

1        **Rheological properties of concentrated solutions of galactomannans in an ionic liquid**

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14        Key Words: galactomannan; molecular weight between entanglements; guar gum; tara gum;

15        locust bean gum; ionic liquid

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20 **Abstract**

21           The rheological behavior of galactomannans in concentrated solutions was examined by  
22 using dynamic viscoelasticity measurements. Concentrated solutions of three galactomannans,  
23 guar gum, tara gum, and locust bean gum were prepared with an ionic liquid  
24 1-butyl-3-methylimidazolium chloride as the solvent. Each galactomannan solution showed  
25 angular frequency dependence curves of the storage modulus and the loss modulus which were  
26 characteristic of a solution of entangled polymer chains. The molecular weight between  
27 entanglements ( $M_e$ ) was obtained from the plateau modulus and the concentration dependence  
28 of  $M_e$  showed  $M_e$  in the molten state ( $M_{e,melt}$ ) to be  $4.6 \times 10^3$ ,  $3.2 \times 10^3$ , and  $2.7 \times 10^3$  for guar gum,  
29 tara gum, and locust bean gum, respectively. It was found that the material constant  $M_{e,melt}$   
30 depends on the mannose/galactose ratio of the galactomannans. The number of monosaccharide  
31 units between entanglements in the molten state for the galactomannans varied within the range  
32 found for other polysaccharides such as cellulose and agarose in ionic liquids, suggesting that  
33 all the galactomannans take a random-coil conformation in ionic liquid solutions.

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36 **1. Introduction**

37 Galactomannans consist of a main chain of (1, 4)- $\beta$ -D-mannose as units and a side group of  
38 (1, 6)- $\alpha$ -linked D-galactose. Among them guar gum (g-gum), tara gum (t-gum) and locust bean  
39 gum (lb-gum) are specifically well-known. They differ in the mannose/galactose (m/g) ratio: ~2  
40 for g-gum, ~3 for t-gum, and ~4 for lb-gum (Sittikijyothin, Torres, & Goncalves, 2005; Wientjes,  
41 Duit, Jongschaap, & Mellema, 2000; Wu, Cui, Eskin, & Goff, 2009; Wu, Li, Cui, Eskin, & Goff,  
42 2012). The three galactomannans have been widely used in the food industry as ingredients to  
43 enhance viscosities in processing (Cerqueira, Bourbon, Pinheiro, Martins, Souza, Teixeira, &  
44 Vicente, 2011), but the degree of enhancement depends on the species, or more precisely the  
45 m/g ratio. Similarly, how the m/g ratio is important to consider the viscoelastic properties of the  
46 solutions has been reported by many research groups (Sittikijyothin, Torres, & Goncalves, 2005;  
47 Wu, Cui, Eskin, & Goff, 2009; Wu, Li, Cui, Eskin, & Goff, 2012). The m/g ratio is really one of  
48 important factors determining the solution properties of the galactomannans, but the origin on  
49 the molecular basis is still controversial (Morris, Cutler, Ross-Murphy, & Rees, 1981;  
50 Richardson, & Ross-Murphy, 1987; Robinson, Ross-Murphy, & Morris, 1982; Wu, Cui, Eskin,  
51 & Goff, 2009). The galactose units are not randomly distributed along the main chain made of  
52 mannose for galactomannans, which generates a blockiness: galactose-poor blocks (g-poor  
53 blocks, i.e., mannose-rich blocks) and galactose-rich (g-rich) blocks on a chain. Of course, the

54 blockiness is not clear, but the mannose blocks easily form molecular association through  
55 hydrogen bonds, while such attractive interaction is small for the g-rich blocks (Sanderson,  
56 1990; Urlacher, & Dalbe, 1994). This intermolecular association, enhanced with increasing the  
57 m/g ratio, may explain the difference in solution properties of the galactomannans.

58       The viscoelastic properties of the concentrated solutions of galactomannans are controlled  
59 firstly by the number density of entanglements on a polymer chain, as is the case of other  
60 homogeneous polymer liquids (Ferry, 1980; Doi, & Edwards, 1986), and the number density is a  
61 material constant reflecting the molecular parameters of the polymer chains such as the stiffness  
62 of the polymer chain. The molecular weight between entanglements ( $M_e$ ) is often used to  
63 describe the spacing between entanglements and  $M_e$  in the molten state ( $M_{e,melt}$ ) becomes a  
64 material constant. It is interesting to know if the chain stiffness and accordingly the spacing  
65 between entanglements change with the m/g ratio (McCleary, Amado, Waibel, & Neukom,  
66 1981). However, we have no information of the values of  $M_{e,melt}$  for the galactomannans at  
67 present. This is partly due to the difficulty in preparing concentrated solutions, solutions of  
68 overlapping polymers, of the galactomannans with conventional solvents. The aim of this study  
69 is to estimate  $M_{e,melt}$  for the galactomannans. It should be noted that the rheological behavior  
70 reflecting  $M_{e,melt}$  (or  $M_e$ ) appears in much shorter time region than the intermolecular  
71 associations described above. Dynamic viscoelasticity is examined for concentrated solutions by

72 using an ionic liquid as a good solvent. Ionic liquids are known to dissolve several  
73 polysaccharides which are insoluble to conventional organic solvents. For each of  
74 galactomannans,  $M_e$  is determined as a function of the polymer concentration ( $c$ ), and then  
75  $M_{e,melt}$  is estimated by extrapolation of the  $c$ -dependence curve of  $M_e$ .

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## 77 **2. Experimental**

### 78 2.1. Materials

79 Galactomannan powders (g-gum, t-gum and lb-gum) were provided from  
80 MRC-Polysaccharide Co., Japan. All samples were used without further purification. A solvent  
81 1-butyl-3-methylimidazolium chloride (BmimCl; Aldrich, USA) was used as received.  
82 According to the manufacturer's data sheet, the melting temperatures ( $T_m$ ) of BmimCl was  
83 reported to be 70 °C. The galactomannan solutions in BmimCl were prepared as follows: The  
84 powders were added into liquid BmimCl in a dry glass vessel, and then the mixture was quickly  
85 stirred with a stainless steel spatula on a hot plate at about 80 °C. After that the glass vessel was  
86 sealed and was left on the hot plate for complete melting. For every galactomannan  $c$  ranged  
87 from  $5.4 \times 10^1$  to  $2.1 \times 10^2 \text{ kgm}^{-3}$  (ca. 5 to 20 wt %), and in the calculation of  $c$ , the density of  
88 BmimCl was assumed to be  $1.08 \times 10^3 \text{ kgm}^{-3}$ , as reported previously (Horinaka, Yasuda,  
89 Takigawa, 2011a; Horinaka, Yasuda, Takigawa, 2011b). The densities for the galactomannans

90 were commonly assumed to be  $10^3 \text{ kgm}^{-3}$ , since the values for the purely amorphous polymers  
91 are not available (Horinaka, Yasuda, Takigawa, 2011a). The viscoelasticity measurements were  
92 started just after finishing the sample preparation.

93

## 94 2.2. Measurements

95 The dynamic viscoelasticity measurements were carried out with an ARES rheometer (now  
96 TA Instruments, USA) under a nitrogen atmosphere with a cone-plate geometry. The diameter of  
97 the plates was 25 mm and the cone angle was 0.1 rad. The angular frequency ( $\omega$ ) dependence  
98 curves of the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) were measured in the range of  $\omega$   
99 from 0.01 to  $100 \text{ s}^{-1}$ . The amplitude of the oscillatory strain ( $\gamma$ ) was settled to be 0.1 so that the  
100 linear viscoelasticity was realized. The measurement temperature ( $T$ ) ranged from 20 to  $100 \text{ }^\circ\text{C}$ .  
101 The viscoelasticity measurements were successfully taken even at  $20 \text{ }^\circ\text{C}$ , since the supercooled  
102 state of the BmimCl solutions was rather stable below  $T_m$  of  $70 \text{ }^\circ\text{C}$ . (Horinaka, Honda, Takigawa,  
103 2009; Horinaka, Yasuda, Takigawa, 2011a)

104

## 105 3. Results and Discussion

106 Figure 1 (a) shows the master curves of  $G'$  and  $G''$  at the reference temperature ( $T_r$ ) of  $80$   
107  $^\circ\text{C}$  for the solutions of g-gum at  $c =$  for  $5.4 \times 10^1$  and  $2.1 \times 10^2 \text{ kgm}^{-3}$ . At both concentrations,

108 the  $\omega$  dependence curves at different temperatures were well superimposed to give the master  
109 curves only by a horizontal shift ( $a_T$ : the shift factor). This means that the time (or, angular  
110 frequency)-temperature superposition principle holds for these systems. The  
111 frequency-dependence of loss tangent ( $\tan\delta = G''/G'$ ) is also shown for the region in which the  
112 curves pass through a minimum. The zero-shear viscosity ( $\eta_0$ ) of the solvent, BmimCl, at  $T_r$  of  
113 80 °C was much smaller than that of the solutions examined here, and therefore the contribution  
114 of  $\eta_0$  of the solvent to  $G''$  was ignored. At low  $\omega a_T$  the flow region can be seen clearly on the  $G'$   
115 and  $G''$  curves. In the middle  $\omega a_T$  region in the figure the rubbery plateau exists on both  $G'$   
116 curves. The rubbery plateau originates from the entanglement coupling between polymer chains,  
117 indicating the existence of entanglements between g-gum chains. The tilted plateau suggests  
118 that the molecular weight distribution of the g-gum is broad.

119 Figures 1 (b) and (c) show the master curves of  $G'$  and  $G''$  for the solutions of t-gum and  
120 lb-gum, respectively. Similar viscoelastic behavior to the g-gum solutions is observed for these  
121 galactomannans.

122 Figures 2 shows  $\log a_T (T_r = 80 \text{ }^\circ\text{C})$  plotted against  $1/T$  from 20 to 100 °C for the solutions  
123 of g-gum, t-gum and lb-gum. The shift factor  $a_T$  at a given  $T$  is almost the same regardless of  $c$   
124 and all data points fall on a single line. These are common to the three figures ((a) to (c)). The  
125 above indicates that the  $T$ -dependence curve of  $a_T$  can be represented by an Arrhenius-type

126 equation and that even below the melting point of BmimCl,  $a_T$  has the same  $T$  dependence as  
127 above the melting point. Similar behavior has been observed for other polysaccharides in  
128 BmimCl (Horinaka, Yasuda, Takigawa, 2011a; Horinaka, Yasuda, Takigawa, 2012).

129 From the analogy with the rubber elasticity,  $M_e$  for a polymer at a concentration  $c$  can be  
130 calculated by

$$131 \quad M_e = \frac{10^3 cRT}{G_N^0} \quad (1)$$

132 Here,  $G_N^0$  is the plateau modulus in the rubbery region and  $R$  is the gas constant. (Ferry, 1980;  
133 Doi, & Edwards, 1986; Onogi, Masuda, & Kitagawa 1970) As stated previously, the actual  $G'$   
134 curves in this study were tilted, so that we defined here  $G_N^0$  as the  $G'$  value at  $\omega a_T$  where the  
135  $\tan\delta$  versus  $\omega$  curve stays at a minimum. This leads to the results that the  $5.4 \times 10^1$  and  $2.1 \times 10^2$   
136  $\text{kgm}^{-3}$  solutions of g-gum respectively have  $G_N^0$  of  $1.6 \times 10^3$  and  $3.2 \times 10^4$  Pa (Figure 1(a)),  
137 finally giving  $M_e$  of  $9.8 \times 10^4$  and  $2.0 \times 10^4$ , respectively. The values of  $M_e$  for the solutions of  
138 other galactomannans were obtained in a similar way.

139 Figure 3 shows double-logarithmic plots of  $M_e$  against  $c$  for the three galactomannans. For  
140 each galactomannan, a straight line with a slope of  $-1$  is drawn with the best fit method. This is  
141 based on the assumption that a relation for polymers  $M_e \propto c^{-1}$  is also applied to the  
142 galactomannans (Doi, & Edwards, 1986; Masuda, Toda, Aoto, & Onogi, 1972; Nemoto, Ogawa,  
143 Odani, & Kurata, 1972). It is seen that data points for each galactomannan are fitted well by the



144 line of slope  $-1$ , indicating that the  $c^{-1}$  dependence of  $M_e$  also holds well for the galactomannan  
145 solutions examined in this study. Comparing the values of  $M_e$  at a given  $c$ , we have the order  
146 g-gum > t-gum > lb-gum although the difference between t-gum and lb-gum is rather small. The  
147 quantity,  $M_{e,melt}$  for the galactomannans can be determined as a value of the intercept on the  
148 right-hand ordinate in Figure 3 (or, more precisely, the value of  $M_e$  at  $c = 10^3 \text{ kgm}^{-3}$ ), by  
149 assuming the density of all galactomannans to be  $1.0 \times 10^3 \text{ kgm}^{-3}$ . The obtained values of  $M_{e,melt}$   
150 are  $4.6 \times 10^3$ ,  $3.2 \times 10^3$ , and  $2.7 \times 10^3$  for g-gum, t-gum and lb-gum, respectively; namely,  $M_{e,melt}$   
151 becomes smaller with increasing the m/g ratio. Since  $M_{e,melt}$  is a material constant, it is  
152 interesting to calculate the number of monosaccharide units between entanglements in the  
153 molten state ( $N_{unit}$ ) from  $M_{e,melt}$  and  $M_{unit}$ , with  $M_{unit}$  being the molecular weight of a repeating  
154 unit for the galactomannans. Here,  $M_{unit}$  was calculated based on the assumption that the m/g  
155 ratios are the typical values, i.e., 2 for g-gum, 3 for t-gum, and 4 for lb-gum, and that a galactose  
156 side group was included in a unit. We define  $N_{unit}$  as the number of mannose units along the  
157 main chain, not counting a galactose side group, i.e.,  $N_{unit} = (\text{the number of mannose units in a}$   
158  $\text{unit}) \times (M_{e,melt} / M_{unit})$ . Table 1 lists  $N_{unit}$  for the galactomannans together with  $M_{e,melt}$  and  $M_{unit}$ .  
159 The values of  $N_{unit}$  lie in almost the same range (13 to 19). If we see them more precisely,  
160 however, we may have a tendency that  $N_{unit}$  decreases with increasing the m/g ratio. The values  
161 for the galactomannans can also be compared with those for other polysaccharides estimated in

162 our previous studies. We have 19 for cellulose, 15 for agarose and 14 for gellan, which are  
163 almost the same and are typical for polysaccharides with the random-coil conformation in the  
164 ionic liquid (Horinaka, Yasuda, & Takigawa, 2011a). The values for the galactomannans are  
165 really close to those of the other polysaccharides with the random coil conformation, suggesting  
166 that the galactomannans in the ionic liquid here take the random coil conformation. This is, at  
167 least for g-gum, consistent with the previous prediction made from the intrinsic viscosity  
168 measurement that a g-gum molecule behaves as a random coil in water (Robinson,  
169 Ross-Murphy, & Morris, 1982).

170

#### 171 **4. Conclusions**

172 Dynamic viscoelasticity of concentrated solutions of g-gum, t-gum, and lb-gum in  
173 BmimCl was examined to estimate  $M_{e,melt}$  of the galactomannans. The values of  $M_{e,melt}$  are  
174  $4.6 \times 10^3$ ,  $3.2 \times 10^3$ , and  $2.7 \times 10^3$  for g-gum, t-gum, and lb-gum, respectively; namely,  $M_{e,melt}$  for  
175 the galactomannans is dependent on the m/g ratio. As a whole, however,  $N_{unit}$  for the three  
176 galactomannans are rather close to each other being in the same range as for other  
177 polysaccharides such as cellulose and agarose. This suggests that the galactomannans take the  
178 random coil conformation in ionic liquid. It seems that a galactose side group causes no  
179 conformational changes of galactomannans, for example, to a helix.

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182 **References**

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## Figure Captions

Figure 1 Master curves of  $\omega$  dependence of  $G'$  and  $G''$  for  $5.4 \times 10^1$  and  $2.1 \times 10^2 \text{ kgm}^{-3}$  solutions of (a) g-gum, (b) t-gum, and (c) lb-gum.  $T_r = 80 \text{ }^\circ\text{C}$ . The  $\tan\delta$  curve is also included.

Figure 2 Shift factor for (a) g-gum, (b) t-gum, and (c) lb-gum solutions of  $c$  from  $5.4 \times 10^1$  to  $2.1 \times 10^2 \text{ kgm}^{-3}$  plotted against the reciprocal of  $T$ . In each figure, all data points fall on a single line

Figure 3 Double-logarithmic plot of  $M_e$  against  $c$  for galactomannans in solution. Each line is the best fit with a slope of  $\approx 1$ .  $M_{e,\text{melt}}$  for galactomannans are determined as  $M_e$  at  $c = 10^3 \text{ kgm}^{-3}$ .

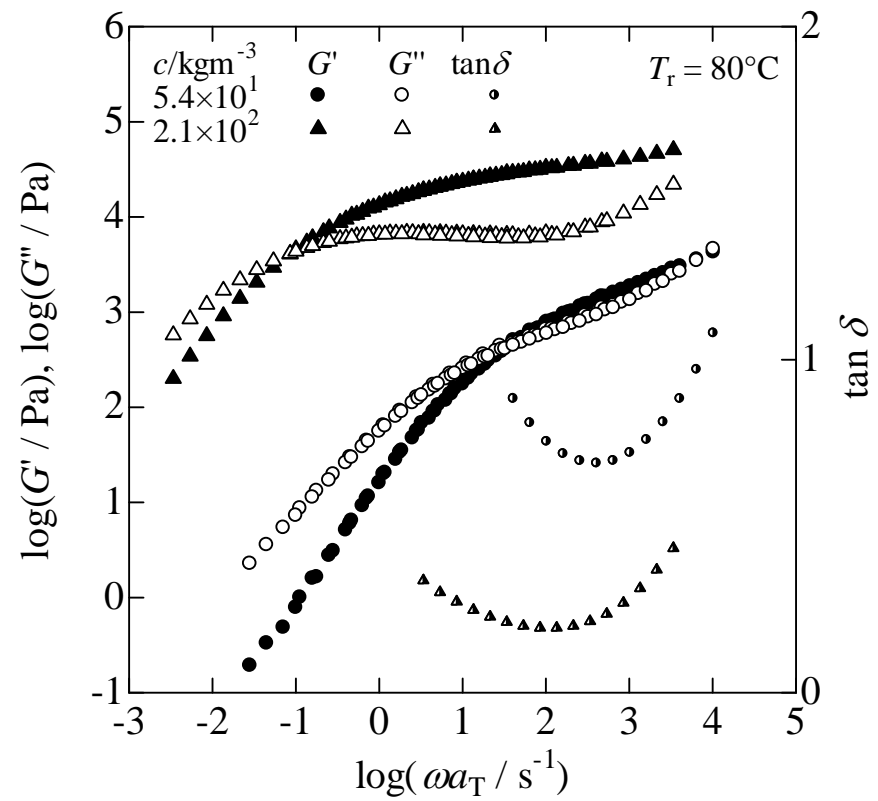


Fig. 1(a)



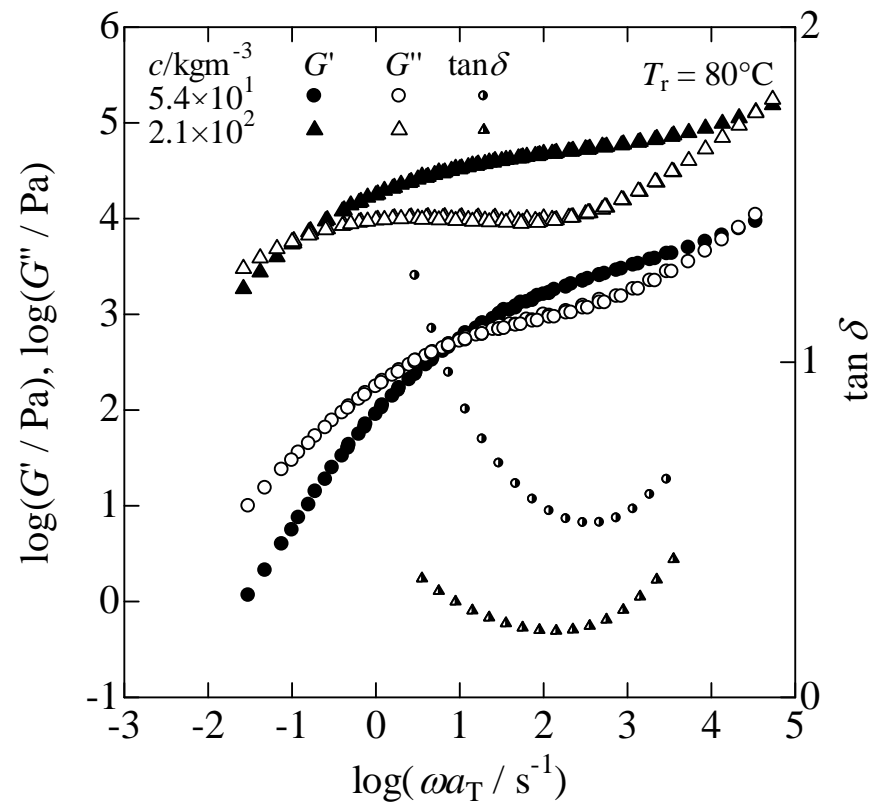


Fig. 1(b)

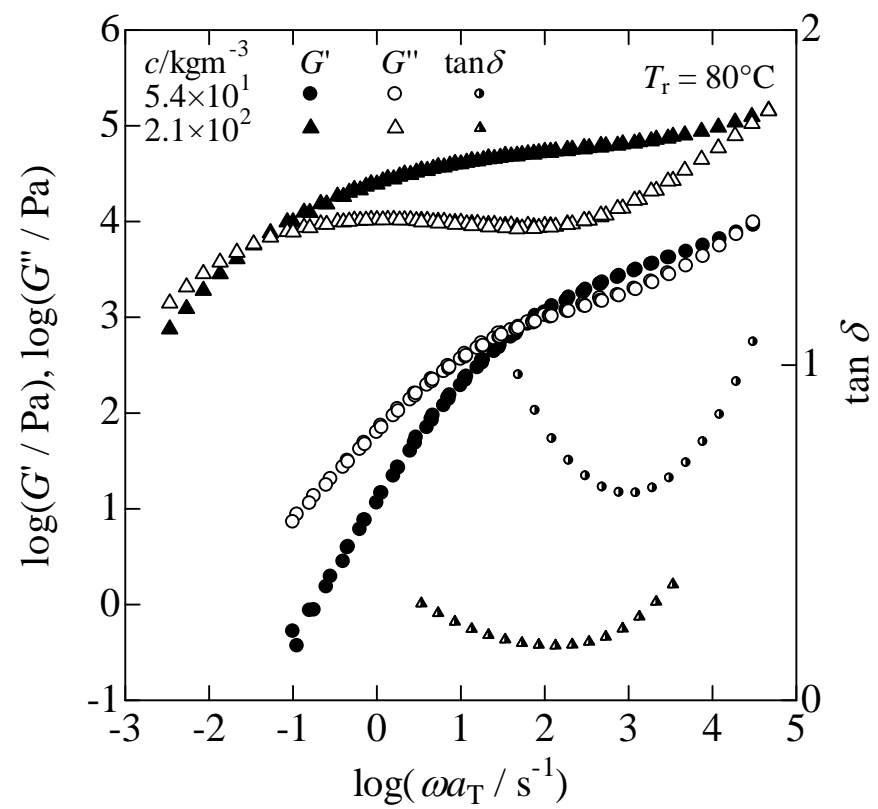


Fig. 1(c)

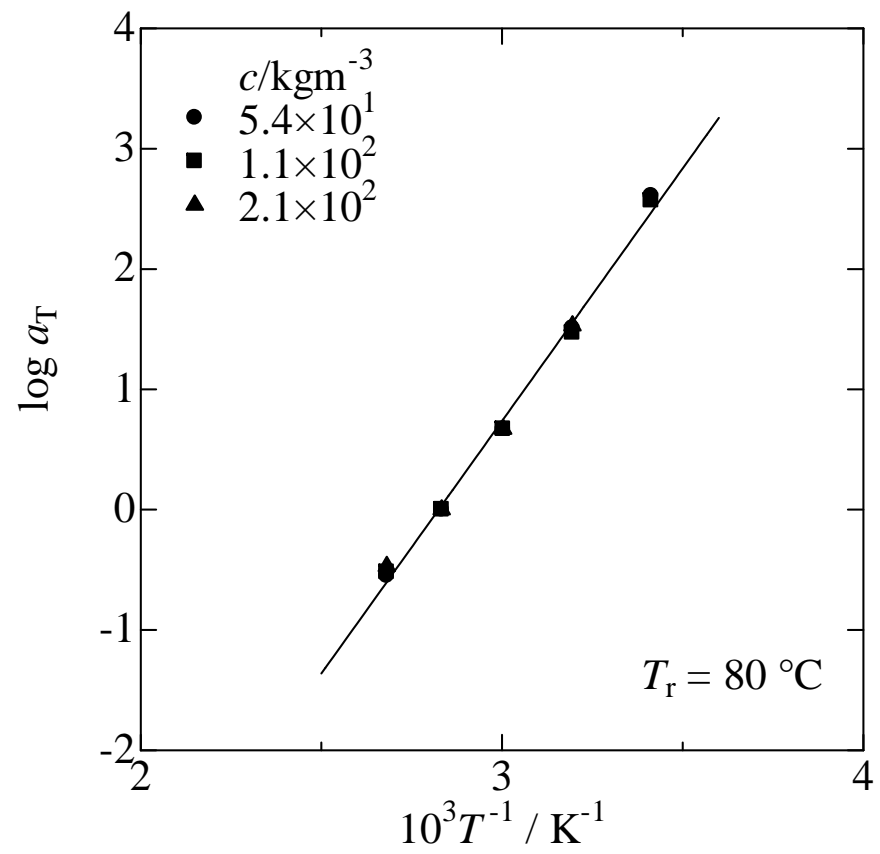


Fig. 2(a)

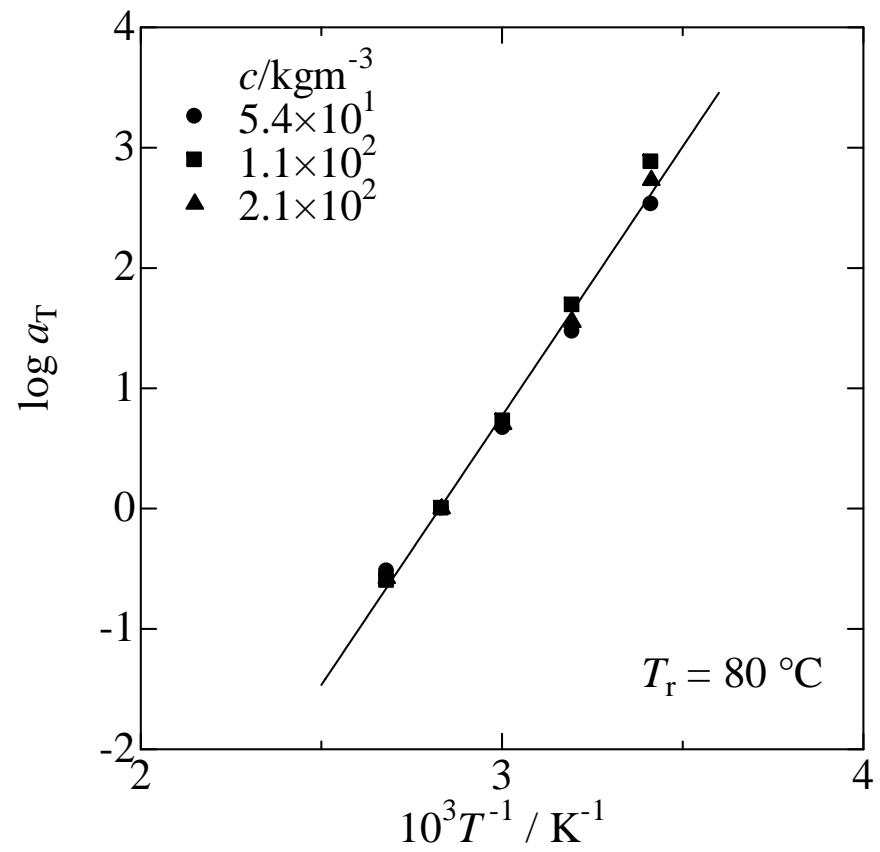


Fig. 2(b)

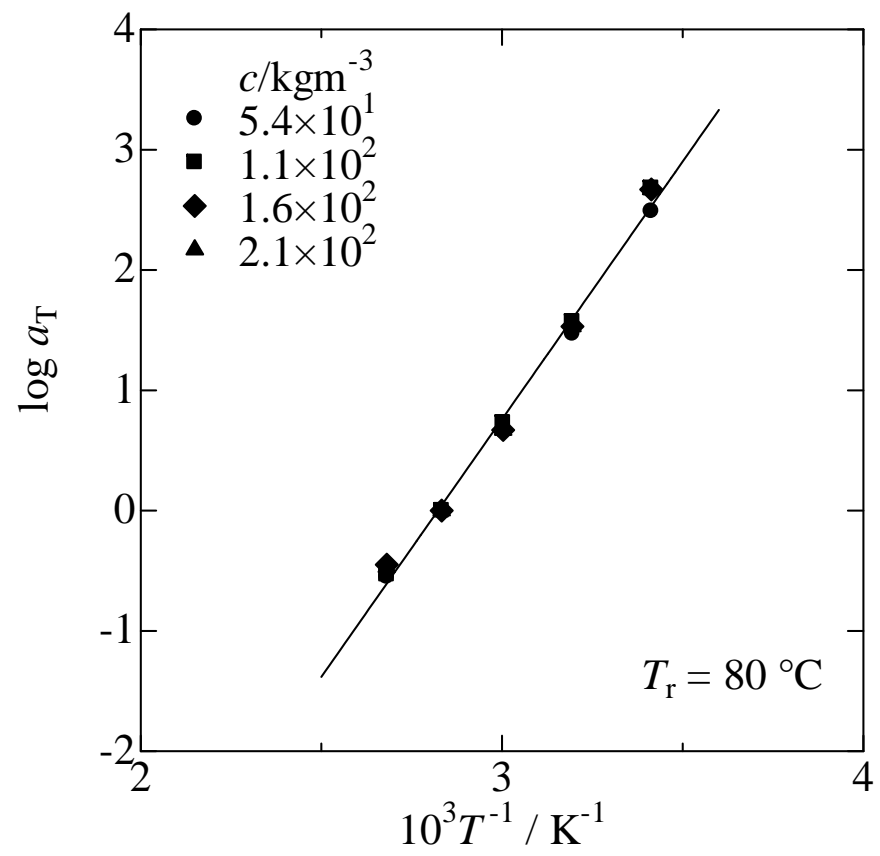


Fig. 2(c)

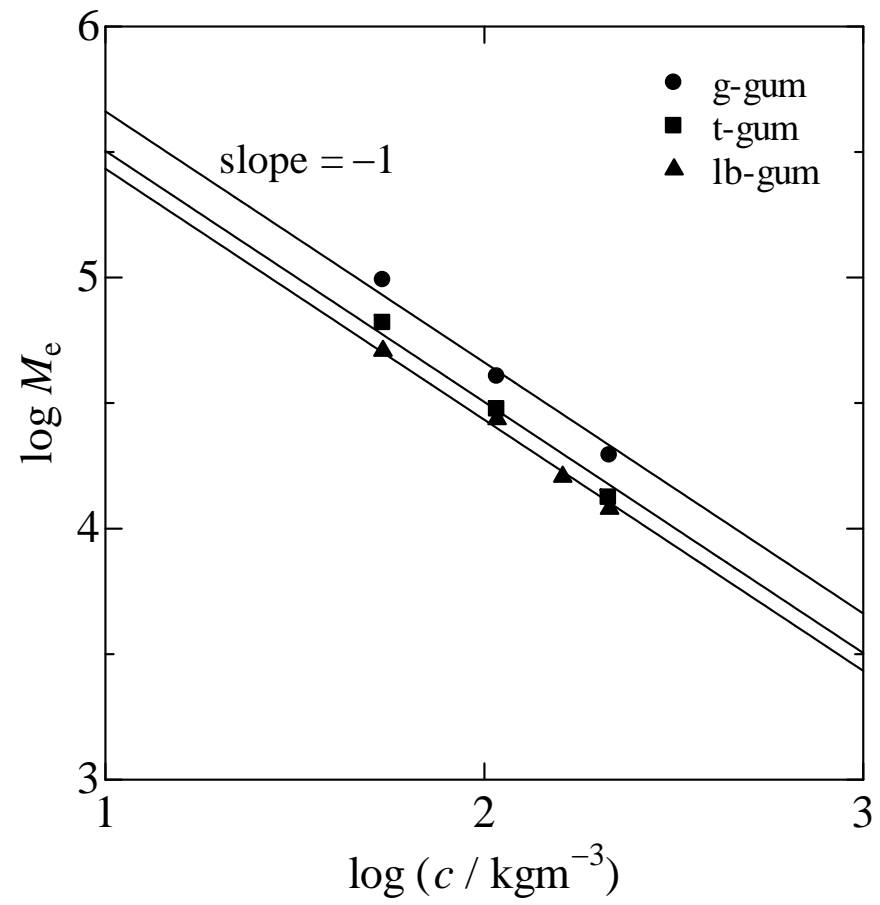


Fig. 3

Table 1. Material constants for galactomannans

sample	$M_{\text{unit}}$	$M_{\text{e,melt}}$	$N_{\text{unit}}^*$
g-gum	486	$4.6 \times 10^3$	19
t-gum	648	$3.2 \times 10^3$	15
lb-gum	810	$2.7 \times 10^3$	13

\* excluding a galactose side group