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The Effect of Pyruvate on Viscosity Properties of Xanthan

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ABSTRACT

It is shown that the viscosity of concentrated (~ 1%) solutions of high-pyruvate xanthan in water is increased by the addition of salt. On decreasing the concentration of polymer to ~ 0·4% a cross-over in this behaviour is observed, i.e. addition of salt decreases the viscosity. In low-pyruvate xanthan samples the salt effect is greatly reduced, confirming the predictions of Smith et al.

1 INTRODUCTION

The rheological behaviour of solutions of xanthans varying in pyruvate content was studied by Sandford *et al.* (1977), who concluded that solution viscosity increases with increasing pyruvate content for 0·1% and 0·5% xanthan in 1% aqueous KCl. Thus high- and low-pyruvate xanthans behave differently, and this phenomenon warranted further study.

Smith *et al.* (1981) studied the influence of pyruvate on xanthan association in solution, and showed that the extent of association under given conditions of concentration, ionic strength, temperature and shear rate is related directly to the degree of pyruvate substitution. A rapid increase in the extent of macromolecular association with increasing ionic strength, only for xanthan samples substituted above ~ 0·31 degree of pyruvate substitution, was noted. This was taken as the rationale for the atypical increase in viscosity when salt is added to relatively concentrated [above 0·2%] solutions of xanthan.

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Subsequently, Bradshaw *et al.* (1983) claimed that removal of pyruvate (and acetate) did not affect the viscosity of 0·3% w/v xanthan solution in either water or 1% KCl solution. These authors argued on the basis of the above results that, in contrast to the earlier reports of Sandford *et al.* and Smith *et al.*, pyruvate and acetate levels had no effect on xanthan properties. Bradshaw *et al.* pointed out that the conclusions concerning the effect of pyruvate on xanthan solution viscosity were based on comparisons of xanthans from different culture batches or different *X. campestris* strains. They suggested that the results could be attributed to changes in polymer characteristics other than pyruvate and acetate levels, and that the assessment of the contribution of pyruvate groups to the viscosity could only be made when the xanthans were all derived from the same batch, e.g. by partial removal of pyruvate with 5 mM trifluoroacetic acid at 100°C.

In reply, Smith *et al.* (1984) showed that at the concentration of xanthan used by Bradshaw *et al.* (0·3%), differences between the viscosities of solutions of low and high ionic strength were slight. This was so because there was a 'cross-over' in viscosity between solutions of high and low ionic strength at about the 0·3% concentration level. Above a 0·3% concentration of polymer, addition of KCl considerably *enhanced* the viscosity of xanthan solutions, while below a 0·3% concentration, a decrease in viscosity was observed.

The results of Bradshaw *et al.* and Smith *et al.* were not incompatible, but merely inconclusive due to the choice of experimental conditions.

In order to clarify the situation, we have, as suggested by Smith *et al.* (1984), compared the viscosity of high- and low-pyruvate xanthan solutions in water and 0·1 M KCl, over a range of concentrations and shear rates. We conclude that pyruvate content does indeed affect the viscosity of xanthan solutions, in a manner similar to that proposed by Smith *et al.* (1981, 1984), Symes (1980) and Frangou *et al.* (1982).

2 EXPERIMENTAL

A Rheomat 115 (Contraves AG) rotational viscometer was used, with an MS-0 measuring system (20 ml volume, hollow concentric cylinder type), at shear rates of 2·4, 10·1 and 61 s^{-1}. Viscosity measurements were made over the concentrate range 0·05–1·0% w/v, in water and in 0·1 M KCl. Temperature was maintained at 28°C by a Haake circulating water-bath. The xanthan used (Keltrol, food grade, Kelco Division of Merck & Co.), was purified by the method of Holzwarth (1976) and converted to the potassium form. It was dissolved by allowing it to swell in water overnight, followed by stirring at 90°C for 30 min. Pyruvate-free xanthan was prepared by heating xanthan solutions (0·5% w/v) in 5 mM trifluoroacetic acid at 100°C for 90 min (Bradshaw *et al.*, 1983). Pyruvate in the native xanthan and in the TFA-treated sample was determined by HPLC (Cheetham & Punruckvong, 1985) and colorimetrically (Slonecker & Orentas, 1962).

3 RESULTS AND DISCUSSION

The native xanthan had a degree of pyruvate substitution, $x = 0{\cdot}5$ (x = fraction of side chains carrying pyruvate), while the TFA-treated sample had $x = 0{\cdot}1$. Solutions (~ 2% w/v) of the native and pyruvate-free xanthan were prepared in water, and diluted to 1% w/v with either distilled water, or 0·2 M KCl. The apparent viscosity η of each sample was determined at three rates of shear, over the concentration range 1·0–0·05%, the latter being the limit of sensitivity of the measuring system.

The $\log \eta$ versus log concentration curves for native xanthan are shown in Fig. 1. The samples in 0·1 M KCl all show enhanced viscosity relative to those in water alone, above a concentration of ~ 0·4%. Below this concentration, the 'cross-over' in viscosity noted by Smith *et al.* (1984) occurred. The enhancement in viscosity at 1% concentration (~ $2\frac{1}{2}$ fold) was not as marked as that observed by those authors (~ 4 fold).

The pyruvate-free sample ($x = 0{\cdot}1$) shows much smaller differences between viscosities in water and KCl (Fig. 2). The 'cross-over' is at ~ 0·1% although this is near the limit of accurate measurement with the MS-0 measuring system. Also the results show that $\Delta\eta$, the fractional change in viscosity resulting from addition of KCl, is small but positive above 0·1% concentration, even at low pyruvate level ($x = 0{\cdot}1$). Smith *et al.* (1981) found $\Delta\eta$ to be small but negative up to $x = 0{\cdot}31$, above which it increased rapidly with increasing pyruvate substitution. The differences in sign between $\Delta\eta$ values in the present results and those of Smith *et al.* are probably due to slight differences between the samples used, and/or to differences in the dissolving procedures. It has been shown (Cheetham & Punruckvong (1985)) that autoclaving removes substantial amounts of pyruvate, and some acetate. The present results were obtained from samples dissolved by the heat/stir method. The high-pyruvate sample in salt has a high viscosity partly because it is salt-stabilized ($T_m = 65$°C) in the rigid, ordered conformation, and partly because of the specific, nonpolar intermolecular interactions between pyruvate

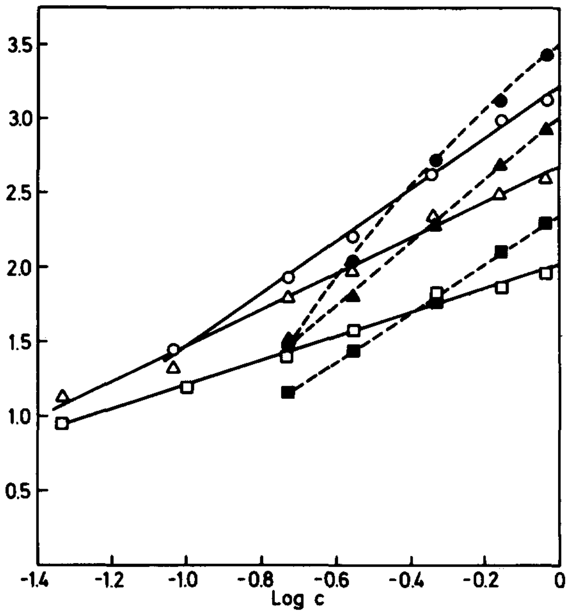

Fig. 1. Plots of log η versus log concentration of native xanthan in water (——) and in 0·1 M KCl (- - -) at rates of shear: 2·4 s^{-1} (○, ●), 10·1 s^{-1} (△, ▲) and 61 s^{-1} (□, ■).

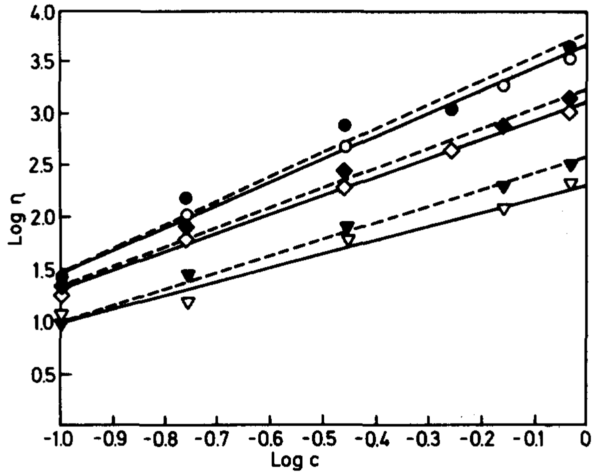

Fig. 2. Plots of log η versus log concentration of pyruvate-free xanthan in water (——) and in 0·1 M KCl (- - -) at rates of shear; 2·4 s^{-1} (○, ●), 10·1 s^{-1} (◇, ◆) and 61 s^{-1} (▽, ▼).

methyl groups (Smith *et al.*, 1981). As the concentration of polymer decreases, the viscosity falls as expected. The high pyruvate sample in water ($T_m = 42°C$) experiences no electrostatic shielding, and the ordered conformation is not stabilized by salt. The charged chains repel one another and the viscosity is less than that in salt. On dilution, polyelectrolyte expansion is relatively large and there is a consequent increase in viscous drag, which eventually (at 0·4% concentration) results in the viscosity in water exceeding that in salt.

For the pyruvate-free sample (which still has ~20% residual pyruvate) the effect of salt at high concentrations is far less than that experienced by the fully pyruvylated sample, there being fewer methyl groups for intermolecular association. The situation in water again involves no shielding, but lower pyruvate means less polyelectrolyte expansion. As the concentration of polymer is lowered, expansion occurs, but to a lower extent than in the high-pyruvate sample. The cross-over point with the sample in KCl occurs at lower concentration (~ 0·1%) than that of the fully pyruvylated sample (~ 0·4%).

Depending upon the ionic strength, the pyruvate substituent is implicated in both attractive and repulsive interactions between xanthan chains. The level of pyruvate affects the stability of the ordered conformation, high pyruvate levels being destabilizing, as shown by increases in T_m on progressive removal of pyruvate (Holzwarth & Ogletree, 1979).

Another contribution to intermolecular association between (ordered) xanthan chains appears to be hydrogen bonding. It was shown (Frangou *et al.*, 1982) that urea stabilized the ordered conformation of xanthan, but had the effect of causing both the dynamic and steady-shear properties to become typical of normal semi-dilute polymer solutions. This behaviour was attributed to disruption of noncovalent interactions, including hydrogen bonding, between conformationally ordered xanthan chains. It is proposed that those interactions, rather than the ordered structure as such, lead to the unusual rheological properties of xanthan solutions. Further study of the role of pyruvate (and acetate) levels on both inter- and intramolecular properties of xanthan is obviously warranted.

4 CONCLUSION

The results presented above confirm the observations of Smith *et al.* (1981), that concentrated solutions of xanthan highly substituted with pyruvate experience a significant viscosity increase on the addition of salt, while those of low pyruvate substitution do not.

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