A Comparative Study of the Viscosity of Ion Conducting Polymers based on the Bond Strength-Coordination Number Fluctuation Model and Other Models

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Abstract

According to the Bond Strength-Coordination Number Fluctuation (BSCNF) model of the viscosity proposed some years ago by one of the authors, the viscosity is controlled by the relaxation of structural units that form the melt, and is described in terms of the average bond strength, coordination number and their fluctuations of the structural units. In the present paper, a comparative study of the viscosity of ion conducting polymeric system is presented. The analysis has been done though the BSCNF model and other models widely used in the literature such as Vogel-Fulcher-Tamman (VFT) and Williams-Landel-Ferry (WLF) equations. The result reveals that the three models describe well the temperature dependence of the viscosity reported experimentally. As a gross trend, the fragility of the polymeric system in consideration increases with the increase in the concentration of salts. Based on the analysis with the BSCNF model, such a behavior has been interpreted to arise from the disruption of the network that results by the addition of salts. The comparative study also reveals that the BSCNF model could provide a physical interpretation to the empirical parameters used in other models.

Keywords: Bond Strength-Coordination Number Fluctuation Model, Viscosity, Ion Conducting Polymer, Vogel-Fulcher-Tamman Equation, Williams-Landel-Ferry Equation.

Introduction

Studies of physical properties of ion conducting polymeric materials are interesting from both, the academic and applied science points of views. These materials are characterized by their high ionic conductivity and high energy density power [1]. Potential applications of these materials in rechargeable lithium-ion batteries, electrochemical devices such as fuel cells, electrochromic displays, sensor, etc. have been investigated intensively [2,3]. Many studies have been also conducted in order to enhance the ionic conductivity and the mechanical stability of the materials [4]. However, fundamental understanding of the physical properties of the materials is not sufficient. For instance, previous study has indicated that the optimization of the ionic conductivity could be searched by studying the viscosity-conductivity relation [5,6]. However, its physical background was not clear.

Some years ago, one of the authors proposed the bond strength-coordination number fluctuation (BSCNF) model of the viscosity [7]. According to this model, viscosity is controlled by the relaxation of structural units that form the melt, and is described in terms of the average bond strength, coordination number and their fluctuations of the structural units. In a recent study, we have applied the model to analyze the temperature dependence of the viscosity or the fragility of trehalose-water-lithium iodide system [8]. The result indicated that the viscosity of the system is controlled by the connectivity of the structural units of trehalose molecules. It has been also shown that good ionic conductors have intermediate values of fragility [5].

In order to gain further understanding on the behavior of the system and extend the applicability of the model, it is necessary to verify the model in other systems. In the present paper, the temperature dependence of the viscosity of ion conducting polymeric materials will be analyzed by the BSCNF model, the Vogel-Fulcher-Tamman (VFT) equation and the Williams-Landel-Ferry (WLF) equation. From a comparison of the analysis, the interrelation

between the parameters of these models is obtained. Since the physical properties such as viscosity and fragility of the material under consideration here are not sufficiently understood, it is expected that our result will provide a hint to understand these properties.

Models for viscosity

In order to present clearly the different expressions used in the analysis, in the following, a brief summary of the models are given.

The bond strength-coordination number fluctuation model

The BSCNF model provides an expression for the temperature dependence of viscosity. It has been applied in oxides, semiconducting chalcogenides, metallic and some polymeric systems [5]. In this 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 breaking and twisting the bonds connecting them. Each structural unit is bound to other structural units by certain bond strength [7].

Based on these considerations, the temperature dependence of the viscosity can be written as

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

where

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2}, \qquad C = \frac{E_0 Z_0}{R T_g}, \qquad \text{and} \qquad x = \frac{T_g}{T} \quad . \tag{2}$$

In Eq.1, η_0 and η_{Tg} denote the viscosities at high temperature limit and at the glass transition temperature, respectively. For their values we adopted the usual values $\eta_0 = 10^{-5}$ Pa·s and $\eta_{Tg} = 10^{12}$ Pa·s [9]. The quantity 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 B and C as [7,10]

$$m = \frac{B - C + 2\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \ln(1-B)}{(\ln 10)(1-B)} \quad . \tag{3}$$

From Eq. 3, we can learn that a high value of the total bond strength between the structural units C and a low value of its fluctuation B results in a less fragile system [11].

The Vogel-Fulcher-Tamman equation

The VFT equation is the most widely used expression to describe the temperature dependence of the viscosity. It is given by

$$\ln\eta = \ln\eta_0 + \frac{B_{VFT}}{T - T_0} \quad , \tag{4}$$

where B_{VFT} is a constant and T_0 denotes the ideal glass transition temperature known as Vogel temperature. In a recent study, it has been shown that the BSCNF model reproduces exactly the temperature dependence of the viscosity described by the VFT equation [10]. From this

consideration, the parameters of the BSCNF model can be connected with those of the VFT equation. For instance, the expression for the ideal glass temperature is given by

$$\frac{T_0}{T_g} = 1 - \frac{\left(\frac{1+\sqrt{B^*}}{1-B^*}\right)C^* - \frac{1}{2}\ln\left(1-B^*\right)}{\left(\ln 10\right)m} \quad . \tag{5}$$

Here, B^* and C^* denote the values B and C that satisfy the following relation with γ=1 [10].

$$C = \frac{2\gamma(1-B)}{2\gamma+\sqrt{B}\left(1+\gamma^2\right)}\left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right\} \quad , \tag{6}$$

where

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

that is, when the ratio of the normalized bond strength fluctuation to the normalized coordination number fluctuation equal in unity.

The Williams-Landel-Ferry equation

The WLF equation has been used widely to describe the temperature dependence of the viscosity and relaxation time in polymeric systems. It is an empirical equation and is given by

$$\log a_T = \log\left(\frac{\eta}{\eta_{Tg}}\right) = \frac{-C_1\left(T-T_g\right)}{C_2+\left(T-T_g\right)} \quad , \tag{7}$$

where a_T is called shift factor. η is the viscosity at temperature T and η_{Tg} is the viscosity at some reference temperature. In the above expression, we have used the glass transition temperature T_g as the reference temperature. C_1 and C_2 are constants [12]. It has been reported that the values of C_1 and C_2 are 17.4 and 51.6 K respectively, for many materials [12, 13]. In terms of the WLF parameters, the fragility is given by [13]

$$F = 1 - \frac{C_2}{T_g}. \qquad (8)$$

Application of the models to the polymeric systems

In this section, the BSCNF model is applied for the investigation of the temperature dependence of the viscosity of ion conducting polymeric systems. In our study, the experimental data of the viscosity of poly(propylene glycol) (PPG) (4000) [14] and poly(propylene oxide) (PPO) (4000) [15] liquid polymer electrolytes containing the dissolved salts are used as test materials. They have been also analyzed by the VFT and WLF equations. The result shown in Fig. 1 indicates that all three models reproduce well the experimental behavior. From the analysis of the experimental data, we have determined the values of the parameters (B_{VFT}, T_0, η_0), (C_1, C_2) and (B, C) corresponding to each model. They are summarized in Table 1. Concerning the value of the fragility index m and F, they have been determined from Eqs. 3 and 8, respectively.

The relation between the parameters B and C obtained for different ion conducting polymeric materials is shown in Fig. 2. The relation follows a trend suggested in previous studies [5]. That is, B decreases with the increase of C. In the figure, theoretical curves based on the BSCNF model are shown for different values of $\delta = \ln(\eta_{Tg}/\eta_0)$. From the figure, we note that most of the data are distributed between $\delta = 50$ and $\delta = 80$. This means that for the materials in consideration, the viscosities at T_g and at the high temperature limit T_0 are different from the usual values $\eta_{Tg} = 10^{12}$ Pa.s. and $\eta_0 = 10^{-5}$ Pa.s, respectively. The usual value adopted in the Angell's plot is $\delta = 39.1$ [5].

The parameters B and C in the BSCNF model provide physical information of the system in consideration. For instance, it has been shown previously that large value of C and small value of B correspond to strong systems, whereas small value of C and large value of B

correspond to fragile systems [11]. From Fig. 2, we note that systems with high salt concentration have large value of *B* and small value of *C*. It indicates that the system is fragile. According to the BSCNF model, the decrease of *C* and the increase of *B* is related with the decrease of the total bond strength and the increase of the fluctuations between the structural units. The decrease of the bond strength is reflected in the decrease of the connectivity between the structural units. Since the connectivity of the network is destroyed by introducing salts in the system, the BSCNF model catches the essence of the phenomenology of the composition dependence observed.

Concerning the parameters of the WLF equation, from Table 1 we note that C_2 is more sensitive than C_1 to the composition. It has been reported that C_2 is related to the strength parameter *D* of the strong-fragile liquid classification [13]. A comparison between C_2 and the fragility index described by the BSCNF model is shown in Fig. 3. It is noted that *m* decreases with the increase of C_2. Fig. 4 shows a comparison between the fragility index described by the BSCNF model and the values of fragility. It can be understood that there is a good correlation between these two set of values. The result indicates that the parameter C_2 of the WLF equation can be described in terms of the parameters of the BSCNF model which have clear physical meaning as defined in Eq. 2.

The experimental data of the systems considered in the references [14] and [15] are available only in a limited range of temperatures. In Fig. 5, the temperature dependence of the viscosity for various ion conducting polymeric systems calculated through the BSCNF model is shown. For their calculation, values of *B* and *C* reported in Table 1 were used. From the figure, it is noted that the system in consideration is relatively fragile, as expected from the values of *B* and *C* shown in Fig. 2. As discussed above, as a gross behavior, we note that by decreasing the salt content, the fragility index decreases.

Conclusion

The BSCNF model, the VFT equation, and the WLF equation have been used to study the temperature dependence of the viscosity of ion conducting polymeric systems. The result indicates that the three models describe well the temperature dependence of the viscosity reported experimentally. The analysis based on the BSCNF model suggests that by increasing the salt content, the fragility index increases due to the decrease of the connectivity between the structural units. From the comparison of these models, it was shown that the BSCNF model could provide a physical interpretation to the empirical parameters used in other models.

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Table

Table 1 Numerical values of the parameters in the VFT (B_{VFT}, T_0, η_0), BSCNF (B, C) and WLF (C_1, C_2) equations for the polymeric systems.

Compounds	B_{VFT} (K)	T_0 (K)	η_0 (Pa·s)	B	C	C_1	C_2 (K)	T_g (K)	F	m
$NaCF_3SO_3$-PPG (1:8)	1352	217	$2.58\ 10^{-3}$	0.74	11.1	15.2	31.2	262	0.88	118
$NaCF_3SO_3$-PPG (1:16)	1264	191	$2.95\ 10^{-3}$	0.69	13.0	15.3	34.0	224	0.85	95
$NaCF_3SO_3$-PPG (1:40)	1113	178	$3.95\ 10^{-3}$	0.68	13.2	15.8	37.3	205	0.82	91
$LiClO_4$-PPG (1:8)	1283	229	$5.44\ 10^{-3}$	0.66	10.5	15.8	43.1	261	0.84	89
$LiClO_4$-PPG (1:16)	1594	183	$1.32\ 10^{-3}$	0.60	11.7	16.0	46.7	223	0.79	72
$LiClO_4$ -PPG (1:40)	1259	176	$2.70\ 10^{-3}$	0.59	11.8	16.2	44.0	204	0.78	70
$NaClO_4$ -PPO (1:16)	1243	203	$3.35\ 10^{-3}$	0.69	10.6	15.3	33.5	239	0.86	96
$NaClO_4$ -PPO (1:30)	915	205	$7.88\ 10^{-3}$	0.55	12.4	16.8	54.7	201	0.73	63
NaSCN -PPO (1:8)	1619	212	$1.15\ 10^{-3}$	0.70	11.9	15.2	35.8	259	0.86	101

The numbers in the parenthesis in the compounds indicate the mole ratio. The experimental values of the glass transition temperature (T_g) [14-15] and the fragilities calculated from Eq. 3 (m) and 8 (F) are also given.

Figure Captions

Fig. 1 Examples of fitting of the experimental data with the a) BSCNF model, the VFT equation and the b) WLF equation.

Fig. 2 Relationship between the values of parameters *B* and *C* determined for different polymeric systems**.**

Fig. 3 Relationship between the fragility index calculated from the BSCNF model, Eq. 3 and the value of the parameter C_2 in the WLF equation.

Fig. 4 Relationship between the fragility index calculated from the BSCNF model, Eq. 3 and the fragility given by Eq. 8.

Fig. 5 Temperature dependence of viscosity for various compositions of polymeric ion conducting systems obtained from Eq. 1. Experimental values of different polymeric systems are shown by symbols. The behavior of SiO_2 is also shown for comparison.

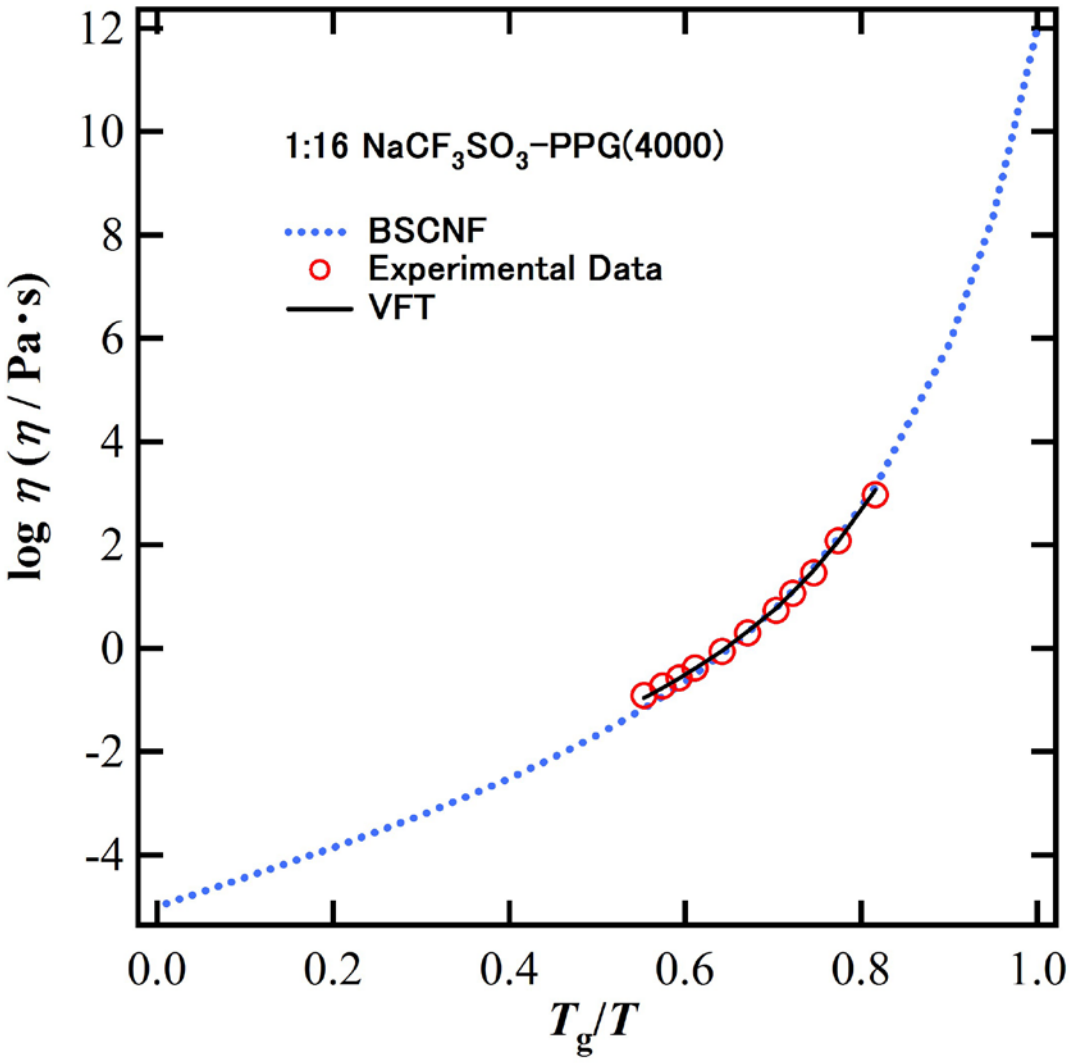
1:16 NaCF3SO3–PPG(4000)
BSCNF
Experimental Data
VFT
log η (η / Pa·s)
Tg/T
12
10
8
6
4
2
0
-2
-4
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 1 (a)

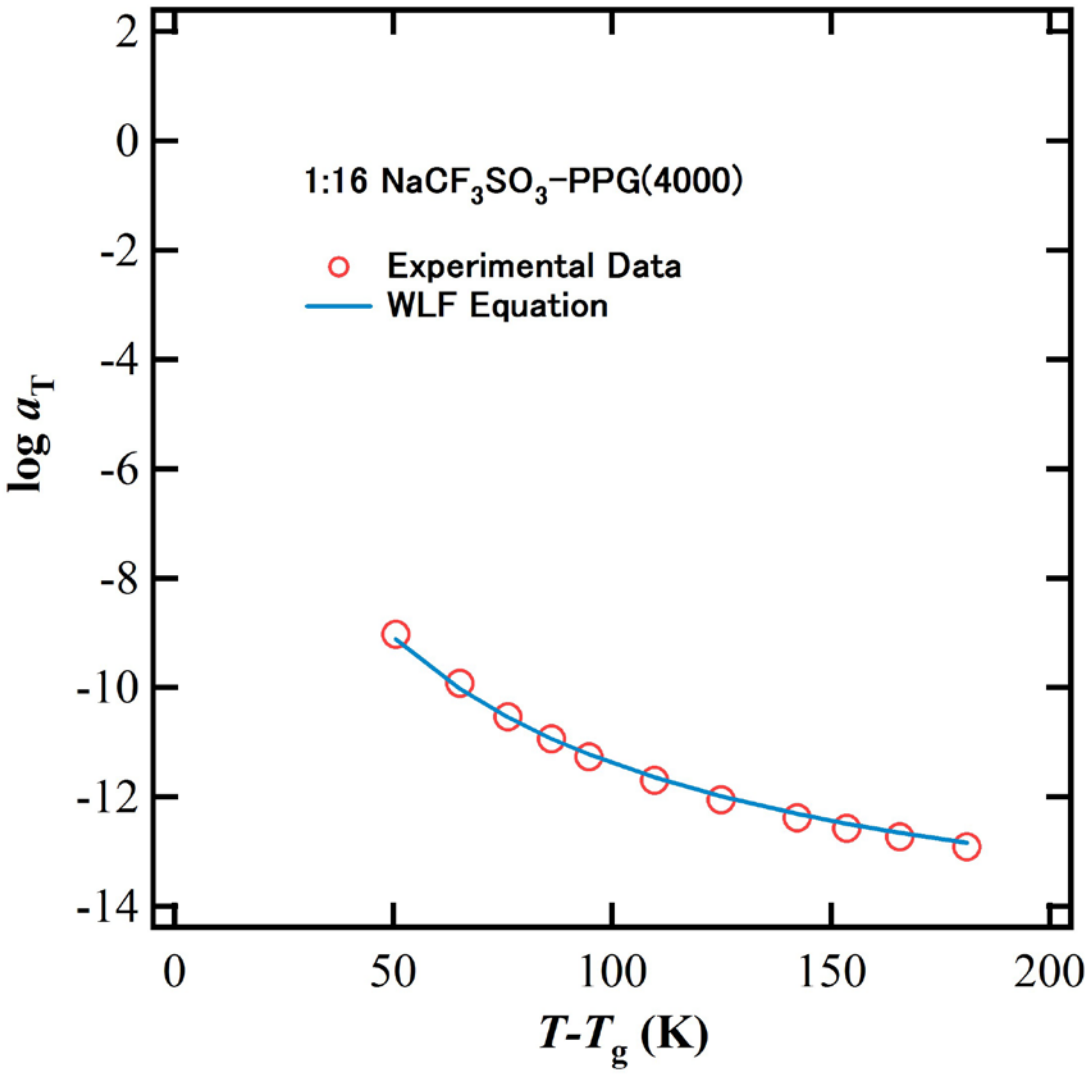
1:16 NaCF3SO3–PPG(4000)
Experimental Data
WLF Equation
log aT
T-Tg (K)
2
0
-2
-4
-6
-8
-10
-12
-14
0
50
100
150
200

Fig. 1 (b)

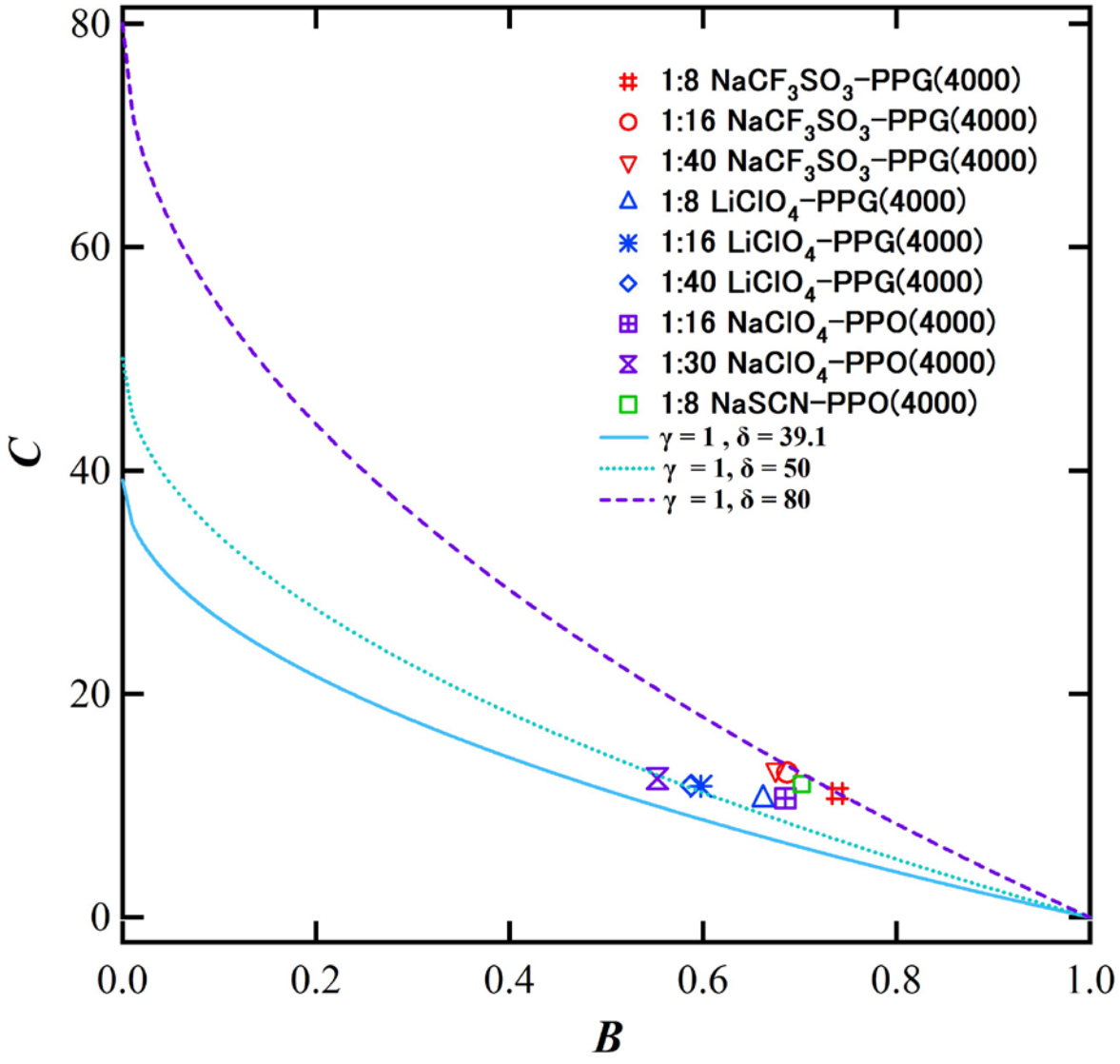
80
60
40
20
0
C
0.0
0.2
0.4
0.6
0.8
1.0
B
1:8 NaCF3SO3–PPG(4000)
1:16 NaCF3SO3–PPG(4000)
1:40 NaCF3SO3–PPG(4000)
1:8 LiClO4–PPG(4000)
1:16 LiClO4–PPG(4000)
1:40 LiClO4–PPG(4000)
1:16 NaClO4–PPO(4000)
1:30 NaClO4–PPO(4000)
1:8 NaSCN–PPO(4000)
γ = 1 , δ = 39.1
γ = 1, δ = 50
γ = 1, δ = 80

Fig. 2

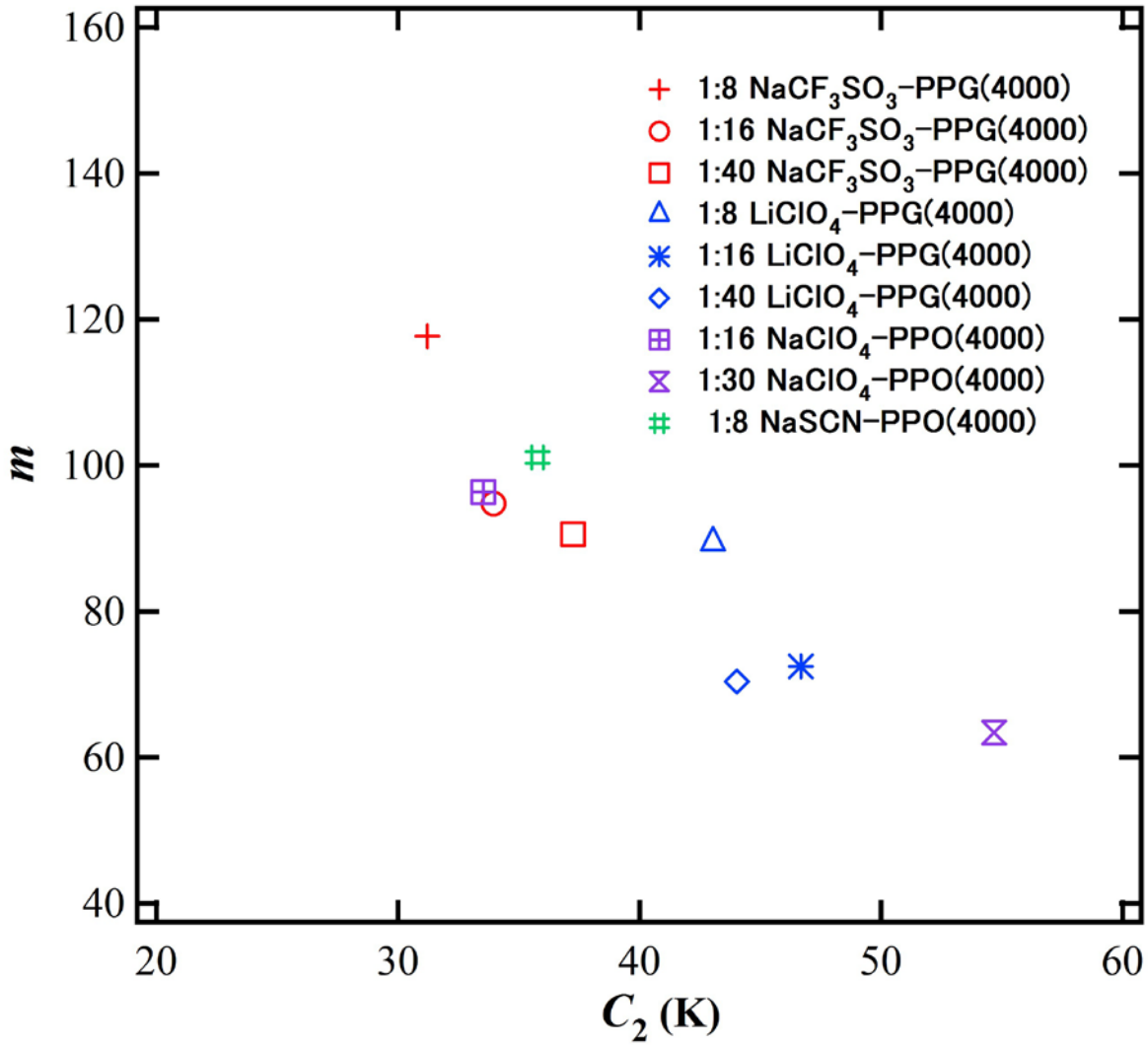
160
140
120
100
80
60
40
m
20
30
40
50
60
C_2 (K)
1:8 $NaCF_3SO_3$–PPG(4000)
1:16 $NaCF_3SO_3$–PPG(4000)
1:40 $NaCF_3SO_3$–PPG(4000)
1:8 $LiClO_4$–PPG(4000)
1:16 $LiClO_4$–PPG(4000)
1:40 $LiClO_4$–PPG(4000)
1:16 $NaClO_4$–PPO(4000)
1:30 $NaClO_4$–PPO(4000)
1:8 NaSCN–PPO(4000)

Fig. 3

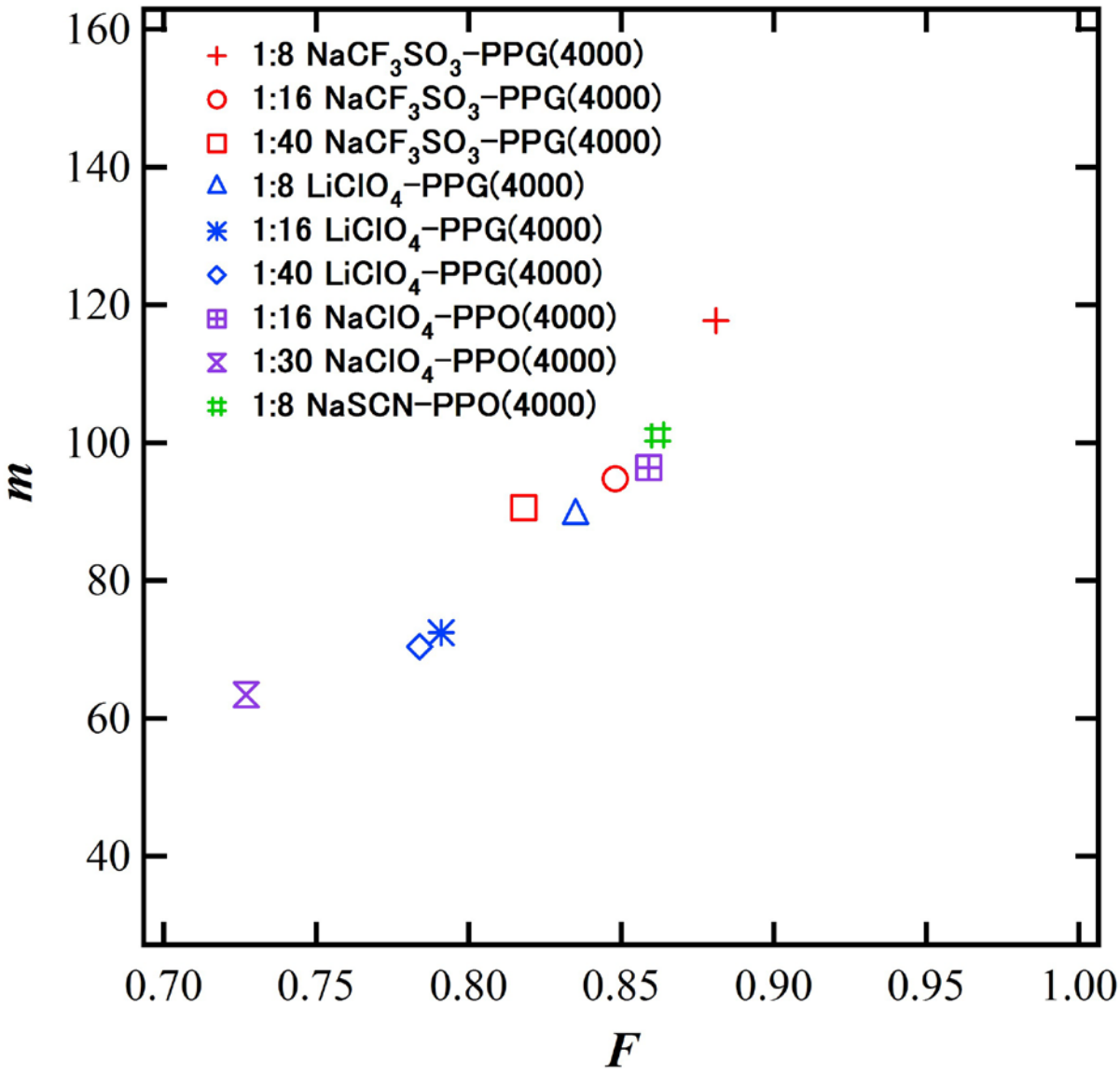
160
140
120
100
80
60
40
m
0.70
0.75
0.80
0.85
0.90
0.95
1.00
F
1:8 NaCF3SO3–PPG(4000)
1:16 NaCF3SO3–PPG(4000)
1:40 NaCF3SO3–PPG(4000)
1:8 LiClO4–PPG(4000)
1:16 LiClO4–PPG(4000)
1:40 LiClO4–PPG(4000)
1:16 NaClO4–PPO(4000)
1:30 NaClO4–PPO(4000)
1:8 NaSCN–PPO(4000)

Fig. 4

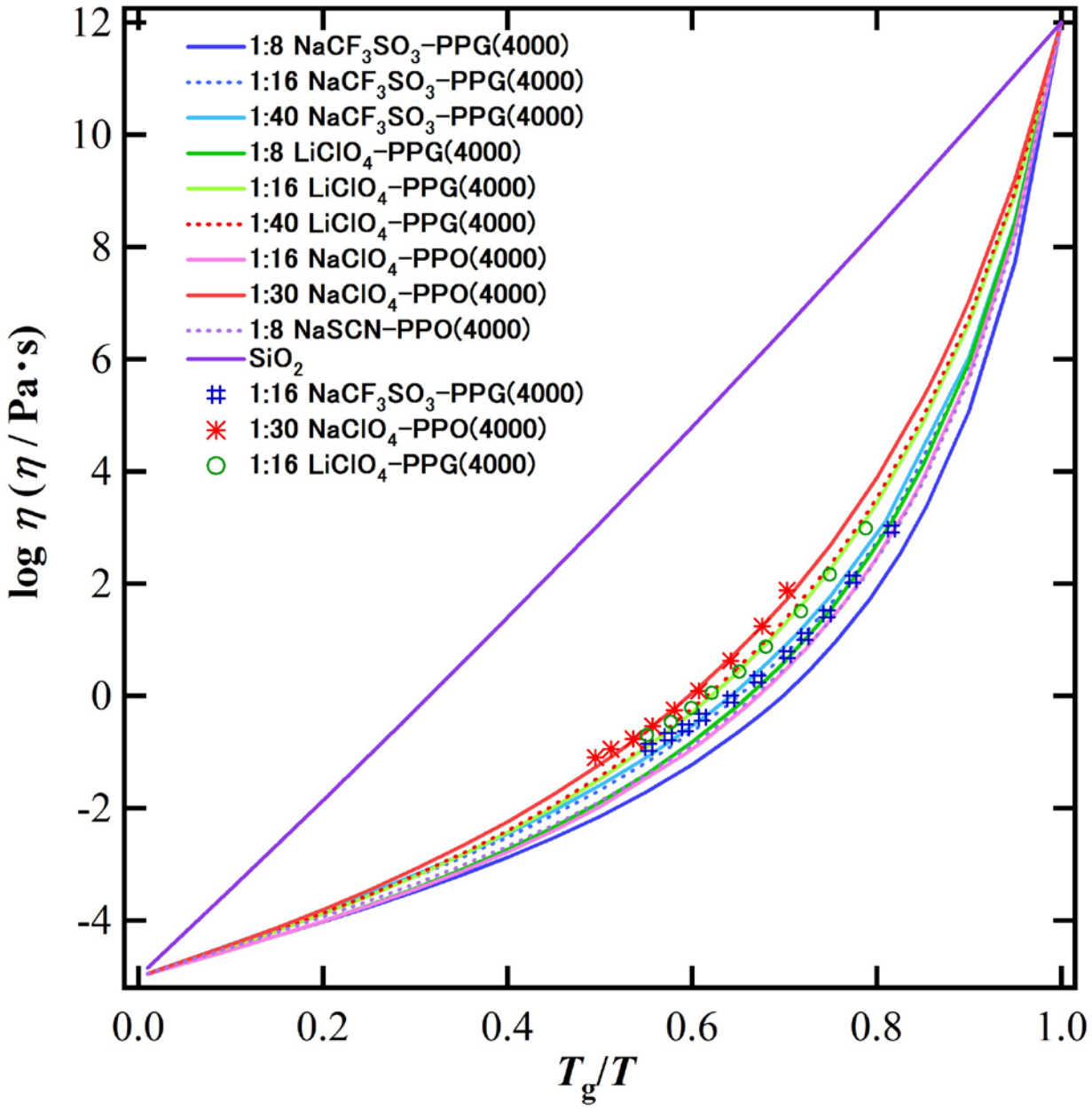
1:8 NaCF3SO3–PPG(4000)
1:16 NaCF3SO3–PPG(4000)
1:40 NaCF3SO3–PPG(4000)
1:8 LiClO4–PPG(4000)
1:16 LiClO4–PPG(4000)
1:40 LiClO4–PPG(4000)
1:16 NaClO4–PPO(4000)
1:30 NaClO4–PPO(4000)
1:8 NaSCN–PPO(4000)
SiO2
1:16 NaCF3SO3–PPG(4000)
1:30 NaClO4–PPO(4000)
1:16 LiClO4–PPG(4000)
log η (η / Pa·s)
Tg/T
12
10
8
6
4
2
0
-2
-4
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 5