THE VISCOSITY AND MOLECULAR CONFORMATION OF GALACTOMANNANS IN SOLUTION

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To Sharyn.

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Abstract

Two galactomannans, from the seeds of Guar (Cyanopsis tetragonoloba) and Carob (Ceretonia siliqua) also known as Locust Bean, have found widespread use as industrial hydrocolloids. Many other galactomannans have been isolated from legume seeds, but so far none have been widely employed in industry.

Measurements of the viscosity of the solutions of some of these latter galactomannans (from Red Clover, Lucerne, Lotus pedunculatus, Sophora japonica, and Soybean) were made along with solutions of Guar and Carob galactomannans. A wide range of viscosities was found for the various samples, with the viscosity of Guar and Carob galactomannan solutions being the highest.

The effects of shear rate, temperature, and galactomannan concentration on the solution viscosities were examined. The measured viscosity changes correlated well with Schutz's (1970) empirical equations explaining the viscous solution behaviour of pseudoplastic carbohydrates (including Guar galactomannan). The effects on viscosity of two common industrial additives, sucrose and sodium chloride, were also examined, and interpreted in terms of a dehydration mechanism.

In order to explain the viscosity results, the galactomannan molecular weights were determined by measuring their sedimentation and diffusion coefficients in an Analytical Ultracentrifuge. Their molecular weight distributions were obtained both from their Schlieren sedimentation diagrams using the method of Gralen and Langermalm (1952), and from the ratio of their apparent diffusion coefficients to their weight-average diffusion coefficients (Henley, 1962).

The dependence of galactomannan intrinsic viscosities, sedimentation coefficients, and diffusion coefficients on molecular weight (weight-weight average and sedimentation-diffusion average) was

examined, and a good linear correlation obtained in each case, with two exceptions. Lucerne galactomannan had a very wide distribution of molecular weights. The galactomannan from Lotus pedunculatus II was thought to differ slightly in structure from the other galactomannans due to its high substitution ratio of one galactose sidechain for every mannose in the molecular backbone which changed the conformation of the mannose backbone.

The dependence of the galactomannan intrinsic viscosities, sedimentation coefficients and weight-average diffusion coefficients on the weight-weight average degree of polymerisation and/or the weight-weight average molecular weight was examined in the light of recent hydrodynamic theories. By use of the theories of Debye, Beuche and Brinkman; Kirkwood and Riseman; Kuhn and Kuhn; Peterlin; and Flory, Fox and Mandelkern it was deduced that the galactomannan molecule approximates to a random coil in solution. The molecule is highly extended, and the presence of the galactose sidechains alters its draining characteristics, making its solution behaviour deviate from that expected from the theories.

Comparison of galactomannan solution behaviour with that of two soluble cellulose ethers, ethylhydroxyethyl cellulose (Manley, 1956) and hydroxyethyl cellulose (Brown, 1962) shows many similarities.

It was concluded that galactomannans in solution can be treated as a linear polymer series provided that the galactose : mannose ratio is not less than 1 : 5 or more than 1 : 1.1, and also that their molecular weight distributions are very similar. This implies that other galactomannans could be used industrially instead of those of Guar and Carob, provided some problems of yields and solubility could be surmounted.

It was also concluded that galactomannans in aqueous solution have

conformations very similar to water-soluble cellulose derivatives. Similarities between mannans and cellulose have already been proved in the solid state.

Preface

This work was originally intended to be a comparison of the viscosity of various galactomannan solutions with that of some of their derivatives (e.g. sulphates).

The purpose of this was to determine whether the derivatives had more desirable properties from an industrial viewpoint than the original galactomannans, especially with regard to viscosity. The idea for this came from the large number of water-soluble cellulose derivates that are used industrially.

For the above work, as simple a picture as possible of viscosity was required, and this led to the neglecting of shear rate in the measurement of the variation of galactomannan viscosity with temperature and concentration.

After these first measurements had been carried out, it was realised that galactomannan solution viscosities were much more complex than had previously been imagined. Accordingly, the original aim of this project was altered, and more complete measurements of viscosity (including shear rate effects) and galactomannan molecular parameters in solution were made, to provide a basis for any future work on galactomannan derivatives.

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