Jurnal Sains Materi Indonesia
Indonesian Journal of Materials Science

Special Edition on Materials for Energy and Device 2010, page : 40 - 43
ISSN : 1411-1098

Akreditasi LIPI Nomor : 452/D/2010
Tanggal 6 Mei 2010

ANALYSIS OF THE PHYSICAL PROPERTIES OF TREHALOSE-WATER-LITHIUM IODIDE BASED ON THE BOND STRENGTH COORDINATION NUMBER FLUCTUATION MODEL

Sahara, Jean L. Ndeugueu and Masaru Aniya
Department of Physics, Graduate School of Science and Technology-Kumamoto University
Kurokami 2-39-1, Kumamoto, 860-8555, Japan
e-mail :093d8113@st.kumamoto-u.ac.jp

ABSTRACT

ANALYSIS OF THE PHYSICAL PROPERTIES OF TREHALOSE-WATER-LITHIUM IODIDE BASED ON THE BOND STRENGTH COORDINATION NUMBER FLUCTUATION MODEL. The temperature dependence of the viscosity of trehalose-water-lithium iodide system has been investigated by the mean of the Bond Strength Coordination Number Fluctuation (BSCNF) model. The result indicates that by increasing the trehalose content, maintaining the content of LiI constant, the fragility decreases due to the increase of the connectivity between the structural units. Our analysis suggests also that the fragility of the system is controlled by the amount of water in the composition. By increasing the water content, the total bond strength decreases and its fluctuation increases, resulting in the increase of the fragility. Based on the analysis of the obtained parameters of the BSCNF model, a physical interpretation of the VFT parameters reported in a previous study has been given.

Key words : Bond Strength Coordination Number Fluctuation Model, Viscosity, Fragility

ABSTRAK

ANALISIS SIFAT-SIFAT FISIS *TREHALOSE*-AIR-*LITHIUM* IODIDA BERDASARKAN MODEL *BOND STRENGTH COORDINATION NUMBER FLUCTUATION*. Telah diinvestigasi viskositas sebagai fungsi suhu terhadap sistem *trehalose*-air-*lithium* iodida dengan menggunakan model *Bond Strength Coordination Number Fluctuation* (*BSCNF*). Hasilnya menunjukkan bahwa dengan penambahan kandungan *trehalose*, mempertahankan kandungan LiI tetap konstan, *fragility* sistem menurun, seiring dengan peningkatan konektivitas antar unit-unit struktur molekul. Hasil analisis juga menyarankan bahwa *fragility* sistem dikontrol oleh banyaknya kandungan air di dalam komposisi. Dengan meningkatkan kandungan air, total kekuatan ikatan terhadap unit struktur lain berkurang dan fluktuasinya meningkat, mengakibatkan peningkatan *fragility* sistem. Interpretasi fisis dari parameter *VFT* yang dilaporkan pada penelitian sebelumnya telah dilakukan berdasarkan analisis dari parameter-parameter model *BSCNF* yang diperoleh.

Kata kunci : Model *Bond Strength Coordination Number Fluctuation*, Viskositas, *Fragility*

INTRODUCTION

Studies on physical properties of lithium-ion conductors are interesting from both academic and applied science points of views. These materials are characterized by their high energy density power and high ionic conductivity. Among the many potential technological applications such as fuel cells, electrochromic displays and smart windows, rechargeable lithium-ion batteries are of outmost importance. However, changes in today's lithium-ion batteries are required. For instance, changes in the chemistry, improvements in environmental sustainability and energy content are mandatory. Many studies have been conducted in order to enhance the conductivity of lithium-ion conductors, including LiI-nH_2O system [1,2]. For this system it has been shown that the addition of trehalose enhances the glass forming ability [3,4].

Recently, the ionic conductivity of trehalose-water-lithium iodide system with different compositions of lithium iodide and trehalose has been measured [4]. The results showed that the addition of trehalose into the aqueous solution of LiI enhances not only the ionic conductivity but also the glass transition temperature. The data were analyzed by the use of the Vogel-Fulcher-

Tammann (VTF) equation. Until now, the physical properties such as conductivity, viscosity and fragility of the material under consideration here are not sufficiently understood.

The purpose of the present work is to gain further insights on the physical properties of trehalose-water-lithium iodide system by using the Bond Strength Coordination Number Fluctuation (BSCNF) model [5], which has been found to be very useful to describe the relaxation behavior of many materials. In this work, we have investigated theoretically the effects of trehalose and water on the aqueous solution of LiI.

THEORY

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 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 [5].

Based on these considerations, the temperature dependence of the viscosity can be written as Equation (1)

$$ln\left(\frac{\eta}{\eta_o}\right)=\frac{Cx+Cx^2\left\{\left[ln\left(\frac{\eta_{Tg}}{\eta_o}\right)+\frac{1}{2}ln(1-B)\right]\frac{(1-B)}{C}-1\right\}}{1-Bx^2}-\frac{1}{2}ln(1-Bx^2) \quad \text{..... (1)}$$

Where

$$B=\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_g^2}, \quad C=\frac{E_0Z_0}{RT_g}, \quad \text{and} \quad x=\frac{T_g}{T}$$

In Equation (1), η_0 and η_{Tg} denote the viscosities at high temperature limit and at glass transition temperature, respectively. For their values we adopt the usual values $\eta_0 = 10^{-5}$ Pa·s and $\eta_{Tg} = 10^{12}$ Pa·s [6]. C contains information about the total bond strength of the structural unit and B gives its fluctuation. E_0 is the average value of the binding energy and Z_0 is the average value of the coordination number of the structural units. ΔE and ΔZ are the fluctuations of E and Z, respectively. R is the gas constant.

According to the BSCNF model, the fragility index m is written in terms of the parameters and as [5,7,8].

$$m=\frac{1}{\ln(10)}\left\{\frac{B-C+2\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right]}{1-B}\right\} \quad \text{..... (2)}$$

From Equation (2), we can learn that a high value of the total bond strength of the structural unit and a low value of its fluctuation corresponds to a less fragile system [9].

On the other hand, it is well established in the literature that the temperature dependence of the viscosity can be described in term of the VTF equation as

$$Log\eta = Log\eta_0 + \frac{B_{VFT}}{T-T_0} \quad \text{..... (3)}$$

where is a constant and denotes the ideal glass transition temperature known as Vogel temperature. In a recent study, it has been shown that the BFCNF model reproduces exactly the temperature dependence of the viscosity described by the VFT equation [10]. Such a reproduction occurs when the parameters and satisfy the following relation

$$C=\frac{2\gamma(1-B)}{2\gamma+\sqrt{B}(1+\gamma^2)}\left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right\} \quad \text{..... (4)}$$

Where

$$\gamma=\frac{|\Delta E|/E_0}{|\Delta Z|/Z_0}=1$$

that is, when the ratio of the normalized bond strength fluctuation to the normalized coordination number fluctuation equals unity. At the glass transition temperature, the VTF equation given by Equation (3) can be written as

$$\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)=\frac{\left(\frac{B_{VFT}}{T_g}\right)}{1-\frac{T_0}{T_g}} \quad \text{..... (5)}$$

Table 1. Compositions (mole ratio) of trehalose-water-lithium iodide system and corresponding values of VFT parameters [4].

Glass No.	Composition			T_g (K)	T_0 (K)	T_0/T_g (K)	B_{VFT}
	LiI	H_20	Trehalose				
I	14.3	85.7	0.0	143	112	0.78	385
II	15.7	83.3	1.0	154	120	0.78	421
III	12.5	81.1	6.4	204	143	0.70	686
IV	13.0	74.0	13.0	227	152	0.67	820
V	14.0	68.4	17.7	264	188	0.71	850
VI	46.0	43.4	10.7	263	129	0.49	1387
VII	61.4	32.8	5.8	275	147	0.53	1173

Special Edition on Materials for Energy and Device 2010, page : 40 - 43
ISSN : 1411-1098

Table 2. Values of the parameters and the fragility index of trehalose-water-lithium iodide system determined from the BSCNF model

Glass No.	*B*	*C*	*m*
I	0.460	12.496	50.02
II	0.456	12.612	49.58
III	0.255	19.304	32.49
IV	0.196	21.753	28.66
V	0.272	18.653	33.64
VI	0.022	33.328	17.67
VII	0.015	34.343	17.20

In terms of the VFT parameters, the fragility index is written as

$$m = \frac{\left(\frac{B_{VFT}}{T_g}\right)}{\left(1-\frac{T_0}{T_g}\right)^2} \quad \text{.....} \quad (6)$$

By using Equations (4), (5) and (6), we can obtain the following relationship between the VFT parameters and the BSCNF model parameters

$$\frac{T_0}{T_g} = 1 - \frac{\left(\frac{1+\sqrt{B^*}}{1-B^*}\right)C^* - \frac{1}{2}\ln\left(1-B^*\right)}{\ln(10)m} \quad \text{.....} \quad (7)$$

Here, and denote the values and that satisfy Equation (4) in the case of [10].

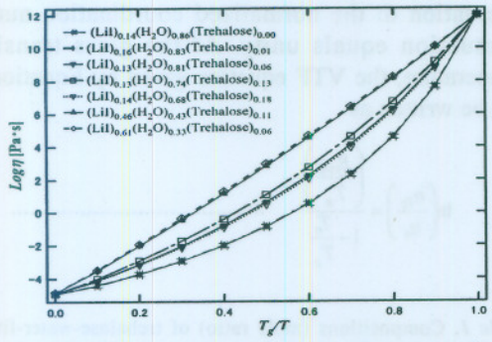

Figure 1. Temperature dependence of viscosity for various compositions of trehalose-water-lithium iodide system, obtained from Equation (1).

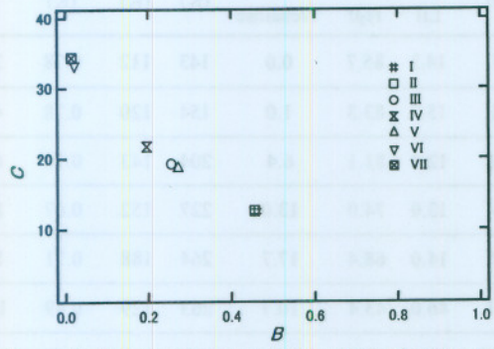

Figure 2. Relationship between the values of parameter and determined for different composition

RESULTS AND DISCUSSION

In this section the BSCNF model is applied to predict the temperature dependence of the viscosity of trehalose-water-lithium iodide system. The ratio and the value of for each composition reported in [4] are given in Table 1. It has been shown that the ionic conductivity of the system follows the VFT behavior [4]. Therefore, by assuming that the viscosity also follows the VFT behavior, we have used Equation (7) to determine the values of and for each composition. For the fragility index *m*, we used the values calculated from Equation (6). Thanks to Equation (2), the obtained values of and enable us to obtain the values of the fragility index given in Table 2, which coincide exactly with that of Equation (6). This coincidence reconfirms that the behavior described by the BSCNF model reproduces the behavior described by the VFT equation.

Once having the values of and, we can describe theoretically the temperature dependence of the viscosity thanks to Equation (1). The result is shown in Figure 1. It is of utmost importance to mention that, as far as we are informed, experimental studies on viscosity in trehalose-water-lithium iodide system has not been reported.

Figure 2 shows the relationship between the parameters and, determined for trehalose-water-lithium iodide system. It has been shown previously that large value of and small value of correspond to strong systems, whereas small value of and large value of correspond to fragile systems [9]. The addition of trehalose to the aqueous solution of LiI (data points I-V) results in the decrease of and the increase of. This trend indicates that the fragility of the system decreases as shown in Table 2.

According to the BSCNF model, this behavior is related to the increase of the strength of the connectivity between the structural units. In the present case, the connectivity is primary caused by the interconnection between trehalose molecules. This interpretation is consistent with a study reported in aqueous mixture of trehalose with sodium chloride [11]. There, based on conductivity measurements and simulation results, it is reported that the heterogeneity prevails in the system and that the domains consisting mostly of trehalose move slowly, whereas the domains consisting of ions and their accompanying hydration shells move faster.

From Figure 2, we note that by increasing the water content (from VII to I), of gross manner, the fragility increases. This behavior is interpreted as due to the low connectivity of water molecules as compared to that of trehalose. The result reported for some sugar solutions seems consistent with this picture [12-14].

To avoid confusion, some comment should be given here. By looking at Figure 1 or by comparing the values of *B* and *C* obtained here for the LiI-H_2O-trehalose system with those of other systems

[15], we note that the system in consideration is relatively strong. This behavior arises quite probably from the route of how the parameters B and C were obtained. In the present study, these were obtained through VFT parameters determined from conductivity measurements [4]. On the other hand, for the other systems, B and C were determined by fitting directly to viscosity data [15].

In our analysis, we have shown that the VFT parameters can be described in terms of the parameters of the BSCNF model. This indicates that the BSCNF model provides a physical interpretation of the phenomenological VFT parameters. For instance, in Ref. [4] the VFT parameters were determined from conductivity measurements. However, no physical interpretation was given. By reanalyzing their data in the light of our BSCNF model, we have discussed what happens in the composition dependence. Specifically, we have shown that such parameters carry information on the degree of connectivity between the structural units. In addition, by using the model, the temperature dependence of the viscosity was predicted.

CONCLUSION

The Bond Strength-Coordination Number Fluctuation (BSCNF) model has been used to study some physical properties of LiI-H_2O-Trehalose mixtures. The result suggests that by increasing the content of trehalose, maintaining the content of LiI constant, the fragility index decreases due to the increase of the connectivity between the structural units. We have also found that by increasing the water content, the total bond strength decreases and its fluctuation increases, resulting in the increase of the fragility of the system. The physical interpretation of the phenomenological VFT parameters has been given based on the BSCNF model. The result indicates that such parameters carry information on the degree of connectivity between the structural units

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014). Sahara acknowledges for the Monbukagakusho Scholarship.

REFERENCES

[1]. P.O. MAURIN, J.F. JAL, J. DUPUY-PHILON, N. ASAHI, J. KAWAMURA, T. KAMIYAMA and Y. NAKAMURA, *Ber. Bungsenges. Phys. Chem.*, **102** (1998) 152-155

[2]. P.O. MAURIN, J. DUPUY-PHILON, J.F. JAL, N. ASAHI, T. KAMIYAMA, J. KAWAMURA, and Y. NAKAMURA, *Prog. Theor. Phys. Suppl.*, **126** (1997) 141-146

[3]. C.A. ANGELL, *Solid State Ionics*, **9** and **10** (1983) 3-16

[4]. R. TAKEKAWA, Y. IWAI AND J. KAWAMURA, *Solid State Ionics*, Ed. B.V.R. CHOWDARI et al, Wuhan Univ. Press, China (2010) 463-469

[5]. M. ANIYA, *J. Therm Anal. Calorim.*, **69** (2002) 971-978

[6]. L.M. MARTINEZ and C.A ANGELL. *Nature*, **410** (2001) 663-667

[7]. M. IKEDA and M. ANIYA, Ed. B.V.R. CHOWDARI et al, *Solid State Ionics*, Macmillan India, (2008) 409-415

[8]. M. IKEDA and M. ANIYA, *Solid State Ionics*, **180** (2009) 522-526

[9]. M.ANIYA and T.SHINKAWA, *Mater. Trans.*, **48** (2007) 1793-1796

[10]. M. IKEDA, *Ph.D Thesis Kumamoto University*, Japan, (2010)

[11]. D.P. MILLER, P.B. CONRAD, S. FUCITO, H.R. CORTI and J.J. de PABLO, *J. Phys. Chem.* B, **104** (2000) 10419-10425

[12]. M. RAMPP, C. BUTTERSACK and H. D. LÜDEMANN, *Carbohydr. Res.*, **328** (2000) 561-572

[13]. V. MOLINERO, T. CAGIN and W.A. GODDARD III, *Chem. Phys. Lett.*, **377** (2003) 469-474

[14] C. BRANCA, S. MAGAZÙ, G. MAISANO, F. MIGLIARDO, P. MIGLIARDO and G. ROMEO. *J. Phys. Chem. B*, **105** (2001) 10140-10145

[15] M.ANIYA and M.IKEDA, *Ionics*, **16** (2010) 7-11