Analysis of Apparent Viscosity of Aqueous Macromolecule Solutions Containing Sucrose

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The apparent viscosity ($\eta_a$) of aqueous macromolecule solutions with and without sucrose was measured. In addition, the apparent reduced viscosity ($\eta_{a,\text{red}}$), the intrinsic viscosity ([\eta]), the dependence of apparent specific viscosity ($\eta_{a,sp}$) on water activity ($A_w$), and the activation energy of apparent viscosity ($E_a$) were analyzed to compare the inter-macromolecular interactions among six aqueous macromolecule solutions at a fixed concentration. The macromolecule solutions tested were 2% polyethylene glycol (PEG35000, MW = 35 kDa), dextran (DexT40, MW = 40 kDa), apple pectin, citrus pectin, sodium alginate, and 0.5% xanthan. Based on the dependence of $\eta_{a,sp}$ and $E_a$ on $A_w$, as well as the difference in $\eta_{a,\text{red}}$ and its relationship with [\eta], the apparent viscosity behavior of the macromolecule solutions tested was classified into three groups. In Group A which consists of PEG35000 and DexT40, the macromolecules are diluted enough such that intermolecular interactions are very weak. In Group B which consists of pectins and alginate, the macromolecules are in contact with one another such that inter-macromolecular interactions become stronger and the addition of sucrose affects the macromolecular interactions. In Group C which consists of xanthan, macromolecular chains are physically entangled with partial aggregations such that inter-macromolecular interactions are very strong, but the addition of sucrose has almost no effect on the interaction.

Keywords: macromolecular interaction, viscosity, activation energy, reduced viscosity, specific viscosity, water activity

Introduction

Food macromolecules are the basic ingredients for modifying pasting properties and the texture of food (Sudhakar et al., 1995). It is important to understand the molecular interactions of food macromolecules in water for a critical view in the functionalities of macromolecules (Shi and BeMiller, 2002). The various functionalities of macromolecules are influenced by their structure, composition, and physical properties due to inter-macromolecular interactions (Lodge et al., 1987; Kar and Arslan, 1999b). Viscosity measurement is a method used to analyze inter-macromolecular interactions in solutions. Moreover, inter-macromolecular interactions are affected by the coexistence of low-molecules, which also affects water activity ($A_w$) (Sato et al., 2004; Sato and Miyawaki, 2008). In this paper, the apparent viscosity ($\eta_{a,sp}$) behaviors of six different macromolecules with their various dimension levels in aqueous solutions, with and without sucrose due to its well-known $A_w$ depressor, were measured to analyze macromolecular interactions. The macromolecules used here were 2% polyethylene glycol (PEG35000), dextran (DexT40), apple and citrus pectins, sodium alginate, and 0.5% xanthan. PEG35000 is a linear branched uncharged polyether (Bertoluzzo et al., 2007) and DexT40 is composed of $\alpha$-1,6 linked glucose with a variable $\alpha$-1,3 and occasional $\alpha$-1,2 or $\alpha$-1,4 branched chains (Sidebotham, 1974; Aquino and Franco, 2009). Apple and citrus pectins are high methoxyl-pectins and are based on a backbone of 1,4-linked $\alpha$-D-galacturonic acid and its methyl ester interspersed by 2-linked $\alpha$-L-rhamnopyranosyl residues (Kar and Arslan, 1999a; Kjønnsen et al., 2005). Sodium alginate consists of a family of linear polymers of $\beta$-D-mannuronic acid (M) and $\alpha$-L-guluronic acid (G), and has three types of blocks, MM block, MG block,
and GG block (Gomez et al., 2009), characterized by the M/G ratio. Xanthan gum is composed of a cellulose backbone, oligosaccharide repeating-units, and a β-D-mannopyranosyl terminal group which links pyruvate acetal via C-4 and C-6 in pyranose (Jasson et al., 1975; Bradshaw et al., 1983).

From the $\eta'_H$ of the macromolecule solution at a fixed concentration, the apparent reduced viscosity ($\eta''_r$), the dependence of apparent specific viscosity ($\eta''_s$) on $A_w$ in solutions containing sucrose, and the activation energy ($E_a$) for $\eta''_H$ were obtained and analyzed with the intrinsic viscosity ($[\eta]$) of the macromolecule in water to estimate the difference in inter-macromolecular interactions among the macromolecule solutions tested.

Materials and Methods

Materials Polyethyleneglycol 35000 (PEG35000, MW = 35 kDa) was purchased from Merck (Tokyo, Japan) and Dextran T40 (DexT40, MW = 40 kDa) from GE Healthcare (Tokyo, Japan). Xanthan gum, apple and citrus pectins, as well as sodium alginate (low viscosity) were purchased from Sigma (St. Louis, MO, USA). These macromolecules were selected depending on the dimension level of the macromolecules, but not considered the charge of each macromolecule in water since the electrostatic contribution is more complicated for physical interpretations. Sucrose was obtained from Nacalai Tesque (Kyoto, Japan). For citrus pectin, its high-methoxyl pectins (Glenn, 1953). Sodium alginate showed a M/G ratio of 1.3 by the simple chemical method involving partial hydrolysis with an acid (Huang et al., 1974). All the reagents used were of reagent grade and were used without further purification. The water content was analyzed by drying in an oven at 110 °C to 120°C to calculate their concentration accurately.

Measurement of apparent and reduced viscosity of macromolecule solutions The macromolecule powder was suspended and dissolved in distilled water at 50°C. The concentration of the macromolecules except xanthan was fixed at 2 wt%. The concentration of xanthan was adjusted at 0.5 wt%. The sample solution was kept overnight at 50°C until use. The temperature and incubation time were fixed among the macromolecules to avoid degradation; citrus pectin degrades upon heating, resulting in a decrease in molecular weight (Diaz et al., 2007). Then, 7 mL of the sample solution was poured into the cell, and $\eta''_H$ was measured using a rotational viscometer (B8L, Tokimec, Tokyo, Japan) at a shear rate of 15.8 s$^{-1}$ for both PEG35000 and DexT40, and 16.8 s$^{-1}$ for the others with rotational speeds varying from 0.5 to 100 rpm at 25°C. The apparent reduced viscosity ($\eta''_r$) was determined from $\eta''_H$ using the following equation. 

$$\eta''_r = (\eta''_H - \eta_w) / \eta_w / C$$ (1)

where $\eta_w$ is the viscosity of pure water and $C$ is the concentration of the macromolecule (g/dL).

Measurement of intrinsic viscosity of macromolecule solutions in pure water The concentrations of the diluted macromolecule solutions were adjusted to 0.01 – 0.03 g/dL with water, and the viscosity ($\eta_H$) was measured using a Cannon-Fenske capillary viscometer (Sibata Co., Ltd., Tokyo) and a density meter (DMA4500, Anton Paar, Austria) at 25°C. The intrinsic viscosity ([\eta]) was determined by the following Huggins’s equation (Huggins, 1942; Migliori et al., 2010) according to Launay et al. (1997).

$$[\eta] = [(\eta_H - \eta_w) / \eta_w / C_{c...o}]$$ (2)

Activation energy for apparent viscosity of macromolecule solutions The activation energy ($E_a$) for $\eta''_H$ of the macromolecule solutions with and without sucrose at 5 – 40°C was determined using the following Arrhenius-type equation (Kar and Arslan, 1999b).

$$\eta''_H = \eta_b \exp (E_a / RT)$$ (3)

where $\eta_b$ is a pre-exponential factor (mPa·s), $R$ is the gas constant (= 8.3145 J/mol/K), and $T$ is the absolute temperature (K).

Apparent specific viscosity of macromolecule solutions containing sucrose The apparent specific viscosity ($\eta''_s$) of the macromolecule solution was determined using the following equation.

$$\eta''_s = (\eta''_H - \eta_s) / \eta_s$$ (4)

In this case, $\eta''_H$ is the apparent viscosity of the macromolecule solution containing sucrose and $\eta_s$ is the viscosity of the sucrose solution. $\eta_s$ has been described as a function of $A_w$ as follows (Sato and Miyawaki, 2008).

$$\eta_s = \eta_w + a(1 - A_w) + b(1 - A_w)^2$$ (5)

The parameters $a$ and $b$ in this equation have been determined as a function of temperature in previous literature (Sato and Miyawaki, 2008).

Determination of water activity The water activity ($A_w$) of the sucrose solutions, could be described by the following equation (Kozak et al., 1968):

$$A_w = (1 - X_s) \exp (aX_s^2)$$ (6)

where $X_s$ is the molar fraction of sucrose. The parameter $a$
intermolecular interactions among the macromolecules.

\[ \eta_a \text{red} = \frac{[\ln (\eta_H / \eta_W)]}{C} \quad C \rightarrow 0 \] 

(7)

### Results and Discussion

**Flowing property of macromolecule solutions in pure water**

Figure 1 shows the effect of shear rate on \( \eta_H \) of the aqueous macromolecule solutions without sucrose at 25°C. The concentrations of the macromolecules were fixed at 2% except that of xanthan, which was 0.5% due to its high apparent viscosity in this case. Flowing properties of the macromolecule solutions often show non-Newtonianity (Jeanes et al., 1961; Launay et al., 1997; Marcotte et al., 2001). In the present case, the apple and citrus pectin solutions showed shear thinning properties at low shear rates, but the apparent viscosity became constant at shear rates higher than 6.33 s\(^{-1}\). On the contrary, the sodium alginate, PEG35000, and DexT40 solutions showed Newtonian property at all shear rates. The xanthan solution showed shear thinning property at a shear rate below 16.8 s\(^{-1}\), at which its apparent viscosity was determined. This macromolecule is reported to be incompletely solvated in water with a weak gel-like structure (Morris et al., 1983). However, the apparent viscosity at a shear rate of 16.8 s\(^{-1}\) was employed to analyze the intermolecular interactions.

\[ \eta_a \text{red} \] was calculated from \( \eta_H \) and \( \eta_W \), and compared with \( [\eta] \) in Table 1. \( [\eta] \) is the reduced viscosity of a solution in the infinitely diluted state, at which the macromolecules in the solution are isolated from one another with negligible intermolecular interactions. To obtain \( [\eta] \), several equations have been shown (Vahid et al., 2011). In the present case, the Huggins’s equation (Huggins, 1942) described in Eq.(2) was used as shown in Fig. 2. In Fig. 2, the following Kraemer’s equation (1938) was also employed for comparision.

A similar order of \( [\eta] \) was obtained with a high determination coefficient \( (R^2) \) of more than 0.926 in each equation for the three typical macromolecules: PEG35000, citrus pectin, and xanthan, while \( [\eta] \) calculated using the Kraemer’s equation was slightly lower. Thus, only \( [\eta] \) obtained by Eq.(2) is shown in Table 1.

**Table 1. Apparent viscosity and activation energy of fluidization for macromolecule solutions.**

<table>
<thead>
<tr>
<th>Macromolecule</th>
<th>Concentration (wt%)</th>
<th>( \eta_a \text{red} ) (dL/g)</th>
<th>( [\eta] ) (dL/g)</th>
<th>MW (kDa)</th>
<th>( E_a ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG35000</td>
<td>2</td>
<td>1.3</td>
<td>3.2</td>
<td>35</td>
<td>17.4</td>
</tr>
<tr>
<td>DexT40</td>
<td>2</td>
<td>0.6</td>
<td>4.0</td>
<td>40</td>
<td>12.3</td>
</tr>
<tr>
<td>Apple pectin</td>
<td>2</td>
<td>61.3</td>
<td>16.3</td>
<td>~100</td>
<td>27.4</td>
</tr>
<tr>
<td>Citrus pectin</td>
<td>2</td>
<td>39.9</td>
<td>24.5</td>
<td>~100</td>
<td>31.9</td>
</tr>
<tr>
<td>Alginate</td>
<td>2</td>
<td>46.7</td>
<td>44.0</td>
<td>~100</td>
<td>27.4</td>
</tr>
<tr>
<td>Xanthan</td>
<td>0.5</td>
<td>573</td>
<td>64.4</td>
<td>~1000</td>
<td>1.9</td>
</tr>
<tr>
<td>Water</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>17.4</td>
</tr>
</tbody>
</table>
[\eta] has been known to change along with MW of the macromolecule (Tanglertpaibul and Rao, 1987). MWs of PEG35000 and DexT40 are the smallest in the order of 10 kDa, those of alginate (Pongsawatmanit et al., 1999) and pectin (Oakenful and Scott, 1984; Kar and Arslan, 1999b) are moderate in the order of 100 kDa, and that of xanthan (Bradshaw et al., 1983; Ptaszek et al., 2007) is the largest in the order of 1,000 kDa. In the literature, [\eta] for a high-methoxyl pectin was reported to be 21.5 dL/g in water (Yoo et al., 2006). In the present case, [\eta] for alginate seems to be slightly higher at 44.0 dL/g. In contrast, [\eta] for xanthan gum obtained in this study was 64.4 dL/g which is comparable to 87.5 dL/g as reported in a previous reference (Launay et al., 1997).

Effect of temperature on apparent viscosity of macromolecule solutions

Figure 3 shows the effect of temperature on \( \eta^H \) of the macromolecules in pure water. According to Eq. (3), the logarithm of \( \eta^H \) was plotted against 1/T, giving straight lines. From the slope of this plot, the activation energy for fluidization of the macromolecule solution (\( E_a \)) was determined and summarized in Table 1 along with that of water. At the concentration level of macromolecules tested here, \( E_a \) is not much different from that of water for PEG3500 and DexT40, slightly higher for pectins and alginate, and very

Fig. 2. Comparison of the Huggins’s plot with the Kraemer plot for three typical macromolecules in water.
Open symbols with the straight line are the Huggins’s plots. Closed symbols with the dotted line are the Kraemer plots. ○ and ●, xanthan gum; □ and ■, citrus pectin; △ and ▲, PEG35000.

Fig. 3. Arrhenius plots for apparent viscosity of aqueous macromolecule solutions. Symbol descriptions are the same as in Fig. 1.

Fig. 4. Apparent viscosity of macromolecule solutions containing sucrose at 25°C. Symbol descriptions are the same as in Fig. 1. Open cross symbols (△) with a smooth solid line correspond to the sucrose solution (Sato et al., 2008).
Effect of sucrose on activation energy for apparent viscosity of macromolecule solutions

Figure 6 shows the effect of \( A_w \) on \( E_a \) of the apparent viscosity of the macromolecule solution containing sucrose. Within the \( A_w \) range of 1 to 0.98, \( E_a \) increased from 17.4 to 22.6 kJ/mol for PEG35000, from 12.3 to 20.7 kJ/mol for DexT40, from 27.4 to 36.1 kJ/mol for apple pectin, from 31.9 to 45.5 kJ/mol for citrus pectin, and from 24.9 to 31.2 kJ/mol for sodium alginate. For xanthan, almost no increase in \( E_a \) was observed (1.9-2.7 kJ/mol). In lower for xanthan. In the literature, \( E_a \) has been reported to be 19.5 kJ/mol for a 2.5 % orange pectin solution (Kar and Arslan, 1999b), 19.6 kJ/mol for a 1 % pectin solution, and 5.74 kJ/mol for a 1 % xanthan solution (Marcotte et al., 2001). \( E_a \) is dependent on the concentration of the macromolecule. As for the citrus pectin solution, the \( E_a \) measured was very close to that of pure water in a dilute solution and increased along with an increase in the pectin concentration (Sato et al., 2008), showing an increase in pectin-pectin interactions.

Effect of sucrose on apparent viscosity of aqueous macromolecule solutions

Figure 4 shows the effect of the coexistence of sucrose on \( \eta_{sp}^a \) of the macromolecule solutions at 25°C. With a decrease in \( A_w \) due to an increase in the sucrose concentration, \( \eta_{sp}^a \) increased significantly for pectins and alginate, and increased slightly for PEG35000, DexT40, and xanthan. With an increase in sucrose concentration, the viscosity of the sucrose solution also increased as described by Eq. (5). Therefore, the apparent specific viscosity \( (\eta_{sp}^a) \) defined by Eq. (4) will be convenient to compensate the change in the viscosity of the background sucrose solution.

Figures 5a and 5b show the effect of sucrose, expressed as a function of \( A_w \) on \( \eta_{sp}^a \) of the macromolecule solution at 25°C. For PEG35000 and DexT40, \( -d\eta_{sp}^a/dA_w \) is almost zero, showing that the change in viscosity of the macromolecule solution is determined almost only by the viscosity change in the background sucrose solution in this case. On the contrary, \( -d\eta_{sp}^a/dA_w \) is positive for pectins and alginate suggesting that the coexistence of sucrose causes an increase in the intermolecular interactions among macromolecules. As for pectin, inter-macromolecular interaction comprises hydrogen bonding and hydrophobic interaction (Oakenful and Scott, 1984), both of which have been reported to increase by the coexistence of sugars (Sato and Miyawaki, 2008). For xanthan, \( -d\eta_{sp}^a/dA_w \) interestingly gave a negative value, suggesting that the coexistence of sucrose weaken the inter-macromolecular interactions in this case. A decrease in the intrinsic viscosity of xanthan is reported in the highly concentrated sucrose solution (Launay et al., 1997), which may correspond to the negative value of \( -d\eta_{sp}^a/dA_w \) observed here.

Figures 5a and 5b. Apparent specific viscosity of macromolecule solutions containing sucrose at 25°C.

Fig. 5a. Apparent specific viscosity of macromolecule solutions containing sucrose at 25°C. Symbol descriptions are the same as in Fig. 1. Apparent specific viscosity was determined using Eq. (4) in the text.

Fig. 5b. Apparent specific viscosity of PEG35000 and DexT40 solutions containing sucrose at 25°C. Symbol descriptions are the same as in Fig. 1.
depending on the concentration of the macromolecule, \( C \), and its relationship with the two critical concentrations, \( C^* \) and \( C^{**} \), (Launay et al., 1997) as follows:

**I. Dilute regime (\( C < C^* \)):** macromolecules are infinitely diluted.

**II. Intermediate regime (\( C^* < C < C^{**} \)):** macromolecules are in contact with one another.

**III. Semidiluted regime (\( C^{**} < C \)):** macromolecule chains are entangled.

This classification seems to correspond well to the classification of the apparent viscosity behavior summarized in Table 2.

Group A in Table 2 corresponds to Category I. For this group, \( \eta_{\text{red}}^a \) is very small and the change in viscosity change upon addition of sucrose is almost solely dependent on the viscosity of the background sucrose solution causing a very small \( -d\eta_{\text{sp}}^a/dA_w \) value. The \( E_a \) value is not much different from that of pure water (~18 kJ/mol) or the sucrose solution (17.5-22.1 kJ/mol). Inter-macromolecular interactions are very weak because of the infinite dilution in this group.

Group B corresponds to Category II. Macromolecules are in contact with one another such that \( \eta_{\text{red}}^a \) became high. In addition, the coexistence of sucrose affected intermolecular interactions among the macromolecules through hydrogen bonding and hydrophobic interaction (Oakenful and Scott, 1984) to give a positive value for \( -d\eta_{\text{sp}}^a/dA_w \) and a much higher value for \( E_a \) than the sucrose solution.

In Group C, MW of xanthan is very high and macromolecule chains are entangled and partially aggregated to increase \( \eta_{\text{red}}^a \) significantly. The coexistence of sucrose might have affected to shrink the macromolecule to give a negative value for \( -d\eta_{\text{sp}}^a/dA_w \). Since intermolecular physical entanglement is the major mechanism in this case, the temperature dependency of apparent viscosity is low such that \( E_a \) is almost zero. The critical concentration \( C^{**} \) for xanthan is reported to be around 0.1% (Launay et al., 1997), which is much lower than the present case suggesting that Group C corresponds to Category III. The low sensitivity of the viscosity of the xanthan solution to temperature is favorably evaluated as a stable food thickener.

Table 2. Classification of apparent viscosity of macromolecules in aqueous solutions at the tested condition*.

<table>
<thead>
<tr>
<th>Group</th>
<th>Macromolecule</th>
<th>( \eta_{\text{red}}^a ) (dL/g)</th>
<th>(-d\eta_{\text{sp}}^a/dA_w)</th>
<th>( E_a ) (kJ/mol)</th>
<th>Macromolecular interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PEG35000, DexT40</td>
<td>0.6 – 1.3</td>
<td>~ 0</td>
<td>~ 18</td>
<td>weak</td>
</tr>
<tr>
<td>B</td>
<td>pectin, alginate</td>
<td>40 – 61</td>
<td>positive</td>
<td>&gt; 25</td>
<td>moderate</td>
</tr>
<tr>
<td>C</td>
<td>xanthan</td>
<td>573</td>
<td>negative</td>
<td>~ 0</td>
<td>strong</td>
</tr>
</tbody>
</table>

*The concentration of the macromolecule except for xanthan was fixed at 2 wt%. The concentration of xanthan was adjusted to 0.5 wt%.
The classification in Table 2 also depends on the concentration of the macromolecule, which was fixed in the present case. Each macromolecule, in principle, has its own $C^*$ and $C^{**}$ such that the relationship between the concentration of the macromolecule and $C^*$ and/or $C^{**}$ affects the classification.

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