Development of a model for analyzing the temperature dependence of the viscosity of ion conducting polymers and ionic liquids

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Abstract

The bond strength-coordination number fluctuation (BSCNF) model of the viscosity developed by the authors considers that the viscous flow occurs by breaking and twisting the connections between the structural units that form the melt. The analytical expression of the viscosity that results from such processes is written in terms of the average bond strength, the average coordination number, and their fluctuations of the structural units. In the present study, we use the BSCNF model to investigate the temperature dependence of the viscosity of ion conducting polymers $LiClO_4$-PPG and $NaCF_3SO_3$-PPG, and ionic liquids [bmim][PF_6], [bpy][BF_4], [bmpro][$(CF_3SO_2)_2N$], [bpy] [$(CF_3SO_2)_2N$] and [bmim][$(CF_3SO_2)_2N$]. For ion conducting polymers, the analysis of the α-relaxation process is also presented. A case study done for ionic liquids indicates that the cooperativity for molecular motion which is evaluated from the viscosity analysis can be correlated with the diffusion coefficients and the ionic conductivities. The results of this study indicate that the BSCNF model is an effective model

that could be used to analyze and interpret the measured temperature dependence of the viscosity.

Keywords: viscosity, fragility, ion conducting polymers, ionic liquids, bond strength-coordination number fluctuation model

1. Introduction

It is well known that by decreasing the temperature of the melt, the glass formation process takes place. This process is accompanied by a drastic increase of viscosity. In many practical situations such as processing of materials, industrial plants, petroleum processing, foods, pharmaceutical and medical sciences, geophysical science, etc. controlling the viscosity is of primordial importance [1-5]. It is also important to understand the transport properties in complex liquids, for instance, understand the relationship between viscosity, diffusivity and conductivity [6]. However, from the fundamental point of view, the understanding of this relationship is complex and incomplete. Reflecting this situation, in recent years, much attention has been paid to clarify the mechanism of glass transition and structural relaxation in supercooled liquids and polymeric systems [7-11].

Concerning the temperature dependence of the viscosity, many theories and models have been proposed. Among these, the Vogel-Fulcher-Tamman (VFT) [12-14] and the Williams-Landel-Ferry (WLF) equations [15] are well known. These expressions have been used quite frequently to describe the non-Arrhenius temperature dependence that many supercooled and polymeric systems exhibit. Previously, the bond strength-coordination number fluctuation (BSCNF) model of the viscosity has been proposed by one of the authors [16]. According to this model, the viscosity is described in terms of the average bond strength, the average

coordination number, and their fluctuations of the structural units that form the melt. The viscosity is controlled by the relaxation of these units. The model has been successfully used to analyze the temperature dependence of the viscosity of various kinds of materials including oxides, chalcogenides, metals, ionic conductors and polymeric systems [16-21]. Originally, the BSCNF model was proposed with the aim to understand the origin of the fragility of the materials. Subsequent studies have revealed that the model is more relevant than expected. For instance, as will be shown in this study, the model provides a frame to understand the correlation between different physical quantities.

In the present study, after giving a brief introduction of the BSCNF model, we applied it to some ion conducting polymers and ionic liquids in order to analyze the temperature dependence of the viscosity. Our results indicate that, in addition to the notion gained through traditional models, the BSCNF model provides a new understanding on material properties of these systems. For instance, by linking the parameters of our model to other models such as the VFT equation, an expression that relates to the "ideal glass transition temperature" is obtained. From the application of the BSCNF model to ionic liquids, it is shown that the cooperativity of molecular motion is correlated with the transport properties such as the diffusivity and the conductivity.

2. Model

The BSCNF model was introduced based on the physical picture that the viscous flow of the melt occurs by breaking or twisting the bonds between the structural units that form the glass forming liquids [16]. Generally, amorphous materials and complex liquids are characterized by their disorder or randomness of atomic or molecular configurations [22]. In the BSCNF model, the disordered molecular configuration of glass forming liquids is

considered to be formed by an agglomeration of structural units. Therefore, according to this model, the temperature dependence of the viscosity is described in terms of the mean bond strength E_0 [J·mol^{-1}], the mean coordination number Z_0, and the fluctuations ΔE [J·mol^{-1}], ΔZ, of the structural units that form the melt. The expression of the viscosity is given by [16]

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

where

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

In the above equation, $x = T_g/T$, where T_g [K] is the glass transition temperature. $R = 8.314$ [J·mol^{-1}·K^{-1}] is the gas constant. η_0 [Pa·s] and η_{T_g} [Pa·s] are the viscosities at the high temperature limit and at T_g respectively. In the present analysis, the shift factor $a_T = \ln(\eta_{T_g}/\eta_0)$ is used as a parameter to fit the experimental data.

In the BSCNF model, the glass-forming liquids are characterized by the parameters B and C, whose numerical values are determined by fitting to the experimental data. From Eq. (2) we note that B gives the degree of the fluctuation and C gives the degree of the mean binding energy between the structural units. Furthermore, the values of B and C obtained have been used to locate the glassy materials in a map defined in the B-C plane [16, 17, 23, 24]. The mapping provides a way to understand the trends of physical properties and the composition dependence of glassy materials [17, 18, 24, 25]. Further explanations of the model are given elsewhere [16-21, 23-25].

3. Results and discussion

3.1 Polymer electrolytes

Ion conducting polymers have received tremendous interest due to their technological importance in a wide variety of devices such as batteries, fuel cells, supercapacitors, sensors, etc. [10, 26, 27]. In this section, fundamental aspects of these materials are considered based on the BSCNF model described above. The effectiveness of the model in the analysis of the temperature dependence of the viscosity is shown in Fig. 1 and Fig. 2, for the cases of polymer electrolytes and ionic liquids, respectively. Figure 1 (a) shows the temperature dependence of the viscosity η of polymer electrolytes LiClO$_4$-PPG (poly propylene glycol) and NaCF$_3$SO$_3$-PPG. The experimental values of the viscosity measured using conventional viscometer are taken from the literature [28]. The numbers before the compound names indicate the mole ratio between salt and polymer. On the other hand, Figure 1 (b) shows the temperature dependence of the relaxation time τ of the α-process for poly ethylene oxide (PEO)-based neat and plasticized polymers with dioctyl phthalate (DOP) and dimethyl sulfoxide (DMSO), which were determined from dielectric impedance spectra measurements [29]. It is noted that the theoretical curves described by Eq. (1) fit well the experimental data. The degree of reproducibility of the experimental data is high as indicated by the R^2 parameters given in Table 1. The relaxation time τ and the viscosity η are connected mutually through the Maxwell relation $\eta = G_\infty \tau$, where G_∞ is the infinite frequency shear modulus.

In Figure 1, the experimental data [28, 29] are also analyzed by the VFT equation. The values of the parameters of both equations are given in Table 1. We note that the behaviors of the BSCNF model and the VFT equation are indistinguishable from each other. This observation indicates that the non-Arrhenius temperature dependence usually described by the

VFT equation can be understood in the light of the BSCNF model. In our previous study, it was shown that the VFT-like behavior arises when

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

(3)

In other words, the VFT-like behavior is observed when the magnitudes of the energy and coordination number fluctuation are equal [23]. In this sense, the applicability of the BSCNF model is wider than that of VFT equation.

Traditionally, in most of the cases, the dependence of the viscosity or the relaxation time with temperature has been analyzed using the VFT equation or the WLF equation [12-15]. These equations are given respectively by

$$\eta = \eta_0 \exp\left(\frac{B_{\text{VFT}}}{T - T_0}\right),$$

(4)

and

$$\eta = \eta_{Tg} \exp\left(\frac{-C_1(T - T_g)}{C_2 + (T - T_g)}\right)$$

(5)

In Eq. (4), η_0 [Pa·s] is the viscosity at the high temperature limit, and B_{VFT} [K] and T_0 [K] are the parameters related with the activation barrier and the glass transition, respectively. In particular, T_0 is usually called "Vogel temperature" or "ideal glass transition temperature" which describes the divergence of the viscosity. Meanwhile, in the WLF equation written as Eq. (5), η_{Tg} [Pa·s] is the viscosity at T_g [K] which is used as the reference temperature to fit the experimental data. C_1 and C_2 [K] are constants [22]. The VFT and the WLF equations are mathematically equivalent and the parameters of Eqs. (4) and (5) are interrelated by [30]

$$B_{\text{VFT}} = C_1 C_2,$$

(6)

$$T_0 = T_g - C_2,$$

(7)

and

$$\eta_0 = \eta_{Tg}\exp(-C_1). \tag{8}$$

In our previous studies [19, 20, 23], we reported that the parameters of the BSCNF model defined in Eq. (2) are related with T_0. This relationship is given by

$$\frac{T_0}{T_g} = 1 - \frac{\left(\frac{1+\sqrt{B^*}}{1-B^*}\right)C^* - \frac{1}{2}\ln(1-B^*)}{\ln(10)m} , \tag{9}$$

where B^* and C^* are the parameters of the BSCNF model satisfying the condition given in Eq. (3) and m is the fragility index [23]. As mentioned above, the VFT equation implies the divergence of the viscosity when the temperature decreases, from T to T_0. However, such a behavior is not observed experimentally [31]. In other words, even nowadays, the interpretation of T_0 is still controversial. In this regards, it should be noted that Eq. (9) provides an expression that relates T_0 to other quantities which are observable. Based on this equation, we have reported the relationship between T_0 and the temperature range of cooperativity [19, 20]. The analysis applied to ion conducting polymers revealed that the fragility is correlated with the cooperativity of the molecular motions and that the high value of fragility corresponds to weak molecular interactions. We have also reported the relation between T_0 evaluated through the BSCNF model and the stretched exponent β [32] of the Kohlrausch-Williams-Watts (KWW) relaxation function, $\phi(t) = \phi_0\exp[-(t/\tau)^\beta]$ [33, 34]. As it is well documented, the KWW function is often used to describe the behavior of relaxation in glassy and polymeric materials [35-38]. β takes the values less than unity, resulting in the non-Debye relaxation. ϕ_0 is the initial relaxation function. Interestingly, it has been discussed that β can be related with the parameters of the VFT equation and the dimensionality of glass-

forming materials [39]. This observation implies that the dimensionality of the cross-linked network structure in glassy materials and polymers can be discussed in terms of the parameters of the BSCNF model.

3.2 Ionic liquids

In the fields of environmental science and materials science [40-43], the room temperature ionic liquids or simply called "ionic liquids" have gained much interest due to the excellent material properties such as non-flammability, negligible vapor pressure, high ionic conductivity, etc. [44]. Analogously with the polymeric systems, the VFT equation has been commonly used in the analysis of the transport property of ionic liquids [45-48].

In our previous works we used the BSCNF model to discuss the transport property of ionic liquids [49, 50]. The results indicated that the model could be a promising model to analyze the experimental data of these materials. Figure 2 shows the analysis of the viscosity of ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]), 1-butylpyridinium tetrafluoroborate ([bpy][BF$_4$]), N-butyl-N-methylpyrrolidinium, 1-butylpyridinium, and 1-butyl-3-methylimidazolium as cations with bis(trifluoromethane sulfonyl)imide as anion ([bmpro][(CF$_3$SO$_2$)$_2$N], [bpy] [(CF$_3$SO$_2$)$_2$N], and [bmim][(CF$_3$SO$_2$)$_2$N]. With the exception of [bmim][(CF$_3$SO$_2$)$_2$N]), these compounds are analyzed for the first time in this study. The parameters of the model for these materials are given in Table 1. As we can see from Figure 2 (a), Eq. (1) reproduces quite well the viscosity data of the ionic liquids investigated. For comparison, in Figure 2 (a), the same data are analyzed using the VFT equation. The experimental data of the viscosity shown in this figure, as well as the data of diffusion coefficients and ionic conductivities that will be shown in Figure 3 are taken from refs. [45-48]. The measurement techniques used in the determination

of the transport coefficients were viscometer for the viscosity, pulse-field-gradient spin-echo NMR for the diffusion coefficients, and impedance spectroscopy for the conductivity [46-48]. In Figure 2 (a), it is observed that both equations reproduce with a good agreement the observed behaviors. This result suggests that the physical property of the ionic liquids can be understood from a point of view that differs from the VFT equation. For instance, the application of the BSCNF model to the viscosity analysis enables one to discuss the cooperativity among cations and anions in ionic liquids.

In the BSCNF model, the cooperativity involved in the thermally activated viscous flow is defined as $N_B = E_\eta / (E_0 Z_0)$ [17], where E_η is the activation energy for the viscous flow and $E_0 Z_0$ is the average binding energy per structural unit. In the case where the BSCNF model is applied to ionic liquids, the cations and anions are regarded as the structural units. The temperature dependence of the cooperativity $N_B(T)$ is given by

$$N_{\mathrm{B}}(T) = \frac{\ln(10)}{C} \frac{\mathrm{d}}{\mathrm{d}(T_{\mathrm{g}}/T)} \log \eta(B,C,T). \tag{10}$$

At $T = T_{\mathrm{g}}$, this expression reduces to the original definition mentioned above. It is also noted that at T_{g}, the term $\mathrm{d}\log\eta/\mathrm{d}(T_{\mathrm{g}}/T)$ is the expression of the fragility index m [37], which is widely used as a parameter to characterize the glass-forming materials [9]. Figure 2 (b) shows the behavior of $N_{\mathrm{B}}(T)$ for the ionic liquids whose viscosities are investigated in Figure 2 (a). We can see that N_{B}, or in other words, the number of ions moving cooperatively increases with the decrease of temperature. Figure 2 (b) suggests that in the viscous flow of ionic liquids, the rearrangement of about 4-10 ions is involved. This result reinforces the idea that the BSCNF model is functional and relevant in the study of the properties of materials, such as ion conducting polymers and ionic liquids.

Furthermore, the expression given in Eq. (10) allows one to investigate the relationships with other transport coefficients [50]. As shown in Figure 3, it is interesting to note that the cooperativity N_B can be correlated to the diffusivity and the ionic conductivity. In Figure 3 (a), the relation between the diffusion coefficient D and the cooperativity N_B is plotted for some typical ionic liquids. The straight lines shown in the figure are described by $\ln(D /\mathrm{cm}^2\mathrm{s}^{-1}) = \zeta \ln(N_B^{-1}) + \mathrm{const.}$. The slope of the line gives the ratio between the activation energies for D and N_B (i.e., $\zeta = E_D/E_{NB}$). On the other hand, Figure 3 (b) shows the relation between the ionic conductivity σ and the cooperativity N_B. The straight lines shown are described by $\ln(1/\sigma T /\mathrm{S}^{-1}\mathrm{cm}\cdot\mathrm{K}^{-1}) = \zeta \ln(N_B) + \mathrm{const.}$ From both figures, a clear linear relationship between these quantities is confirmed. We also note that the slopes shown in the figures are almost temperature independent. This means that the ratio between the activation energies, for instance, between E_D and E_{NB} in Figure 3 (a), is almost constant. Here, E_D and E_{NB} are defined by $D = D_0\exp(-E_D/RT)$ and $N_B = N_{B0}\exp(E_{N_B}/RT)$, respectively [50]. In the framework of the BSCNF model, the pre-exponential factor $N_{B0}=1$ holds, which physically indicates that at the high temperature limit, each structural unit relaxes independently. Concerning the relationship between $\ln[(\sigma T)^{-1}]$ and $\ln(N_B)$ given in Figure 3 (b), the Nernst-Einstein (NE) relation, $\sigma T \propto D$ [6, 51], is taken into consideration. On the other hand, Figure 3 (a) suggests the relation $D \propto (N_B^{-1})^\zeta$, where ζ is given by $\zeta = E_D/E_{N_B}$ which is almost temperature independent. Thus, we obtain

$$\sigma T \propto D \propto (N_B^{-1})^\zeta. \tag{11}$$

According to the BSCNF model, N_B gives the number of structural units involved in the viscous flow. In other words, the viscous flow occurs by breaking or twisting the weaker parts

of the bonds that connect the structural units. With this in mind, the result showed in Figure 3 suggests that the process of diffusivity and ionic migration is closely related with the bond-breaking and bond-switching between the diffusing elements (or the charge careers) and the structural units. This picture does not contradict the results of MD simulations [52] which have revealed a hopping mechanism in lithium-salt containing ionic liquids. It is thus thought that in structurally disordered materials, the diffusion process is not likely to occur without involving the formation and disruption of bonds. This picture of ion transport has much in common with the bond fluctuation model of superionic conductors [53]. The result of cooperativity N_B described above illustrates how the BSCNF model can be used to discuss the transport property of ionic liquids.

4. Conclusion

In the present study, the BSCNF model was used to investigate the temperature dependence of the viscosity of ion conducting polymers and ionic liquids. It was shown that the BSCNF model describes quite well the experimental behaviors observed in these materials. The analysis indicates that the BSCNF model is a relevant model to discuss the transport property of ion conducting polymers and ionic liquids in addition to the traditional VFT and WLF equations. The analysis of the cooperativity based on the BSCNF model indicated that about 4-10 structural units are involved in the viscous flow of ionic liquids. Furthermore, it was shown that the cooperativity of molecular motion N_B can be correlated with the diffusion coefficient D and the ionic conductivity σ. A relationship between σ, D and N_B was presented. This relation enables one to discuss quantitatively the transport coefficients of ionic liquids in terms of cooperativity.

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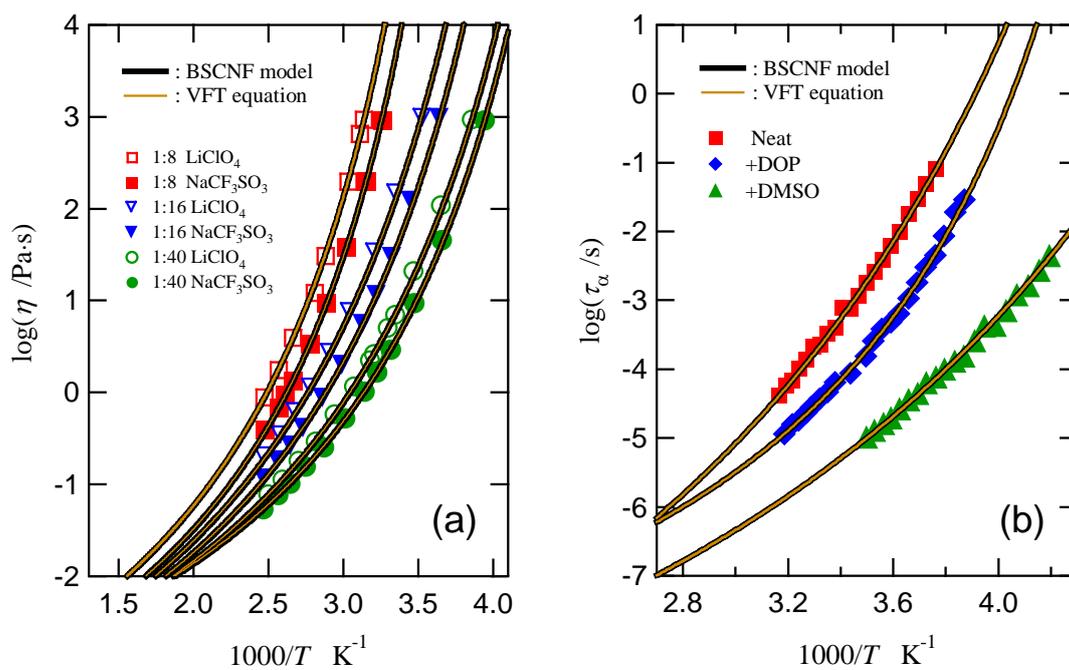
Figure 1. (a) Temperature dependence of the viscosity of polymer electrolytes LiClO$_4$-PPG (poly propylene glycol) and NaCF$_3$SO$_3$-PPG. (b) Temperature dependence of the α-relaxation time of PEO-based neat and plasticized polymers with dioctyl phthalate (DOP) and dimethyl sulfoxide (DMSO).
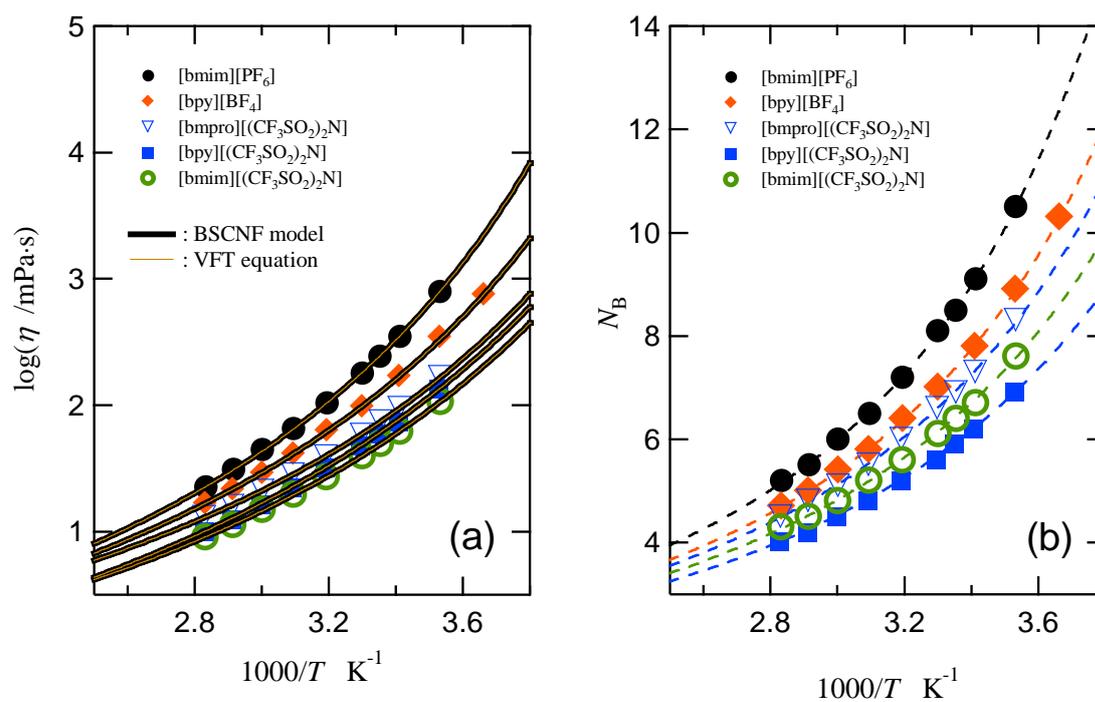
Figure 2. (a) Temperature dependence of the viscosity of ionic liquids analyzed using the BSCNF model and the VFT equation. (b) Temperature dependence of the cooperativity N_B of ionic liquids. The broken lines are the theoretical curves calculated using the BSCNF model.
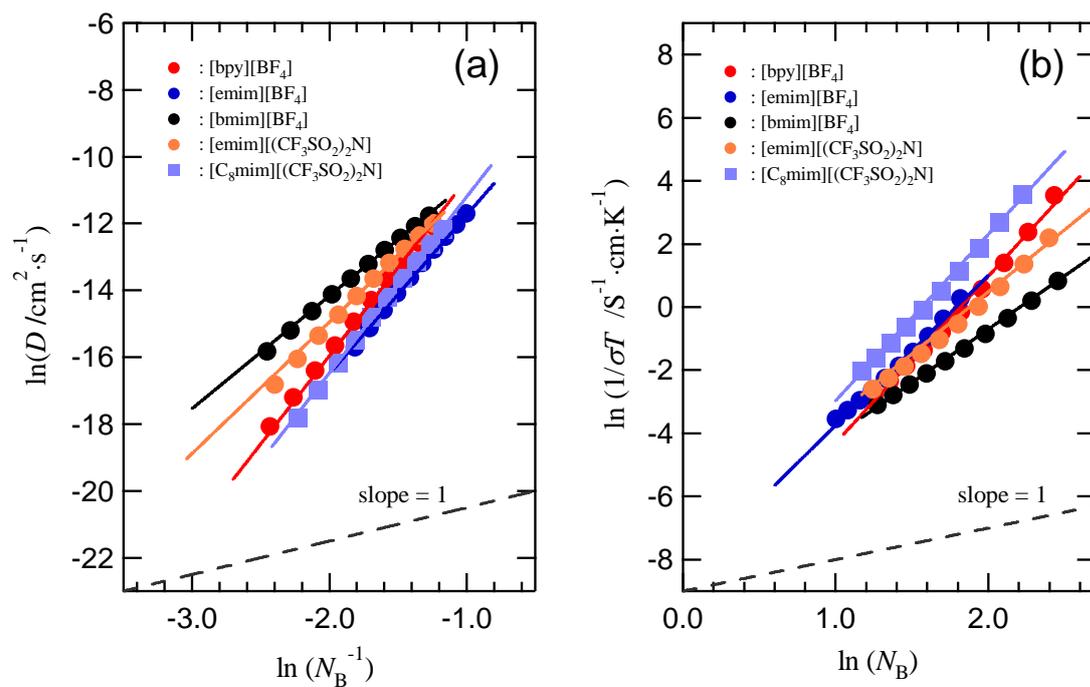
Figure 3. (a) Relation between $\ln D$ and $\ln(N_B^{-1})$. (b) Relation between $\ln[(\sigma T)^{-1}]$ and $\ln(N_B)$.

	VFT equation			BSCNF model			
Polymer electrolytes	B_{VFT} (K)	T_0 (K)	$\log(\eta_0/\text{Pa·s})$	B	C	a_T	R^2
1:8 LiClO$_4$ in PPG(4000)	1454	221	-3.50	0.715	5.42	35.68	0.99906
1:8 NaCF$_3$SO$_3$ in PPG(4000)	1311	219	-3.52	0.736	4.99	35.73	0.99984
1:16 LiClO$_4$ in PPG(4000)	1434	190	-3.63	0.685	6.11	35.98	0.99953
1:16 NaCF$_3$SO$_3$ in PPG(4000)	1290	189	-3.55	0.707	5.61	35.79	0.99947
1:40 LiClO$_4$ in PPG(4000)	1181	179	-3.44	0.713	5.43	35.54	0.99958
1:40 NaCF$_3$SO$_3$ in PPG(4000)	1031	182	-3.27	0.743	4.76	35.17	0.99979
PEO-based neat and plasticized ionomers	B_{VFT} (K)	T_0 (K)	$\log(\tau_0/\text{s})$	B	C	$a_T{}^*$	R^2
Neat	2368	163	-11.12	0.618	11.27	53.24	0.99751
with dioctyl phthalate (DOP)	1142	192	-8.99	0.794	5.18	48.34	0.99847
with dimethyl sulfoxide (DMSO)	1801	141	-10.40	0.643	10.11	51.58	0.99749
Ionic liquids	B_{VFT} (K)	T_0 (K)	$\log(\eta_0/\text{mPa·s})$	B	C	a_T	R^2
[bmim][PF$_6$]	725	194	-0.623	0.735	3.07	22.16	0.99977
[bpy][BF$_4$]	693	186	-0.578	0.735	3.05	22.05	0.99969
[bmpro][(CF$_3$SO$_2$)$_2$N]	626	182	-0.476	0.749	2.84	21.82	0.99962
[bpy][(CF$_3$SO$_2$)$_2$N]	734	173	-0.768	0.711	3.43	22.49	0.99980
[bmim][(CF$_3$SO$_2$)$_2$N]	649	178	-0.649	0.741	3.00	22.22	0.99946

Table 1. Values of the parameters of VFT equation and BSCNF model for the materials investigated in Figure 1 and Figure 2. The shift factors are defined by $a_T = \ln(\eta_{Tg}/\eta_0)$ and $a_T{}^* = \ln(\eta_{Tg}/\eta_0)$, respectively. The last column indicates the R^2 parameter.