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Aggregation in Aqueous Solutions of Some Cationic Amphiphilic Polyelectrolytes

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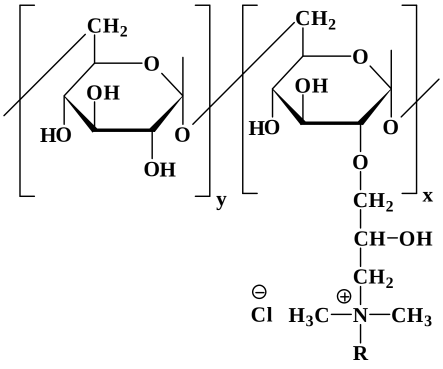
Abstract: Aqueous solutions of amphiphilic polyelectrolytes, based on polysaccharides having N-(2-hydroxypropyl)-N, N-dimethyl-N-alkyl ammonium chloride as pendant groups are used for the discrimination between intra- and intermolecular hydrophobic interactions as a function of polymer physico-chemical characteristics, with a special attention paid to molecular weight and polysaccharide backbone.

The aggregates characteristics are determined by steady-state fluorescence (critical aggregation concentration - *CAC* and micropolarity), fluorescence anisotropy (microviscosity) and capillary viscometry (macroviscosity) measurements. The results highlight the dependence of aggregate characteristics on degree of substitution with hydrophobic pendant groups, the length of alkyl substituent R, molecular weight and type of polysaccharides. *CAC* values decrease with the increase of the R length. The molecular weight and the nature of the polysaccharide have a reduced influence on *CAC* values. Higher anisotropy values are obtained for higher molecular weight and lower values of the degree of substitution. Up-level values of the reduced viscosity, at high polymer concentration, are characteristic for polymers with low DS and high M_w or backbone's flexibility.

Keywords: amphiphilic polyelectrolytes, self-aggregation, fluorescence, capillary viscometry

1. Introduction

Amphiphilic polyelectrolytes can be obtained by chemical modification of water-soluble polymers and hydrophobic groups are distributed either randomly or as blocks along the polymer backbone. The charges and hydrophobes can be located at different positions or can belong to the same side chain. In the last case, pendant groups are surfactants bound as side groups to the polymeric backbone via their headgroup or hydrophobic tail. The self-association of hydrophobes can occur by intra- and/or intermolecular interactions.



Scheme 1. Chemical structure of cationic amphiphilic polyelectrolytes obtained by chemical modification of dextran. R = Oct (C_8), Dod (C_{12}) and Cet (C_{16}), DS = 100x/(x + y)

The purpose of the this study is to analyze the characteristics of the aggregates formed in aqueous solutions of new hydrophobically modified cationic polymers based on polysaccharides carrying pendant N - alkyl N,N-dimethyl- N- (2-hydroxypropyl) ammonium chloride groups, where alkyl is an octyl, dodecyl, or cetyl group (Scheme 1) and the polysaccharide is dextran or pullulan. Pendant groups are randomly distributed and head attached to the polysaccharide backbone.

Fluorescence techniques and viscometric measurements, carried out in dilute and semidilute solutions, were used to characterize the self-aggregates that are formed by these polymers as a function of their chemical composition and concentration.

2. Experimental

2.1. Materials

Two dextran samples were supplied by Sicomed S.A. Bucharest: D40 with M_w = 40 000 and M_w/M_n = 1.12, and D200 with M_w = 210.000 and M_w/M_n = 1.45 (as determined by capillary viscometry and static light scattering in water solution). A sample of dextran with M_w = 465000 (D465) was purchased from Sigma. One pullulan sample P200 with M_w = 200 000 and M_w/M_n = 1.40 was obtained from Hayashibara, Okayama, Japan. N-phenyl naphthylamine (NPN) was from Sigma and was used after appropriate re-crystallization. Doubly distilled deionized water obtained with an Millipore purification system was used for preparation of aqueous solutions.

Cationic polymers with pendant quaternary ammonium groups were synthesized by chemical modification of polysaccharides. 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 general code of cationic polysaccharides is D(or P)MRX, where D stands for dextran and P for pullulan, M represents the molecular weight of the polysaccharide, R is the abbreviation for the alkyl substituent at amino group, according to Scheme 1, and X indicates the average degree of substitution with amino groups carrying the R substituent (X = ± 2-3 mol%).

Polymer stock solutions for fluorescence measurements were prepared in 1×10^{-6} M aqueous solution of NPN, and diluted to the desired concentration with the same fluorophore solution.

2.2. Methods

Steady-state fluorescence spectra and fluorescence anisotropy values where obtained with a SPEX Fluorolog 212 in L conformation, with slits set to 1 nm. Emission spectra of NPN were obtained with excitation wavelength fixed at 340 nm. In the case of fluorescence anisotropy, the emission wavelength was set at 430 nm for NPN. All fluorescence measurements were performed at ambient temperature.

Capillary viscometry was performed with Ubbelhode viscometer immersed in a thermostatted bath at 25 ± 0.1 °C.

3. Results and Discussion

3.1. Critical Aggregation Concentration of the Polymers

Fluorescent probes can provide different information about the hydrophobic domain characteristics, such as micropolarity and microviscosity [1, 2]. NPN is frequently used in the characterization of the aggregates formed by amphiphilic polymers due to its known ability to change the emission intensity maximum and to undergo a batochromic shift of this maximum with decreasing polarity and increasing viscosity of the environment [3].

The fluorescence properties variation of a cromophore probe is due to a sequential partition between water and hydrophobic microdomains (where they are solubilized) until equilibrium between the two regions occurs.

NPN steady-state fluorescence is used to determine the value of critical aggregation concentration (*CAC*)(concentration below which no significant aggregation can be detected) for the amphiphilic polymers. Critical aggregation concentration values are determined as the onset of NPN emission intensity increase with C_p.

The value of CAC depends mostly on the chemical structure of the amphiphilic polyelectrolyte and the specific variation of the polyelectrolyte conformation with concentration [4 - 7].

In Fig. 1 is shown the influence of DS, R length, the molecular weight and nature of the polysaccharide on *CAC*. When the hydrophobicity of the alkyl substituent of the polymer increases, the aggregation process is favoured and *CAC* values decrease. (Fig. 1a).

The increase of either polymer molecular weight or the polysaccharide flexibility must promote the hydrophobic associations and so, CAC values decrease. However, the influence of M_W and backbone flexibility upon CAC values of polymers D(or P)MRX is low (Fig. 1b).

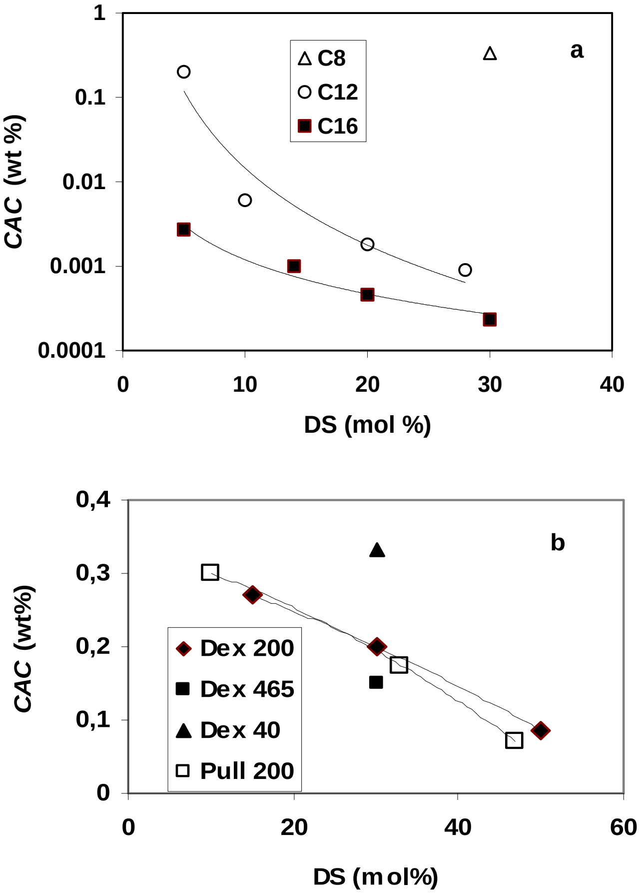


Figure 1a, b. Variation of *CAC* with the degree of substitution of the cationic polymers as a function of the length of R in the polymer D40-RX (a) and as a function of the nature of the polysaccharide backbone and its molecular weight of polymers with R = octyl (b)

3.2. Fluorescence Depolarization

The degree of fluorescence depolarization of the light emitted by a probe can be related to the extent of the motion of that probe during its lifetime in excited state [6, 8, 9, 3]. Therefore, the steady-state fluorescence polarization can be used to determine the apparent microviscosity of the probe environment.

Variation of NPN anisotropy with the polymer concentration is sigmoidal (Fig. 2a, b) which indicates a stepwise partition of the probe between water and hydrophobic microdomains. The maximum values for anisotropy differ as a function of the degree of substitution with hydrophobic groups (Fig. 2a) and molecular weight of the polymer (Fig. 2b).

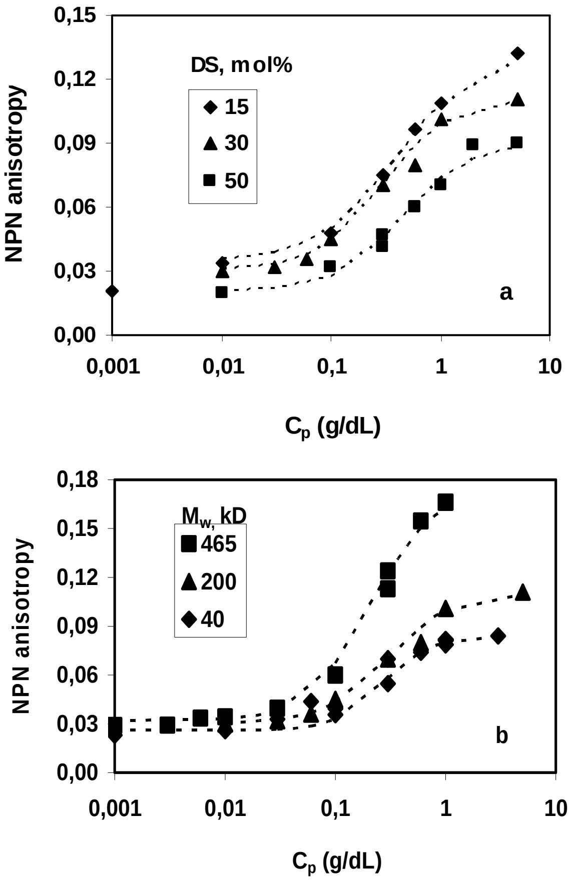


Figure 2a, b. Variation of NPN anisotropy as a function of degree of substitution (D40-OctX) (**a**) and molecular weight of the polymer (DM-Oct30) (**b**)

When DS increases, the values of fluorescence depolarization decrease due to accentuated extension of the polymer chain as a result of enhanced electrostatic repulsions between charges on polymer (Fig. 2a).

For polymers with the same degree of substitution, the anisotropy increases with increase of polymer molecular weight (Fig. 2b). Thus, the highest anisotropy value is found for the polymer with the highest molecular weight (D465) despite of the relatively high polarity of the microdomains.

3.3. Viscosity Measurements

Viscosity studies provide the bulk macroscopic solution behavior, as a balance between electrostatic and hydrophobic forces, acting in aqueous solutions of amphiphilic polymers.

DS, molecular weight and polysaccharide's nature are between the factors that influence the reduced viscosity in aqueous solutions [6, 10 - 15].

The amphiphilic cationic polymers present an upturn of viscosity at very low C_p due to the predominance of electrostatic repulsions over hydrophobic attractions. Tendency is much pronounced for polymers with a high DS due to an elevated charge density which increases electrostatic repulsions (polyelectrolyte behaviour) (Fig. 3a, b, c).

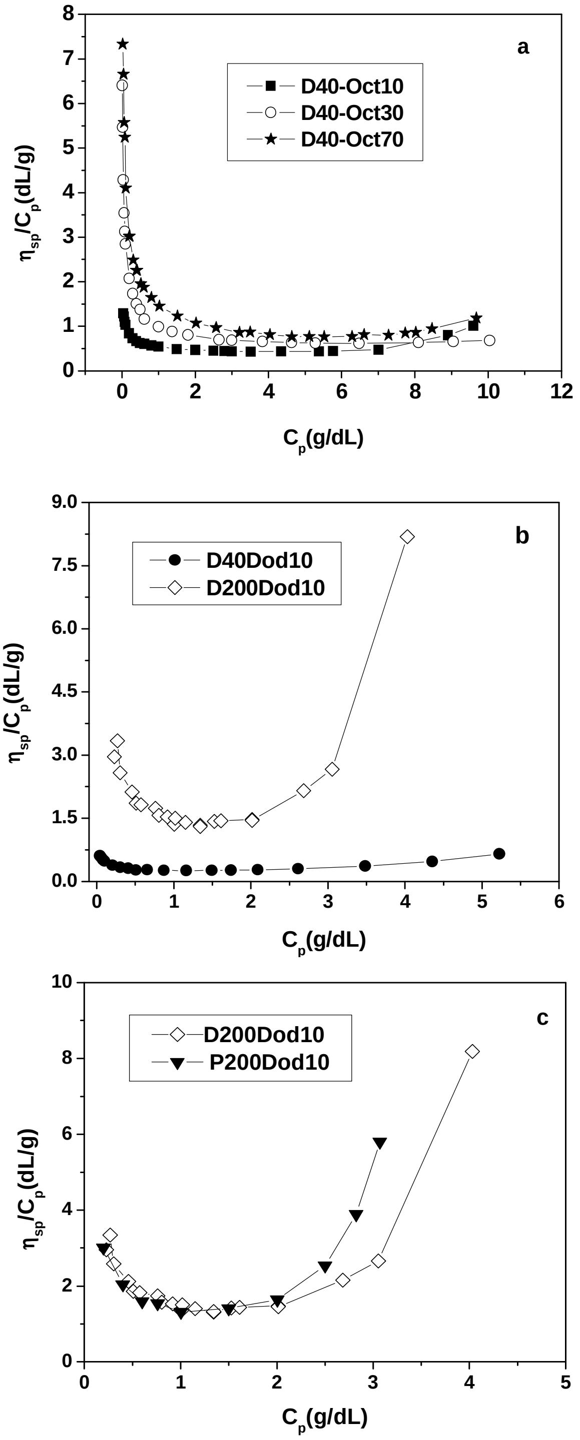


Fig. 3a, b, c. Variation of reduced viscosity as a function of DS (D40-OctX) (**a**), molecular weight of the polymer (DM-Dod10) (**b**) and nature of polymer backbone (**c**)

For amphiphilic polymers, the values of reduced viscosity changes with the decrease of DS as a function of DS and the R length, due to the balance between hydrophobic associations and electrostatic repulsions.

Polymers, with high DS, show a low increase of reduced viscosity values with the increase of polymer concentration, owing to intramolecular hydrophobic interactions (Fig. 3a). At low DS and longer R (dodecyl and cetyl) there is a sharp increase of η_{sp}/C_P with the increase of C_P as a result of the intermolecular hydrophobic associations (Fig. 3b).

The reduced viscosity rises with the augmentation of C_P when M_w or polysaccharide flexibility increases. For polymers, having R = dodecyl (DS = 10 mol%), η_{sp}/C_P values sharply increase for $C_P > 2$ g/dL, thanks to the favorisation of intermolecular hydrophobic associations by increasing M_w and flexibility (Fig. 3b, c).

4. Conclusions

Self-aggregation process of amphiphilic polyelectrolytes is studied using steady-state fluorescence, fluorescence anisotropy and viscosity measurements.

DS, molecular weight and nature of polysaccharide are among the factors that influence the self-aggregation process.

CAC values decrease with the increase of the R length. The molecular weight and the nature of the polysaccharide have a reduced influence on *CAC* values.

Higher NPN anisotropy values are obtained for higher molecular weight and lower values of the DS.

High values of the reduced viscosity with increasing C_P are characteristic for polymers with low DS and high M_w or backbone's flexibility.

REFERENCES

1. Winnik F. M. and Regismond S. S. T., *Colloids Surf.*, A, 118, **1996**, 1-39.
2. Capek, I. *Adv. Colloid Interface Sci.*, 97, **2002**, 91-149.
3. Nichifor M.; Lopes A.; Carpov A. and Melo E., *Macromolecules*, 32, **1999**, 7078-7085.
4. Bataille, I., Huguet J., Muller G., Mocanu G and Carpov A., *Int. J. Biol. Macromol.*, 20, **1997**, 179-191.
5. Nichifor M., Bastos M., Lopes S. and Lopes A., *J. Phys. Chem. B*, 112, **2008**, 15554–15561.
6. Nichifor M., Lopes S., Bastos M. and Lopes A., *J. Phys. Chem. B*, 108, **2004**, 16463-16472.
7. Nichifor M., Zhu X. X., Cristea D. and Carpov A., *J. Phys. Chem. B*, 105, **2001**, 2314-2321.
8. Lee K.Y., Jo, W.H., Kwon I.C. and Jeong S.Y., *Macromolecules*, 31, **1998**, 378-383.
9. Kim Y. H., Gihm S. H. and Park C. R., *Bioconjugate Chem.*, 12, **2001**, 932-938.
10. Tiera M.J., de Oliviera Tiera V.A., de Toledo E.C. and de Sena G.L., *Colloid Polym. Sci.*, 278, **2000**,1052-1060.
11. Mocanu G., Carpov A., Chapelle S., Merle L. and Muller G., *Can. J. Chem.*, 73, **1995**, 1933-1940.
12. Mizusaki M., Morishima Y. and Winnik F.M., *Macromolecules*, 32, **1999**, 4317-4326.
13. Lauten R.A., Marstokk O., Kjøniksen A-L. and Nyström B., *Polym. Bull.*, 49, **2002**, 281-288.
14. Magny B., Iliopoulos I. and Audebert R. in: Dubin P., Bock J., Davies R.M., Schulz D.N. and Thies C. (Eds.), Macromolecular Complexes in Chemistry and Biology, Springer-Verlag, Berlin, **1994**, 51-78.
15. Knudsen D.K., Lauten R.A., Kjøniksen A-L. and Nyström B., *Eur. Polym J.*, 40, **2004**, 721-733.

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