Viscosity of aqueous glucomannan–borate complex solutions

Ryoichi Murakami and Yoshiaki Motozato
Department of Industrial Chemistry, Kumamoto Institute of Technology, Kumamoto 860, Japan
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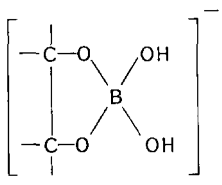
The viscosity of aqueous konjac glucomannan solution in the presence of borate ions was examined. The measurements were made on a rotational viscometer. The apparent viscosity of each sample was determined over the glucomannan concentration range of 0.09–0.45% w/v. In the concentration region above the critical concentration, 0.29% w/v, the viscosity was increased considerably by the presence of borate ions. This may be due to the creation of new interchain crosslinks, involving the formation of a 2:1 anionic complex (dicomplex). On the other hand, in the more dilute region the viscosity was almost independent of the presence of borate ions. In this region the formation of a 1:1 anionic complex (monocomplex) takes place predominantly and does not contribute effectively to the increase in viscosity.

(Keywords: glucomannan; borate complex; viscosity)

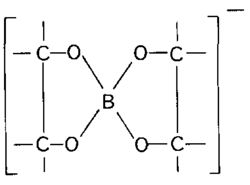
Introduction

The glucomannan from konjac is a polysaccharide consisting of $\beta(1\rightarrow4)$ linked D-glucose and $\beta(1\rightarrow4)$ linked D-mannose. Glucomannan contains hydroxyl groups in a favourable position to react with borate ions, that is, the hydroxyl groups of C2 and C3 of the D-mannose units are adjacent and in the *cis* configuration. The formation of complexes between the borate ion, $B(OH)_4^-$, and polyhydroxyl compounds is well established[1–4].

Diols with a *cis* configuration frequently form two types of complexes:



1:1 anionic complex



2:1 anionic complex

One is formed by splitting two molecules of water between a molecule of polyol and a borate ion, and the other is formed by removal of four molecules of water from two molecules of polyol and a borate ion[5]. In this study the viscosity behaviour of an aqueous glucomannan–borate complex solution was examined and the effect of complex formation on viscosity was discussed.

Experimental

The konjac flour treated with ethanol was dispersed in water and then dissolved by stirring at room temperature for 3 h. The supernatant fluid was used for the experiments after insoluble substances were removed by centrifugation. In this way, ~50% of the original konjac flour was removed. The supernatant can be considered as the fluid containing only glucomannan. In order to inhibit degradation by bacteria present, a few drops of aqueous azide solution were added.

Viscosity measurements were carried out at 25°C using a rotational viscometer (Tokimec B-type). For measurements of glucomannan aqueous solutions, the spindle used was a cylinder with a diameter of 18 mm and a length of 65 mm. The container used had a diameter of 40 mm and was 130 mm deep.

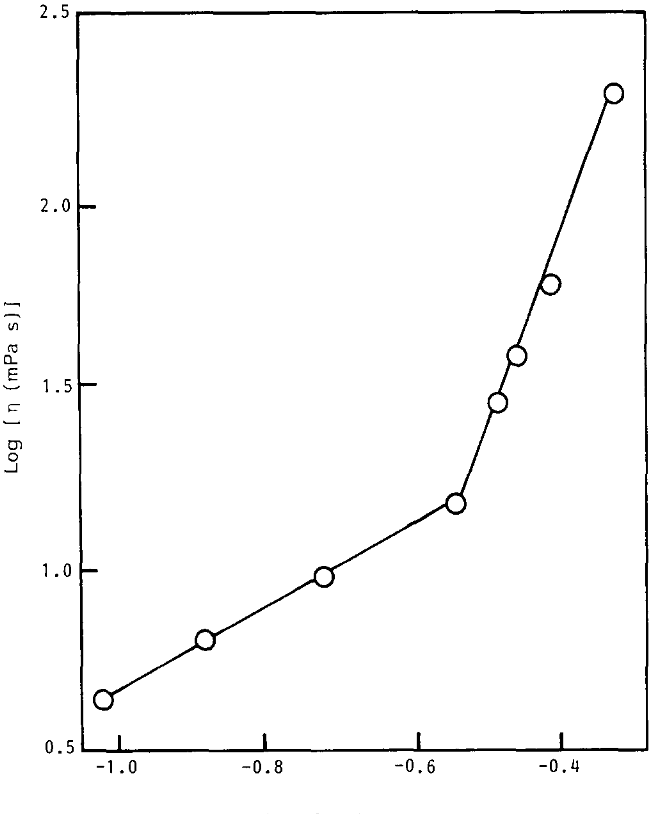


Figure 1 Plot of log η at 25°C (rotational speed 6 rev min^{-1}) *versus* the log of the concentration, C, of aqueous glucomannan solutions

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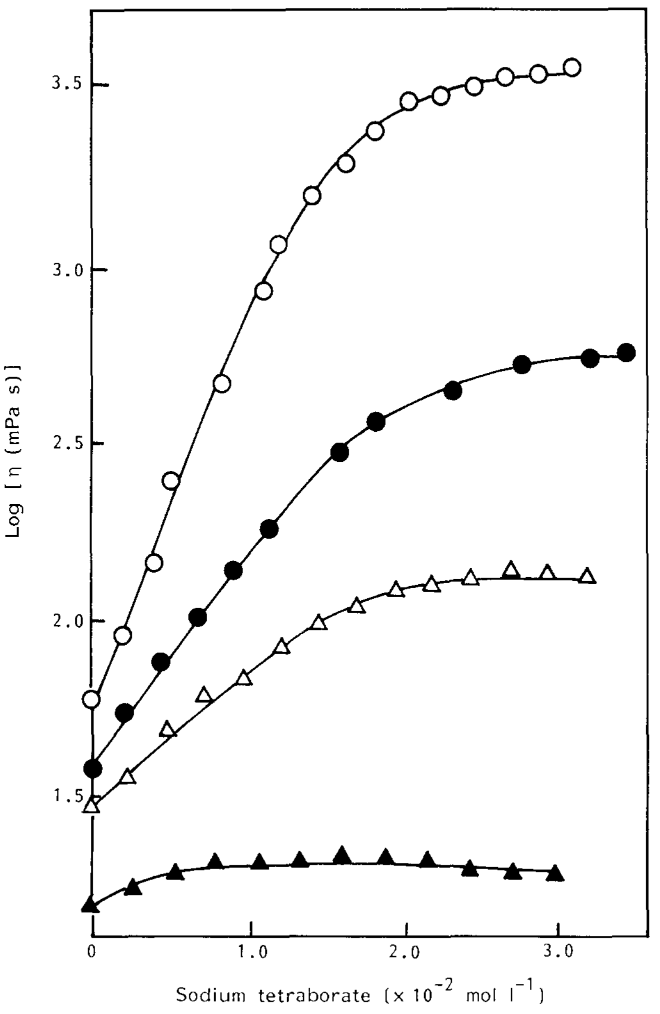

Figure 2 Effect of borate concentration on the viscosity of aqueous glucomannan–borate complex solutions at different glucomannan concentrations: (▲) 0.27% w/v; (△) 0.32% w/v; (●) 0.34% w/v; (○) 0.38% w/v

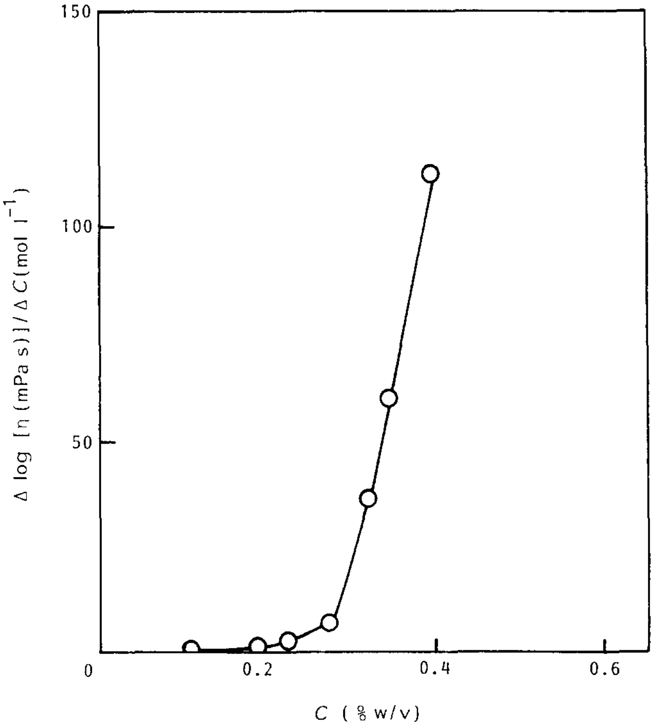

Figure 3 Relationship between the ratio of the increase of viscosity, $\Delta \log(\eta)/\Delta C$, due to the addition of borate and glucomannan concentration C

Results and discussion

The apparent viscosity η of each sample was determined at a rotational speed of 6 rev min^{-1} over the concentration range of 0.09–0.45% w/v. Within this concentration range, non-Newtonian behaviour of the viscosity of the glucomannan aqueous solution is comparably small. On the other hand, in aqueous glucomannan–borate complex solutions considerable non-Newtonian behaviour was observed. By plotting log η *versus* the log of the concentration of glucomannan solutions, two straight lines were obtained which correspond to the dilute and more concentrated regions with slopes of 1.2 and 5.0, respectively, the crosspoint being at a concentration of 0.29% w/v (*Figure 1*). The slope of 1.2 in the dilute region is nearly equal to that reported for different random coil linear polysaccharides in aqueous solution[6]. In this region the hydrodynamic units do not overlap. The slope of 5.0 obtained in the more concentrated region is higher than the values (3.3–3.7) observed for polysaccharide solutions showing purely physical entanglements[7]. In *Figure 2*, the viscosity of aqueous glucomannan–borate complex solutions with different glucomannan concentrations is plotted against sodium tetraborate concentration. At a low concentration (0.27% w/v), corresponding to the region with a slope of 1.2, the viscosity is almost independent of borate concentration and very close to that obtained for aqueous glucomannan solution in the absence of borate ions. On the other hand, at a concentration corresponding to the region with a slope of 5.0, the viscosity increases linearly with increasing borate concentration and levels off beyond borate concentrations of 2 × 10^{-2} mol l^{-1}. The degree of the increase in viscosity is closely related to glucomannan concentration. Plots of the values of the slopes in *Figure 2*, which show the degree of the increase in viscosity, *versus* glucomannan concentration are shown in *Figure 3*. Above the critical concentration (0.29% w/v) the degree of increase in viscosity changes linearly with glucomannan concentration. These results may be explained in the following way. In the dilute region with a slope of 1.2, a 1:1 anionic complex is formed mainly. The viscosity is not greatly affected by the formation of a 1:1 anionic complex. However, in the more concentrated region with a slope of 5.0, a 2:1 anionic complex is formed in preference to a 1:1 anionic complex and this creates new interchain crosslinks resulting in the increase in viscosity. These results lead to the conclusion that in the concentrated region above the critical concentration, which is related to the onset of significant coil overlap, new interchain crosslinks are created on addition of borate ions, involving the formation of a 2:1 anionic complex and causing an increase in viscosity.

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