Canadian Journal of Chemistry*, *73*, 1933–1940.

Molyneaux, P. (Ed.). (1984). *Water-soluble synthetic polymers: properties and behavior*. Boca Raton, FL: CRC Press.

Muthukumar, M. (1997). Dynamics of polyelectrolyte solutions. *Journal of Chemical Physics*, *107*, 2619–2635.

Nichifor, M., Lopes, S., Bastos, M., & Lopes, A. (2004). Self-aggregation of cationic amphiphilic polyelectrolytes based on polysaccharides. *Journal of Physical Chemistry B*, *108*, 16463–16472.

Nichifor, M., Stanciu, M. C., & Simionescu, B. C. (2010a). New cationic hydrophilic and amphiphilic polysaccharides synthesized by one pot procedure. *Carbohydrate Polymers*, *82*, 965–975.

Nichifor, M., Stanciu, M. C., & Simionescu, B. C. (2010b). Fluorescence study of intermolecular interactions in diluted aqueous solutions of some cationic amphiphilic polysaccharides. *Journal of Macromolecular Science Part B: Physics*, *49*, 983–993.

Nichifor, M., Stanciu, M. C., & Zhu, X. X. (2004). Bile acids covalently bound to polysaccharides. 2. Dextran with pendant cholic acid groups. *Reactive and Functional Polymers*, *59*, 141–148.

Odijk, T. (1979). Possible scaling relations for semidilute polyelectrolyte solutions. *Macromolecules*, *12*, 688–693.

Paillet, S., Grassl, B., Khoukh, A., Torres, M., Desbrieres, J., & Muller, A. J. (2009). Rheological behavior of bigrafted hydrophobically modified polyelectrolyte. *Macromolecules*, *42*, 4914–4917.

Qicong, Y. Q., & Chu, B. (1987). Overlap concentration of macromolecules in solution. *Macromolecules*, *20*, 362–366.

Rao, M. V. S. (1993). Viscosity of dilute to moderately concentrated polymer solutions. *Polymer*, *34*, 592–596.

Rotureau, E., Dellacherie, E., & Durand, A. (2006). Viscosity of aqueous solutions of polysaccharides and hydrophobically modified polysaccharides: application of Fedors equation. *European Polymer Journal*, *42*, 1086–1092.

Rubinstein, M., Colby, R. H., & Dobrynin, A. V. (1994). Dynamics of semidilute polyelectrolyte solutions. *Physical Review Letters*, *73*, 2776–2779.

Rubinstein, M., & Semenov, A. N. (1998). Thermoreversible gelation in solutions of associating polymers. 2. Linear dynamics. *Macromolecules*, *31*, 1386–1397.

Rubinstein, M., & Semenov, A. N. (2001). Dynamics of entangled solutions of associating polymers. *Macromolecules*, *34*, 1058–1068.

Rushing, T. S., & Hester, R. D. (2004). Semi-empirical model for polyelectrolyte intrinsic viscosity as a function of solution ionic strength and polymer molecular weight. *Polymer*, *45*, 6587–6594.

Simon, C., Dugast, J. Y., Le Cerf, D., Picton, L., & Muller, G. (2003). Amphiphilic polysaccharides. Evidence for a competition between intra and intermolecular associations in dilute system. *Polymer*, *44*, 7917–7924.

Souguir, Z., Roudesli, S., About-Jaudet, E., Picton, L., & Le Cerf, D. (2010). Novel cationic and amphiphilic pullulan derivatives II: pH dependant physicochemical properties. *Carbohydrate Polymers*, *80*, 123–129.

Strauss, U. P., & Gershfeld, N. L. (1954). The transition from typical polyelectrolyte to polysoap. I. Viscosity and solubilization studies on copolymers of 4-vinyl-N-ethylpyridinium bromide and 4-vinyl-N-n-dodecylpyridinium bromide. *Journal of Physical Chemistry*, *58*, 747–753.

Turner, M. S., & Joanny, J. F. (1993). Static properties of polysoaps in dilute solutions. *Journal of Physical Chemistry*, *97*, 4825–4831.

Yang, Y. (2004). Interpretation of viscosity behavior of a polyelectrolyte in a salt-free polar solvent by ion-association. *Journal of Macromolecular Science Part B: Physics*, *43*, 845–858.