Atypical Viscosity Behavior of Dilute Solutions of Xanthan Gum

INTRODUCTION

Xanthan gum (which will be referred to as xanthan) is an anionic polysaccharide produced by *Xanthomonas campestris*. This branched polymer, produced by fermentation, has a pentasaccharide repeat unit, as shown in Figure 1. The polymer chain is poly[β-(1 → 4)-D-glucose], with the side chain β-D-mannopyranosyl-(1 → 4)-α-D-glucuropyranosyl(1 → 2)-β-D-mannopyranoside 6-O-acetate, linked to alternating glucose residues via a (1 → 3) linkage. About 25–50% of the terminal mannose residues are substituted with a pyruvic acid moiety linked via the 4- and 6-positions. The object of this note is to describe the unusual viscosity behavior of dilute xanthan solutions.

EXPERIMENTAL

The xanthan gum sample, Keltrol (Kelco Co.), had a weight-average molecular weight of 1.75×10^6, which was determined by the Mark–Houwink equation $[\eta] = 1.18 \times 10^{-4} M^{0.85}$.[1] Carboxymethylcellulose (type 7M, Hercules Inc.) had a molecular weight of 3.0×10^5, as determined by intrinsic viscosity.[2] Solutions were prepared by stirring at room temperature with a magnetic stirrer for 24 hr. Complete dissolution was established by following the intrinsic viscosity of the solution. Moisture was determined by drying to constant weight at 105°C. The viscosity data were obtained with Ubbelohde viscometers at 25°C. No shear correction was made.

RESULTS AND DISCUSSION

Dilute solution properties of xanthan were compared to those of carboxymethylcellulose (CMC), a typical polyelectrolyte. Figure 2 is a plot of reduced viscosity (η_{sp}/c) as a function of polymer concentration for xanthan and CMC in water. For CMC, the reduced viscosity, and hence the hydrodynamic volume, increases dramatically as the polymer concentration is decreased. This phenomenon is typical for most polyelectrolytes.[3] The increase in the reduced viscosity for polyelectrolytes in water can be explained by the reduction in concentration of the closely associated counterion layer surrounding the polyelectrolyte. This causes decreased electrostatic shielding between fixed ionic sites on the polymer; the sites are, in this case, carboxyl groups. The polymer expands as a result, increasing the rigidity of the chain and thus its hydrodynamic volume. Also, there is increased solvation of the molecule which contributes to an increased hydrodynamic volume. Furthermore, because of fixed ionic charges on the polymer, intramolecular osmotic pressure also causes molecular expansion.
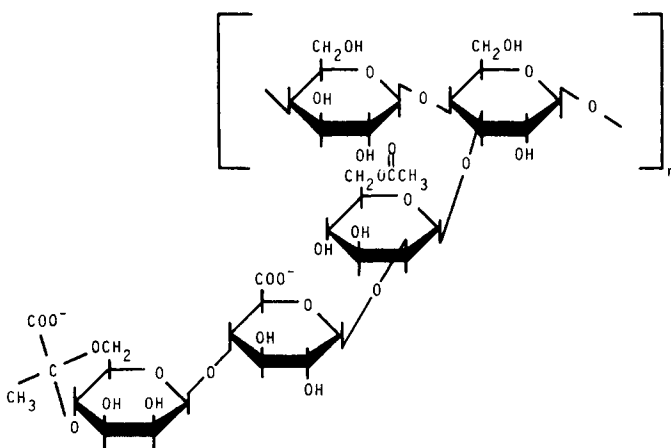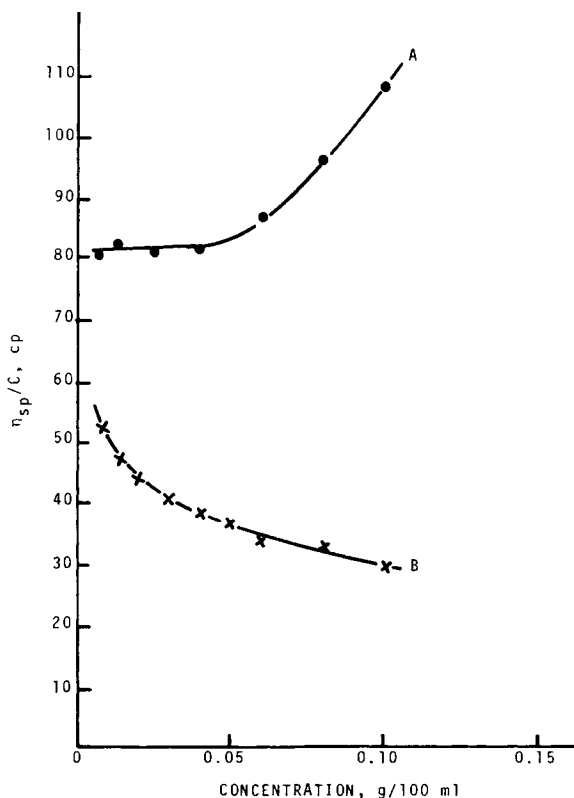

Fig. 1. Repeating unit of xanthan.

Fig. 2. Reduced viscosity (η_{sp}/c) as function of concentration for solutions of (A) xanthan and (B) carboxymethylcellulose in distilled deionized water at 25°C.

The reduced viscosity as a function of concentration is for xanthan, as seen in Figure 2, significantly different from that of CMC. The reduced viscosity drops as the polymer concentration decreases and then levels off; it is essentially constant, below 0.04% (w/v). The constant value of the reduced viscosity at low polymer concentration is atypical of polyelectrolytes and was observed for several different lots of xanthan. Examination of the chemical structure of xanthan gum (Fig. 1) indicates that the highly branched polysaccharide has a relatively long (three saccharide units) and uniformly distributed oligosaccharide side chain. The large volume occupied by the sugar rings of both the backbone and the side chains and the physical constraints imposed by their size create steric factors which influence the conformational mobility of the macromolecule. Furthermore, these steric factors may mitigate the repulsive forces of the carboxyl groups. Analysis of these factors is compounded by the variable and random nature of the pyruvic acid substitution on the terminal mannose residue.

Our results suggest that the shape of the reduced viscosity curve for xanthan in water, which is unlike that of typical polyelectrolytes, may be due to a combination of electrostatic forces, chain conformation, and molecular entanglement. The observed decrease in the reduced viscosity with decreasing polymer concentration may be caused by a decrease in intermolecular interactions related to entanglement. Xanthan is known to be highly entangled in solution. It has been reported that entanglements occur when a xanthan concentration exceeds 0.04%.[4,5] This is the point at which the reduced viscosity levels off. Below this value, there are essentially no entanglements between molecules and electrostatic forces predominate. Owing to the rodlike conformation[6] of the polymer and the position of the carboxyl groups on the pendant side chains, the repulsive forces between the anionic groups are apparently unable to affect the backbone conformation significantly. Other water-soluble polymers, such as CMC, are more flexible, and the electrostatic forces result in chain expansion. Thus, the hydrodynamic volume of xanthan does not undergo the dramatic increase observed for other polyelectrolytes under these conditions.
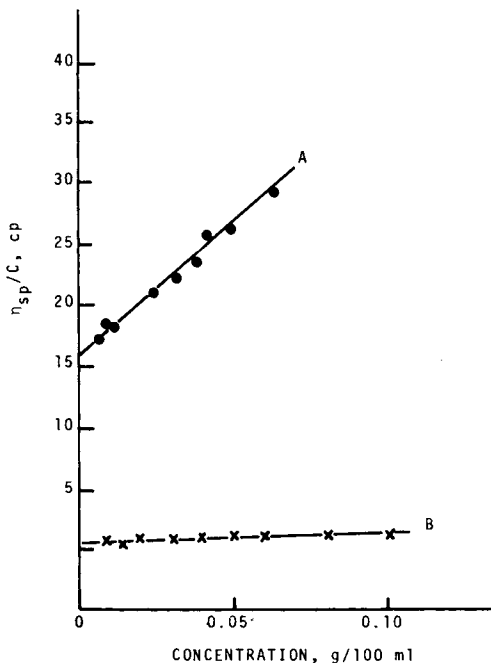
Fig. 3. Reduced viscosity (η_{sp}/c) as function of concentration for solutions of (A) xanthan and (B) carboxymethylcellulose in $0.06M$ sodium acetate at 25°C.

With added electrolyte, the reduced viscosity of xanthan as a function of polymer concentration is linear and, as shown in Figure 3, obeys the Huggins equation, as does CMC. Electrolytes added to polyelectrolyte solutions (1) reduce electrostatic repulsive forces by shielding ionic groups, (2) decrease the thickness of the counterion layer, and (3) diminish intramolecular osmotic forces. As a result, the hydrodynamic volume of the polymer is reduced. The resulting η_{sp}/c-vs.-polymer concentration plots are similar to those of nonionic polymers and obey the Huggins equation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

The Huggins slope constant (k') for xanthan is 0.52, as compared to 0.23 for CMC. The higher slope constant exhibited by xanthan is indicative of increased polymer–polymer interactions caused possibly by either chain entanglement or aggregation.[7]

References

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