Theoretical Analysis of the Viscosity of Disaccharide Solutions

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The temperature dependence of the viscosity of disaccharide solutions such as trehalose, maltose and sucrose has been investigated by means of the Bond Strength-Coordination Number Fluctuation (BSCNF) model. The result indicates that the fragilities of these systems are almost the same and that the values of the materials parameters are determined to be consistent with those of the trehalose-water-lithium iodide system which were observed in a previous study.

§1.　Introduction

The Bond Strength-Coordination Number Fluctuation (BSCNF) model has been found to be very useful to describe the relaxation behavior of many materials.[1] Recently, it has been used to study the properties of trehalose-water-lithium iodide system.[2] The result of the analysis showed that the addition of trehalose into the system results in the decrease of the fragility index due to the increase of the connectivity between the structural units. In the analysis, the material parameters used were obtained from conductivity measurement data.[3] In the present work, with the objective to gain further understanding on the physical properties of the system, the BSCNF model has been applied to investigate the temperature dependence of the viscosity of some disaccharide solutions such as trehalose, maltose and sucrose.

The disaccharides are kinds of sugars which have the same chemical formula ($C_{12}H_{22}O_{11}$, whose molecular weight is 342.3 g/mol) but have different structures.[4] In particular, the trehalose solution has a higher glass transition temperature when compared with other aqueous solutions.[5] Concerning the effect of addition of trehalose on the ionic conductivity of lithium-ion conductors, including the LiI-nH_2O system, many studies have been conducted.[6] For the LiI-nH_2O system, it has been shown that the glass forming ability enhances with the addition of trehalose.[3,7]

In the present report, the temperature dependence of the viscosity of disaccharides in water solutions at weight fraction of $\phi = 0.50$ is calculated by means of the BSCNF model. The result of the calculation indicates that the values of the materials parameters are determined to be consistent with those of the trehalose-water-lithium iodide system which were evaluated from conductivity measurement data. This proves that the ionic conductivity data can be used to determine the values of the parameters necessary to calculate the viscosity.

§2. The bond strength-coordination number fluctuation model

In the BSCNF model, the melt is considered to be formed by an agglomeration of structural units. When the temperature of the system is lowered, the viscosity of the melt increases due to the increase of the connectivity between the structural units and the spatial distribution of the structural unit is frozen at the glass transition temperature T_g. According to the model, the viscous flow occurs when the structural units move from one position to another by twisting and breaking the bonds connecting them. Each structural unit is bound to other structural units by certain bond strength.

Based on the above considerations, the temperature dependence of the viscosity can be written as[8]

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx}{1 - Bx^2}\left[1 + x\left\{\left[\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2}\ln(1 - B)\right]\frac{1 - B}{C} - 1\right\}\right]$$
$$- \frac{1}{2}\ln(1 - Bx^2), \tag{2.1}$$

with

$$B = \left(\frac{\Delta E \Delta Z}{RT_g}\right)^2,$$

$$C = \frac{E_0 Z_0}{RT_g},$$

$$x = \frac{T_g}{T}.$$

Here η_0 and η_{T_g} are the viscosities at the high temperature limit and at the glass transition temperature, respectively. We adopt the usual values[9] $\eta_0 = 10^{-5}$ Pa s and $\eta_{T_g} = 10^{12}$ Pa s. E_0 and Z_0 are the average values of the binding energy and coordination number of the structural units, respectively, ΔE and ΔZ are their fluctuations and R is the gas constant. Note that C contains information about the total bond strength of the structural unit and B gives its fluctuation.

According to the BSCNF model, the fragility index m is written in terms of the parameters B and C as[8],[10],[11]

$$m = \frac{1}{\ln 10}\frac{B - C + 2\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \ln(1 - B)}{1 - B}. \tag{2.2}$$

From Eq. (2.2), we can see that a high value of C and a low value of B corresponds to a less fragile system.[12]

It has been shown that the quantities B and C are related by[11]

$$C = \frac{\gamma(1 - B)}{2\gamma + \sqrt{B}(1 + \gamma^2)}\left[2\ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \ln(1 - B)\right], \tag{2.3}$$

where

$$\gamma = \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0}.$$

When $\gamma = 1$, that is, when the ratio of the normalized bond strength fluctuation to the normalized coordination number fluctuation equals unity, Eq. (2.3) reproduces exactly the well known Vogel-Fulcher-Tammann (VFT) behavior by choosing appropriately the values of B and C.[13]

§3. Results and discussion

The BSCNF model is applied to predict the temperature dependence of the viscosity of disaccharide solutions. The experimental data are given in Table I. The values of B and C given in the Table I are determined from a best fitting of Eq. (2.1) to the experimental data, with the condition that the relation (2.3) is satisfied.

Table I. Experimental data[4] of glass transition temperature T_g, fragility m and viscosity η of water solutions of disaccharide at weight fraction of $\phi = 0.50$. Also given are the values of the parameters B and C obtained from the experimental data.

Disaccharide solution	T_g(K)	m	η (Pa s)	B	C
Trehalose	238	107.4	0.78	0.71	6.06
Maltose	234	109.5	0.69	0.72	5.09
Sucrose	233	111.0	0.65	0.72	5.86

The temperature dependence of the viscosity calculated through Eq. (2.1) is shown in Fig. 1. We note that the viscosity data of the three disaccharides seem almost overlapping. An enlarged view is shown in the inset. It is noted that the theoretical curve do not fit exactly the experimental data. One reason of this disagreement arises from the constraint imposed, i.e., the condition $\gamma = 1$. It has been shown previously that the BSCNF model could reproduce the experimental data better than the VFT equation by relaxing the condition $\gamma = 1$. Another reason of the disagreement arises from the values of the fragility used. The values of the fragility indexes given in Table I are not measured directly. The results of previous analyses based on the BSCNF model suggest that if the values of the fragility of the system in consideration are slightly smaller than the reported values, the agreement between the calculated and measured values of the viscosity will be improved. In any way, for a close quantitative comparison, the temperature range of measurement should be extended, because the temperature range is too limited as illustrated in Fig. 1.

Although the agreement between the calculated and the measured data is not exact, the result shown in Fig. 1 provides an estimation of the values of B and C of disaccharides, that is $B \simeq 0.7$ and $C \simeq 6$. These values are close to the values of parameters determined in a trehalose-water-lithium iodide system by making use conductivity data, $B = 0.3 - 0.7$ and $C = 5 - 18$.[2] As discussed elsewhere, the values of C and B are related with the total bond strength and its fluctuation, respectively, of the structural units that form the melt.[12] Microscopic processes of structural relaxations could be discussed by an improved determination of the values B and C for each material.
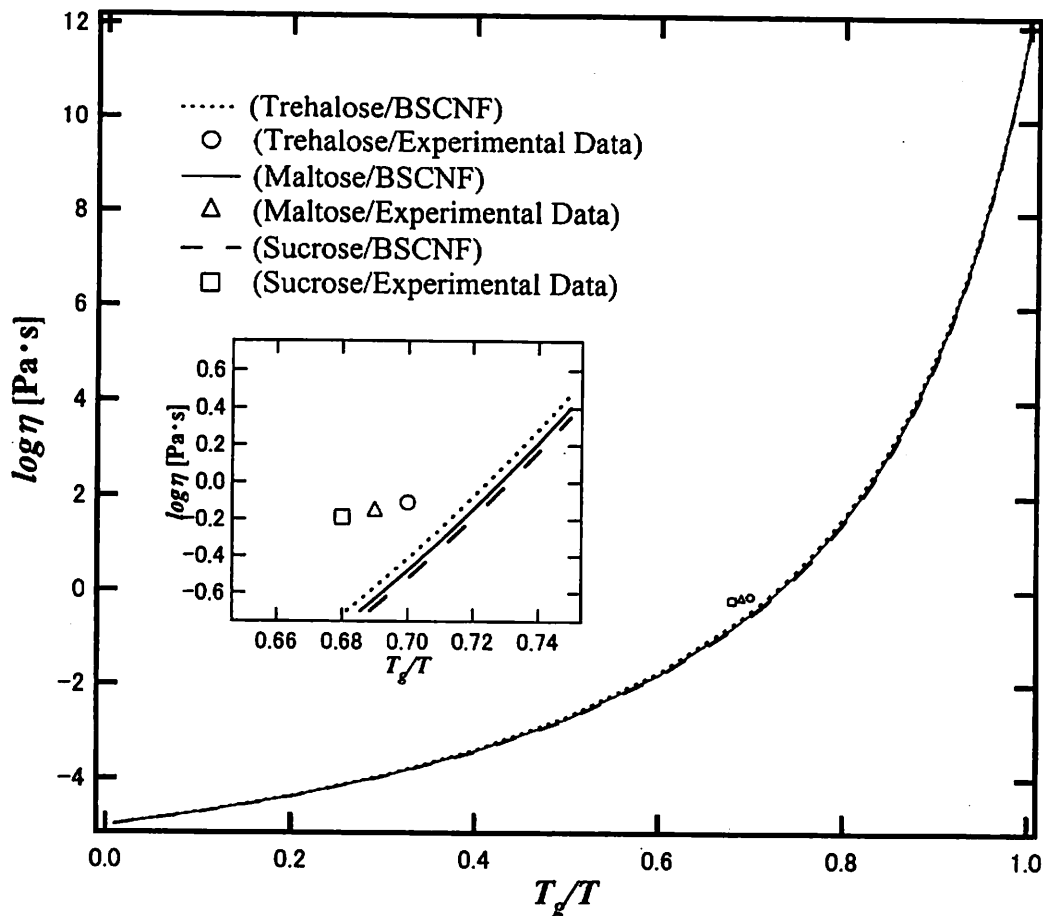
Fig. 1. Temperature dependence of the viscosity for some disaccharide solutions. The theoretical
curves are described by Eq. (2.1). The inset shows an enlarged view of the region where the
experimental data are distributed.

§4. Conclusion

The Bond Strength-Coordination Number Fluctuation (BSCNF) model has been
used to study the temperature dependence of the viscosity of disaccharide solutions
such as trehalose, maltose and sucrose. The result indicates that the fragilities of
these systems are almost the same and that the values of the materials parameters are
determined to be consistent with those of the trehalose-water-lithium iodide system
which have been evaluated by making use of conductivity data.

Acknowledgements

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