



Cationic cellulose and its interaction with chondroitin sulfate. Rheological properties of the polyelectrolyte complex



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ABSTRACT

This work describes the polyelectrolyte complexation between polyquaternium cellulose (PQ-10) and chondroitin 4-sulfate (C-4S), an important structural component of cartilages. The complex shows different behaviors with increasing concentrations of the polyanion. Initially, PQ-10/C-4S interaction forms a soluble, translucent hydrogel that reaches maximum viscosity at a sulfate carboxylate/quaternary ammonium molar ratio lower than 1. After that, the complex begins to aggregate until complete precipitation, and finally, at higher concentrations of C-4S, the resuspension of the aggregate is observed. Further addition of PQ-10 initiates new cycles of precipitation/resuspension for at least seven times.

C-4S contains sulfates and carboxylates able to interact with quaternary ammonium of PQ-10. The results of a comparative study with polymers containing only carboxylate or sulfate to evaluate the influence of each group suggest that the phenomena observed involved, essentially, carboxylate groups.

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1. Introduction

Polyelectrolyte complexes have been subject of thorough research during the last decades. These complexes have huge potential for many practical applications such as additives thickener, membranes with selective retention ability in multilayer assembly or as a model to study complex living systems in which biomacromolecules are ionically associated [1–5]. Their biocompatibility, biodegradability and natural availability are also particularly interesting in many subjects. An example of these involves polyelectrolyte complexes of chitosan with anionic

polymers such as dextran sulfate [6], polygalacturonic acid [7] or poly(acrylic acid) [8], chondroitin sulfate [9–11], hyaluronate [9], and alginate [12] which have been far characterized. These hydrogels exhibit pH responsiveness, especially important for developing “rheologically smart” fluids or carriers for the release of pharmacologically active compounds. Other polysaccharides such as polycationic celluloses have been studied to a lesser extend in combination with polyanions as carbopol [13] or with different glycosaminoglycans, mainly for personal care and medical applications [14,15].

It is known that the formation of polyelectrolyte complexes is governed by the characteristics of the individual components (e.g., properties and position of ionic sites, charge density, macromolecular chain rigidity) and of the chemical environment (e.g., solvent, ionic strength, pH and temperature). Usually, the formation of the complex is possible in a narrow pH range, especially when weak polyelectrolytes are used, and in a way similar to the cooperative binding process of biomacromolecules. This process does not occur with low-molecular-weight substances,

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suggesting that the cause of exchange reactions between oppositely charged polymers lies in the cooperative interaction of sufficiently long sequences of functional groups attached to a chain. The initial contact between two complementary macromolecules takes place at some point along the polymer chains. Further interaction proceeds between ionic groups adjacent to the recently formed links, since these groups are sufficiently close to each other. As a result of such a process, a zipped or double-stranded structure is formed. Previous studies conducted in our laboratory [16], mean field equations were applied to the simulated density profiles in order to assess the entropic contributions. It was found that these are the driving force for the phenomenon, which stems from the release of counterions from the double layers of the polyelectrolyte and the charged surface.

In view of this, the aim of this study is the characterization of the interaction between polyquaternium-10 (PQ-10), more specifically celquat SC-230, a polysaccharide of high molecular weight containing quaternary ammonium groups and having hydrophilicity, biocompatibility and mucoadhesivity [17–20], with oppositely charged polymer involved in the constitution of the intercellular matrix such as chondroitin sulfate (C-4S). The C-4S polymer is a sulfated and carboxylated glycosaminoglycan (GAG) composed of a chain of alternating sugars (N-acetylglucosamine and glucuronic acid). It is a major component of cartilage, usually attached to proteins as part of a proteoglycan. The tightly packed and highly charged sulfate groups of chondroitin sulfate generate electrostatic repulsion that provides much of the resistance of cartilage to compression [21]. Loss of chondroitin sulfate from the cartilage is a major cause of osteoarthritis. Because C-4S has two kinds of negative groups able to interact with PQ-10 (sulfates and carboxylates), we also studied polymers containing only one, carboxylates (alginates) or sulfates (carrageenans), in order to evaluate the relative contribution of each anionic group to the interaction.

2. Materials and methods

2.1. Materials

High-viscosity cationic hydroxyethylcellulose, Polyquaternium-10 (PQ-10), also known as Celquat SC-230, was kindly provided by The National Starch and Chemical Co., (Bridgewater, NJ), MW 1.700 kDa. Chondroitin sulfate (C-4S) in the sodium salt formed was provided by BiotechLab S.R.L (MW 17 kDa). Protanal KF 200 S Potassium Alginate (ALG), with a relation of manuronic acid/guluronic acid (M/G) of 1.6, was supplied by Colorcon S.A. (MW 120 kDa). Carrageenan type I or *kappa* carrageenan (CAR κ), carrageenan type II or *iota* carrageenan (CAR ι), carrageenan type IV or *lambda* carrageenan (CAR λ) were supplied by SIGMA (MW 300–400 kDa). All these polymers were used as received with no further purification. All other reagents were of analytical grade.

Purified water by reverse osmosis (MilliQ[®], Millipore Spain) with resistivity >1.82 M Ω cm was used.

2.2. Preparation of cationic cellulose/polyanion complexes

2.2.1. Dilute dispersions

Samples were prepared by addition of increasing concentrations of water solutions of each polyanion (C-4S from 0% to 0.8%, ALG from 0% to 0.17%, or CAR κ , ι , λ from 0% to 0.33% w/v) into 0.2% w/v of PQ-10 solutions vigorously shaken. Finally, the system was left to stand for 24 h at 4 °C. The pH of the resultants solutions were between 6.5 and 7.

The zero shear viscosities (η°) of these mixtures were obtained from shear rate curve dependence of the viscosity using a rheometer and through concentrated dispersions explained in the paragraph below. These samples were characterized by FTIR, zeta potential, particle size, microscopic and turbidity measurements.

2.2.2. Concentrated dispersions

Similarly, complex of 1% w/v PQ-10 with C-4S, ALG, or CAR ι at 1:0.5, 1:1.5 and 1:5.5 sulfate carboxylate/ammonium group molar ratios was prepared.

The rheological behavior of these samples was evaluated in triplicate at 25 °C in a Physica Rheometer Rheo-plus/32, Anton Paar, Sanico equipped with an AR2500 data analyzer, fitted with a Peltier temperature control. A 5 cm cone-plate measuring geometry was used. Oscillatory shear responses (G' or storage modulus, and G'' or loss modulus) were determined at 0.1 Pa over the frequency range of 0.1–100 rad s⁻¹. The test conditions were within the linearity range of the viscoelastic properties.

2.3. Estimation of the quaternary ammonium groups of PQ-10

The quaternary ammonium groups in the PQ-10 were inferred from the determination of chloride through *Standard Method for the examination of water and wastewater 4500-Cl B, Ed. 19* by the quantification of PQ-10 chloride groups.

2.4. FTIR measurements

IR Spectra were recorded at ambient temperature on a Shimadzu FTIR spectrometer using an accumulation of 16 runs in each sample in the diffuse-reflectance mode.

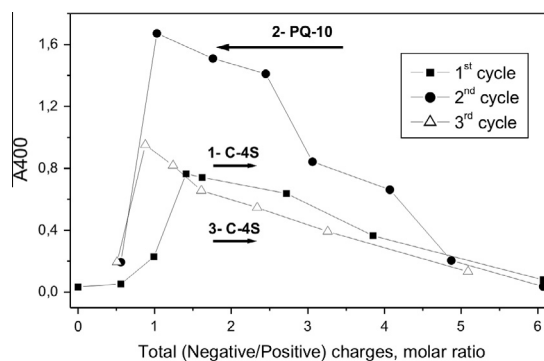


Fig. 1. Turbidity measurements at 400 nm of PQ-10/C-4S complex at different charge molar ratio. 1st and 3rd cycle: constant PQ-10 and increasing C-4S; 2nd cycle: constant C-4S and increasing PQ-10.

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