Carbohydrate Polymers 4 (1984) 153–157

Short Communication

The Effect of Pyruvate on Xanthan Solution Properties

In a recent issue of this Journal, Bradshaw *et al.* (1983) presented evidence to suggest that, contrary to reports by other workers, including ourselves, pyruvate substituents have no effect on the solution properties of xanthan. After critical evaluation of the results on which this conclusion is based, we believe that there is no real conflict of experimental evidence, and that the earlier conclusions are still valid.

The technological value and commercial success of xanthan are largely due to its 'weak gel' properties in solution, including specifically the ability to stabilise emulsions or hold particles in suspension over a long timescale (see, for example, Sandford & Laskin, 1977). This unusual solution behaviour is associated (Morris, 1977) with a rigid, ordered, molecular structure which can be 'melted out' only under conditions of extremely low salt and high temperature. Recently (Frangou *et al.*, 1982) it was shown that the 'weak gel' properties arise from non-covalent interactions between conformationally ordered chain segments, which can be weakened or eliminated by urea, without disruption of the ordered molecular structure.

The primary structure of xanthan (Jansson *et al.*, 1975; Melton *et al.*, 1976) is based on a cellulosic backbone with charge trisaccharide side chains attached to alternate β-D-glucosyl residues. The terminal mannosyl residue of each side chain may carry a pyruvate substituent linked as the 4,6-ketal, but the degree of substitution (x = fraction of side chains carrying pyruvate) varies widely between xanthan samples. Xanthans with a comparatively high level of pyruvate show greater thermal stability

Carbohydrate Polymers 0144-8617/84/$03.00 –

(Nisbet *et al.*, 1982) than samples of low pyruvate content, obtained either microbiologically or by chemical de-pyruvylation (Bradshaw *et al.*, 1983).

Sandford *et al.* (1977, 1978) examined the solution properties of a range of xanthans of different pyruvate content (obtained from different *Xanthomonas* substrains, or by ethanol fractionation of native xanthan) and concluded that 'high-pyruvate' xanthans are more viscous than 'low-pyruvate' samples, particularly in the presence of salt. More recently (Smith *et al.*, 1981) we reported a systematic study of the flow properties of xanthans of different pyruvate content as a function of shear rate ($\dot{\gamma}$), polymer concentration (c) and salt (KCl) concentration. Some results from that investigation are reproduced in Fig. 1. At low concentrations of polymer the viscosity of xanthan in water is higher than that in salt (0·1 M KCl), while at higher polymer concentrations

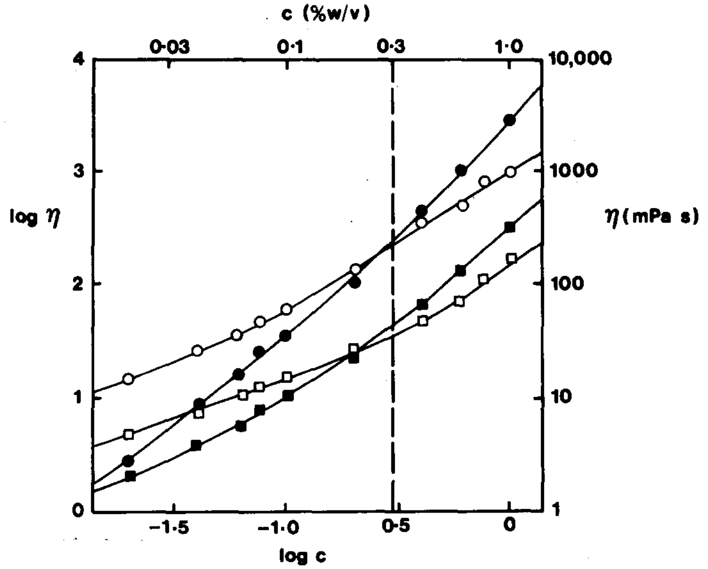

Fig. 1. Concentration dependence of viscosity (η; 25°C) for a typical sample of xanthan (degree of pyruvate substitution, $x = 0{\cdot}39$) in water (open symbols) and in 0·1 M KCl (filled symbols) measured at the same shear rates as were used by Bradshaw *et al.* (1983); $\dot{\gamma} = 10\ \mathrm{s}^{-1}$ (circles) and $\dot{\gamma} = 100\ \mathrm{s}^{-1}$ (squares). The polymer concentration (0·3% w/v) used by Bradshaw *et al.* is indicated (– – –). (Adapted from Smith *et al.* (1981), by permission of Butterworth & Co. (Publishers) Ltd.)

(above ~0·25% w/v) viscosity is enhanced by the presence of salt. For the samples which we studied (purified K^+ salts of commercial xanthans) the magnitude of this enhancement increased systematically with increasing pyruvate content above a minimum critical value of $x \simeq 0{\cdot}31$. One possible interpretation of this behaviour is that pyruvate substituents are specifically implicated in the intermolecular associations which give rise to the 'weak gel' properties of xanthan (Frangou *et al.*, 1982), perhaps by specific chelation of counterions between participating chains as has been demonstrated for a number of gelling polysaccharides (see for example Rees *et al.*, 1982).

In their recent paper, however, Bradshaw *et al.* (1983) have pointed out that in principle the microbiological variations that give rise to different degrees of pyruvate substitution may also lead to other, uncharacterised, structural modifications, and that it may be these accompanying changes, rather than pyruvate content as such, which affect solution behaviour. We accept the validity of this criticism, and congratulate Dr Sutherland and his colleagues on successfully overcoming the problem by development of a chemical technique for selective removal of pyruvate without significant chain cleavage. Using this technique, Bradshaw *et al.* (1983) examined the solution properties of a range of xanthan samples ($x = 0$–$0{\cdot}45$) derived from a single batch of starting material by removing different amounts of pyruvate, and found no significant variation either in solution viscosity or in sensitivity to salt.

Unfortunately, however, the polymer concentration used (0·3% w/v), was very close to the value at which we observed a 'cross-over' in viscosity between solutions of high and low ionic strength (Fig. 1), and thus on the basis of our evidence no appreciable change in viscosity would be expected. The results of Bradshaw *et al.* (1983) therefore do not conflict with our own: they neither test nor disprove our previous conclusion (Smith *et al.*, 1981) that at comparatively *high* concentrations of polymer (typically ~1% w/v) the solution viscosity of xanthans of high pyruvate content is significantly enhanced by salt (~4× at $\dot{\gamma} \simeq 5\ s^{-1}$), while that of 'low-pyruvate' xanthans is not.

A key experiment to resolve this issue would be to compare solution viscosity in water and in 0·1 M KCl for a xanthan sample of high pyruvate content ($x \gg 0{\cdot}31$) and a low-pyruvate sample ($x \ll 0{\cdot}31$) derived from it by the method of Bradshaw *et al.* (1983), using a polymer concentration of ~1% w/v in both cases. We have consulted Dr Sutherland on the possibility of carrying out such an experiment immediately, using materials prepared for the published investigation, but supplies of these samples have unfortunately been exhausted.

Until the necessary experimental work has been done, we suggest that pyruvate should still be regarded as an important determinant of the solution properties of xanthan, in addition to conferring thermal stability (Nisbet *et al.*, 1982).

We thank Dr I. W. Sutherland for helpful discussions.

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