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Intrinsic viscosity and conformational parameters of xanthan in aqueous solutions: Salt addition effect

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ABSTRACT

The intrinsic viscosity and conformational parameters of xanthan in aqueous solutions were investigated at 25 °C as a function of salt nature (NaCl and KCl) and concentration (up to 3×10^{-1} mol/L). The viscometric parameters were evaluated by applying semi-empirical equations proposed by Rao and Wolf. The results show that the new model proposed by Wolf provides accurate intrinsic viscosity values comparable with those obtained by using traditional methods. The experimental data were modeled with Boltzmann sigmoidal equation. The stiffness parameter, hydrodynamic volume and viscometric expansion factor were determined and discussed. With increasing salt concentration, the hydrodynamic volume and the viscometric expansion factor decrease and the critical overlap concentration increases, reaching limiting values above a given salt concentration. The high Huggins constant values suggest the existence of aggregates for salt concentrations above 5×10^{-2} and 3×10^{-3} mol/L for NaCl and KCl, respectively. Stiffness parameter was determined by Smidsrød and Haug method as being 5.45×10^{-3}, indicating a rigid conformation for xanthan macromolecules in solution.

1. Introduction

Polysaccharides are macromolecular compounds with a large variety of structures and chain conformations in solutions, such as coils, semi-flexible chains, stiff chains and helical chains (single, double and triple helical chains) which provide remarkable physicochemical and biological properties (biocompatibility, biodegradability and bioadhesivity) [1–3]. Among them, xanthan is one of the most intensively studied polysaccharides due to its unique properties, i.e., good solubility in hot or cold water, capability to give highly viscous solutions even at very low concentrations, stability over a wide range of temperatures and pHs, ability to modify the surface activity, the rheological properties of the system in which is added, etc. [4]. This heteropolysaccharide of microbial origin produced by the bacterium *Xanthomonas campestris* plays an important role in different food [5,6] and non-food industries (paints and inks, ceramics, pharmaceuticals, pulp and paper, textile, cosmetics, wastewater treatment, oil recovery) [7–9]. In these uses, xanthan is employed as solution, gel, suspension or emulsion. Due to its structure, it can generate different types of interactions (self-interaction or with other macromolecules or low molecules) and hence, nano- and microstructures [10–12].

It has been shown that the primary structure of xanthan consists of a linear main chain of β-(1–4)-D-glucose substituted at every C_3 second glucose residues by charged trisaccharide side chain namely a D-glucuronic acid unit between two D-mannose units. One D-mannose unit is linked to the main chain and contains an acetyl group at position O_6 and the other one contains a pyruvic acid residue linked via keto group to the 4 and 6 positions [5] (Fig. 1); content of pyruvyl groups ranging from a few fractions to 1. Each side chain carried one carboxyl group from the β-D-glucuronic acid unit. The secondary structure of xanthan of double-helix is dependent on temperature and salinity conditions [13–15].

In distilled water, at room temperature, the backbone is disordered and highly extended due to the electrostatic repulsions exhibited between charged groups that belong to the side chains. The high extended structure favors the hydrogen bonding and a randomly broken helix is formed. As the temperature increases, a transition to coil conformation occurs; the macromolecules are dissociated and, as a consequence, rheological properties are changed [16]. At 25 °C, in the presence of salts, the side chains collapse down onto the backbone due to charge screening effects and a disorder–order transition take place when the xanthan chains tend to adopt a stabile helical conformation.

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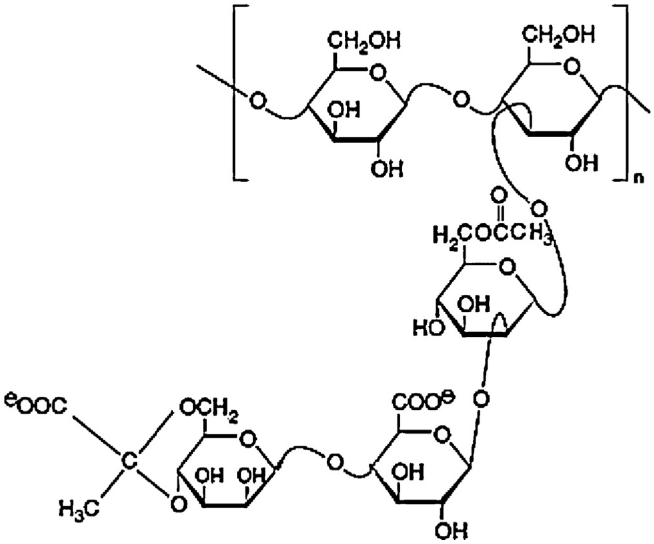

Fig. 1. Primary structure of xanthan.

Paradossi and Brant [17] suggested that interactions between the trisaccharide side chains and backbone might cause a greater conformational constraint in xanthan as compared to other highly substituted cellulose.

Norton et al. [18] have found that the ordered conformation of xanthan in aqueous solutions occurs in the presence of 3.5×10^{-2} mol/L NaCl. Based on optical rotation studies, Muller et al. [19] have shown that a sharp conformational transition occurs in salted solutions of 1×10^{-2} mol/L NaCl; the macromolecular chains of xanthan in 2×10^{-3} mol/L NaCl solution are partially ordered and in 4×10^{-2} mol/L NaCl solution are completely ordered. Rochefort and Middleman [16] considered for a single chain the coexistence of ordered and disordered regions up to 1×10^{-2} mol/L NaCl and above this salt concentration the conformation is completely ordered. Also, they pointed out that the secondary structure of xanthan depends on the sample characteristics, the treatment during and after fermentation [19], solvent, salinity and temperature [13,14].

In comparison with other polysaccharides, xanthan is quite rigid. Tinland and Rinaudo [20] discussed the chain rigidity and they found analogies between the conformations of xanthan with DNA. As it was mentioned above, the presence of ionizable groups located to the trisaccharide side chains, which dissociate in polar solvents, can seriously affect the solution properties of xanthan and the thermodynamic investigation of xanthan in solution has to be done very carefully. The most used method to assess the behavior of polymer in dilute solutions is the viscometry. For polyelectrolytes, the interpretation of the experimental viscometric data requires adequate evaluation methods due to their limits in application. Starting from the realistic assumption that viscosity of dilute solutions constitutes a function of state, Wolf [21] developed a new approach which is able to describe the evolution of the viscosity as a function of polymer concentration. During last years, this model has been applied successfully for salt-free aqueous solutions of poly(*N*-butyl-4-vinylpyridinium bromide) with different quaternization degree [21], aqueous and salted solutions of sodium polystyrene sulfonate [22,23], peripherically charged dendronized poly(methyl methacrylate) [24], carboxymethyl guar [25], cationic polyelectrolytes based on dextran in salt-free or salted aqueous solutions [26], chitosan in solvents with different ionic strength [27] and anionic polysaccharides in the presence or absence of extra salt [28]. In addition, accurate values of the intrinsic viscosity were reported for neutral polymers in solution: poly(vinyl alcohol) in water [29], polyacrylonitrile [30,31] and its mixtures with poly[*N*-(4-carboxyphenyl)-maleimide] [32] in dimethylformamide, for (co)polymers in good solvents [33,34] and in solvent mixtures [35,36].

In this paper, we apply the Wolf model to investigate the viscometric behavior of dilute aqueous xanthan solutions in the presence/absence of monovalent salts, NaCl and KCl. The chain conformation and excluded volume effect are discussed as a function of counterion nature and salt concentration. One motivating factor behind this study is a better understanding of xanthan behavior in water and in the presence of monovalent extra salt. The Wolf approach is adequate to explain how the chain conformation and the solution viscosity are influenced by polymer and salt concentration. On the other hand, the knowledge of the dependence between chain flexibility for this polysaccharide and the type and salt concentrations is of high interest in practical applications.

2. Materials and methods

2.1. Materials

Commercial xanthan was supplied by Sigma-Aldrich as powder and was used as-received without further purification. The viscometric molecular weight of xanthan sample, $M_v = 1.165 \times 10^6$ g/mol, was evaluated by means of the relationship proposed by Milas et al. [37]:

$$[\eta] = 1.7 \times 10^{-6} M_v^{1.14}\,(\mathrm{dL/g}) \qquad (1)$$

The intrinsic viscosity, $[\eta]$, of xanthan in 1×10^{-1} mol/L NaCl solution at 25 °C was determined as being 13.99 dL/g (Table 1) by using Rao method [38] which will be discussed in Section 3.1.

Inorganic monovalent salts (NaCl and KCl) purchased from Sigma-Aldrich were used as-received.

2.2. Preparation of xanthan solutions

Highly purified deionized water obtained from a Mili-Q PF (Millipore, Switzerland) apparatus was used for the solutions preparation. The concentrated stock solution of xanthan in water was prepared by dispersing dry polymer in water and its dissolution under magnetic stirring at room temperature (for 4 h). Salted xanthan solutions were prepared by mixing of concentrated stock solutions of xanthan with those of salt as to achieve the desired concentrations. In order to prevent degradation of xanthan macromolecules, the homogeneous solutions were kept overnight at 5 °C in the refrigerator and thermostated at 25 °C before the viscometric measurements.

2.3. Viscosity measurements

The viscometric measurements of dilute polymer solutions were carried out at 25 °C (±0.01 °C) using an Ubbelohde capillary viscometer for dilution sequences of type I (Schott-Geräte) and capillary diameter of 0.63 mm in combination with an automatic viscosity measurement system (LAUDA LMV 830 Instrument). Flow time for each solution was measured at least five times, until the errors in its determination were lower than 0.1 s.

3. Results and discussion

3.1. Intrinsic viscosity of xanthan solutions in water and in the presence of salts

Viscometry is one of the most used methods and appropriate to explore the behavior of polymer chains in solution. The