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Investigation of equilibrium solubility of a carob galactomannan

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Abstract

The equilibrium aqueous solubility of a commercial carob flour was investigated by determining the percentage of soluble and insoluble components as a function of dissolution temperature. The cumulative polysaccharide yield was ca. 50% at 5 °C, increasing approximately as a linear function of temperature to ca. 90% at 85 °C. Overall molecular weight and intrinsic viscosity of the soluble polysaccharide were determined by size-exclusion chromatography. With increasing dissolution temperature, there was weak trend towards higher overall molecular weight and intrinsic viscosity: M_w from 1060 to 1150 kg/mol, and $[\eta]$ from 11.8 to 12.5 dl/g, between 5 and 65 °C, respectively. Broad, amorphous peaks were evident in the wide-angle X-ray scattering profiles, indicating no role for polysaccharide melting. The continuous increase of molecular weight and decrease of DS_{gal} with dissolution temperature is interpreted as the result of thermodynamic partitioning based on a classical polymer-solvent fractionation, a mechanism that applies only for polysaccharide components with $DS_{gal} < 0.35$ within the accessible temperature range.

Keywords: Locust bean gum; Carob; Galactomannan; Phase behavior; Fractionation

1. Introduction

Carob galactomannans are nonionic, linear polysaccharides used as thickeners/stabilizers, co-gellants, and fat replacers in ice creams, sauces, and other food products. The functional polysaccharide is a poly((1–4)-β-D-mannose) having degree of polymerization ~1000, with a statistical distribution of single-unit (1–6)-α-D-galactose side groups. This polysaccharide is present as enlarged deposits present in the endosperm of mature carob (locust bean) seeds, and are borne in the tree's fruit. The seeds are industrially processed by hull cracking, sifting, and milling operations to isolate and grind the endosperms, which are then sold as a crude flour. Commercially sold flours are reported to contain about 85% pure galactomannan on a mass basis and make an important contribution to the hydrocolloid usage in many food products. Locust bean gum is regarded as essential for providing 'texture' (thus far poorly understood) to premium ice creams for instance. Several reviews are available (Ross-Murphy, 1995; Scherbukhin & Anulov, 1999; Srivastava & Kapoor, 2005).

One of the most important characteristics of the molecular structure of the galactomannan polysaccharide family is the galactose substituents, quantified as an average degree of substitution, DS_{Gal}. Without these groups present in some concentration the isolated polysaccharide is unstable in solution and either crystallizes or precipitates. Galactomannans with DS_{Gal} generally above 0.4 such as guar ($DS_{Gal} = 0.5$) or fenugreek ($DS_{Gal} = 0.9$) are regarded are soluble in dilute and semi-dilute solutions and thermodynamically stable (neglecting possible hydrolysis and bacterial degradation). Carob galactomannan (assumed as $DS_{Gal} = 0.2$–0.4) is generally regarded as partially soluble, and is reported to form weak gels after freeze–thaw treatment, in the presence of high concentrations of sucrose, or in "single-component" solutions when held near the freezing point of water (Richardson, Clark, Russell, Aymark, & Norton, 1999). This polysaccharide has additionally been studied intensively with respect to its role in altering the gel strength when mixed with

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K-carrageenan, often observed as a synergistic effect (Fernandes, Gonçalves, & Doublier, 1991).

The solubility behavior of the polysaccharide flour is itself of interest in some applications, since some of the polysaccharide components dissolve directly in cold water but full dissolution and full viscosity requires a high-temperature soak. It is well established from several studies that the poor solubility of carob flours in water can be used to fractionate the material using water as a solvent medium without extensive sample preparation. This is accomplished simply by dissolving the crude endosperm flour at a given temperature and separating soluble components by centrifugation. Redissolving the insoluble material at a higher temperature gives rise to the next fraction. From these studies it is observed that the chemical composition of the galactomannan, expressed as DS_{Gal}, is inversely related to the dissolution/fractionation temperature: the galactomannan dissolving with increasing temperature is observed to have progressively lower and lower galactose content. The relation between galactomannan chemical structure and this fractionation behavior has been characterized extensively (da Silva & Gonçalves, 1990; Fernandes, 1994; Fernandes et al., 1991; Gaisford, Harding, Mitchell, & Bradley, 1986; Garcia-Ochoa & Casas, 1992; Hui & Neukom, 1964; Mannion et al., 1992; McCleary, Clark, Dea, & Rees, 1985; Richardson et al., 1999) and was recently reviewed (Pollard & Fischer, 2006).

The goal of this study was to clarify the dissolution/extraction process, as obtained from a commercial endosperm flour, in a few key respects. First, we determined the relative partitioning of the components of the polysaccharide between the aqueous solvent phase and the swollen polysaccharide gel phase, by a gravimetric method. As a function of dissolution/extraction temperature, this measurement returns the cumulative yield of polysaccharide which can be correlated to the solution viscosity. Second, we assessed the relative contribution of dissolution kinetics towards the measurement of yield. Third, we examined the X-ray scattering profiles to confirm that the flour does not contain extensive crystallinity. Fourth, we characterized the molecular weight of the dissolved fractions as a function of dissolution/extraction temperature.

2. Materials and methods

2.1. Materials

In this study, commercially available flours were used: carob L-175, tara SP-175, guar GH-200 (all sold by Unipektin), and fenugreek (Fenupure 85, Adium Food Ingredients). The composition of L-175 is, according to product specifications, >75% galactomannan polysaccharide (min), 15% water (max), 4% crude fiber (max), 7% protein (max), and 1.2% ash (max). This flour's particle size distribution was reported as follows: <15% US Mesh 270 (< 53 μm), <40% US Mesh 200–270 (53–74 μm), >60% US Mesh 120–200 (74–125 μm), and <0.5% US Mesh 120 (>125 μm). Sieving (Fritsch) was used to separate the crude L-175 flour into three powder fractions: (1) retained by 100 μm mesh (denoted 100 μm); (2) retained by 43 μm mesh (denoted 43–100 μm); and (3) passing 43 μm mesh (denoted <43 μm).

2.2. Cumulative yield and solution viscosity measurement

Cumulative yield and viscosity measurements were obtained on the unmodified flour and powder fractions 1 and 3. The solubility curves were obtained by using a single-step dissolution procedure. The flour was added to rapidly stirring deionized water at a concentration of $C_{flour} \approx 0.5$ wt% (wet weight) and held for 2 h at the given temperature. Two hours was a compromise based on the need for experimental efficiency. It was later verified using estimates from GPC and yield measurements that full solubilization requires at least 24 h at 25 °C, but was about 85–90% complete on a mass basis after 2 h. The solubility protocol used here is therefore an approximation of the equilibrium solubility.

Insoluble residue (aqueous insoluble matter) containing cell wall material and undissolved polysaccharide was then removed by centrifugation at 40,000*g* for 10 min, decanted, dried, and then weighed. The soluble polysaccharide (aqueous soluble matter) was recovered from the supernatant by precipitation into two parts ethanol, which was then dried, and weighed. Yields of soluble and insoluble matter were obtained in this manner in 20° increments between 5 and 85 °C. Solubility curves are shown on a basis of the crude flour dry matter recovered as a function of temperature. During the experiments, it was found that errors were introduced by the precipitation procedure whenever the ethanol–water slurry was left unstirred, which lowered polysaccharide yield. This accounted for a larger error in total yield between the first data set (≈90%) and the remaining two (≈100%).

Flow curves were obtained using an ARES rheometer at 25 °C after soaking the carob flour for 2 h at the given dissolution temperature. Low-shear viscosities are reported as an approximation to zero-shear viscosity, obtained generally within the Newtonian region and at shear rates high enough to be above the minimum sensitivity of the torque transducer (i.e. no curve fitting was applied). Viscosities were thus obtained as a function of dissolution temperature and reported at a consistent reference temperature. The solutions were then centrifuged at 40,000*g* for 10 min to remove the insoluble residue, and the measurement was repeated.

2.3. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) profiles were obtained on a diffractometer (source Cu-K_α) at room temperature and humidity on four galactomannan flours: carob (L-175), tara (SP-175), guar (GH-200), and fenugreek