# Correlation between Ionic Diffusion and Cooperativity in Ionic Liquids

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A new physical quantity $N_B$ is proposed to analyze the transport properties of ionic liquids. The quantity, which is defined from our model of viscosity, the Bond Strength – Coordination Number Fluctuation (BSCNF) model, quantifies the degree of cooperativity among the constituent elements in viscous liquids. It is shown that the new quantity $N_B$ provides additional information to the conventional transport coefficients such as viscosity, diffusion coefficient, and ionic conductivity. In the present work, the temperature dependence of the activation energies for the diffusion coefficient and the cooperativity described by $N_B$ are discussed for several kinds of ionic liquids. The result obtained suggests that the activation energies for the diffusion coefficient and $N_B$ are strongly correlated.

KEYWORDS: ionic liquids, viscosity, diffusion coefficient, cooperativity, activation energy

## 1. Introduction

During the last years, room-temperature ionic liquids, or simply called ionic liquids have received considerable interest due to their rich properties such as non volatility, negligible vapor pressure, thermal and chemical stability, high ionic conductivity, etc [1, 2]. From an applied point of view, ionic liquid is one of the key energy-related materials, because it has the possibility to replace the conventional electrolytes used in lithium ion batteries [3]. To explore its excellent material properties and extend their further applicability, fundamental studies on physicochemical properties of ionic liquid are indispensable. The main purpose of this study is to give a reliable model to analyze the transport coefficients of ionic liquids in place of the Vogel-Fulcher-Tammann (VFT) equation, and to understand microscopically the transport properties of ionic liquids from a unified point of view.

Previously, a model for the temperature dependence of the viscosity of the melt has been proposed by one of the authors [4]. The model, which is called the Bond Strength – Coordination Number Fluctuation (BSCNF) model, describes the temperature dependence of the viscosity in terms of the mean values of the bond strength $E_0$, the coordination number $Z_0$, and their fluctuations $\Delta E$, $\Delta Z$ of the structural units that form the melt. In our previous study, a quantity $N_B$ which gives the number of structural units involved in the thermally activated viscous flow has been introduced [5]. In addition, it has been shown that [6] the quantity $N_B$ is closely related to the well-known concept used in the glass transition phenomena, the cooperatively rearranging region (CRR) in the theory of Adam and Gibbs [7]. Thus, $N_B$ gives the degree of cooperativity within the viscous liquids. However, $N_B$ was defined at the glass transition temperature $T_g$. In the present report, it is shown that $N_B$ can be described as a function of temperature. From this finding, we can obtain an analytical expression for the temperature dependence of $N_B$.

By applying the extended concept of the cooperativity described by $N_B$ to some ionic liquids, we will discuss the temperature dependence of the viscosity $\eta$ and the diffusion coefficient $D$ for six different kinds of ionic liquids, (1) $BPBF_4$, (2) $EMIBF_4$, (3) EMITFSI, (4) $[bmim][(CF_3SO_2)_2N]$, (5) $[C_6mim][(CF_3SO_2)_2N]$, and (6) $[C_8mim][(CF_3SO_2)_2N]$. The names of these materials are given in Table I. The experimental data used in this work are taken from the literature [8, 9]. More specifically, we will discuss the relations between the activation energies for the diffusion coefficient, the viscosity, and $N_B$. These activation energies are denoted as $E_{Diff.}$, $E_\eta$, and $E_{NB}$, respectively.

Table I. Ionic liquids investigated in the present study. The experimental data are taken from refs. 8 and 9.

| No. | Materials |
|---|---|
| (1) | 1-butylpyridinium tetrafluoroborate |
| (2) | 1-ethyl-3-methylimidazolium tetrafluoroborate |
| (3) | 1-ethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide |
| (4) | 1-butyl-3-methylimidazolium $[(CF_3SO_2)_2N]$ |
| (5) | 1-hexyl-3-methylimidazolium $[(CF_3SO_2)_2N]$ |
| (6) | 1-octyl-3-methylimidazolium $[(CF_3SO_2)_2N]$ |

## 2. Temperature dependence of transport properties in ionic liquids

### *2.1 BSCNF model of viscosity*

Ionic liquids are known as good glass-formers, that is, many ionic liquids can be easily supercooled. For most of the ionic liquids, it is known that the temperature dependence of the viscosity follows the phenomenological VFT equation, $\eta = \eta_0 \exp\{B_{VFT}/(T-T_0)\}$, where, $\eta_0$ is the pre-exponential factor, $B_{VFT}$ and $T_0$ are the fitting parameters determined by the viscosity measurement. It is known that the VFT equation reproduces well the experimental data. On the other hand, the BSCNF model also reproduces well the actual data of the viscosity. According to the BSCNF model, the viscosity is expressed as [4]

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

where

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

Here, $\eta_0$ and $\eta_{Tg}$ are the viscosities at the high temperature limit and at the glass transition temperature $T_g$. $R$ is the gas constant. In our model parameters given in Eq. (2), $B$ gives the degree of the fluctuations described by the binding energy fluctuation $\Delta E$, and the coordination number fluctuation $\Delta Z$. On the other hand, $C$ gives the degree of the mean total binding energy $E_0Z_0$ between the structural units that form the melt. We have demonstrated that many types of glass-forming liquids such as covalent, metallic, molecular, and polymeric systems can be characterized with $B$ and $C$ [5]. Recently, it has been also found that when the parameters $B$ and $C$ satisfy the following relation,

$$C = \frac{2\gamma(1-B)}{2\gamma + \sqrt{B}(1+\gamma^2)} \left[ \ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right], \tag{3}$$

where

$$\gamma = \frac{|\Delta E| / E_0}{|\Delta Z| / Z_0} = 1, \tag{4}$$

the viscosity behavior described by Eq. (1) reproduces perfectly the viscosity behavior described by the VFT equation [10]. In the following, in the case where the BSCNF model and the VFT equation become identical, the set of parameters ($B$, $C$) is denoted as ($B^*$, $C^*$).

In Fig. 1, the temperature dependences of the viscosity for 6 different ionic liquids are shown. The experimental data are taken from refs. 8 and 9. In these papers, the viscosity behaviors are analyzed by the VFT equation. Therefore, the values of the parameters of the VFT equation, $\eta_0$, $B_{VFT}$, and $T_0$ are available [8, 9]. In our model given in Eq. (1), we need the value of $\eta_{Tg}$. However, some ionic liquids given in Table I such as $EMIBF_4$ are known as ionic liquids that crystallize at low temperatures. Thus, in this study, the values of $\eta_{Tg}$ are determined by substituting the glass transition temperature $T_g$ into the VFT equation. The values of $B^*$ and $C^*$ are also shown in Fig. 1. We recognize that the BSCNF model given by Eq. (1) reproduces exactly the behavior described by the VFT equation when the parameters $B^*$ and $C^*$ are used. The material parameters used in the viscosity analysis are given in Table II.

*2.2 Cooperativity of ionic motions: The new quantity $N_B$*

In our previous paper, a new quantity $N_B$ which gives the number of structural units involved in the thermally activated viscous flow has been introduced [5]. The definition of the quantity $N_B$ is given by $N_B \equiv E_\eta/(E_0Z_0)$, where, $E_\eta$ is the activation energy for viscous flow at and near $T_g$. The product $E_0Z_0$ indicates the average total binding energy per one structural unit. Previous studies have shown that for the metallic glass $La_{55}Al_{25}Ni_{20}$, $N_B \approx 7.6$ [5], and for a superionic conducting glass $AgI\text{-}Ag_2O\text{-}B_2O_3$, $N_B \approx 8.3$ [11]. As exemplified in these cases, $N_B$ gives quantitatively the degree of the cooperativity in viscous liquids. More specifically, it indicates how many structural units are

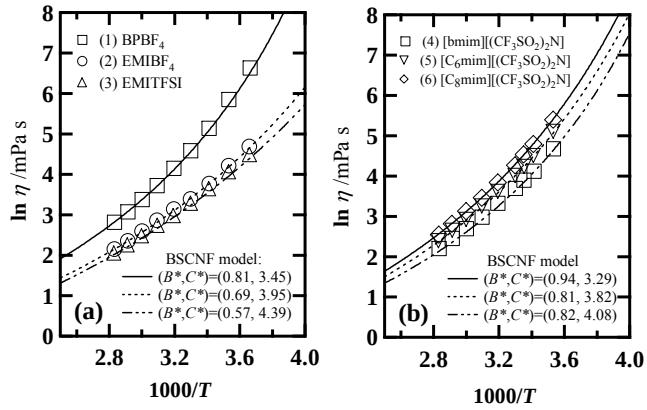


Fig. 1. Temperature dependence of the viscosity for 6 kinds of ionic liquids, Materials (1) - (3) and (4) - (6) are shown in figures (a) and (b), respectively.

involved in the thermally activated viscous flow near $T_g$. In the present study, we consider cations and anions in ionic liquids as structural units.

In our previous study, it has been shown that $N_B$ can be described analytically in terms of $B$ and $C$ [6]. It is written as

$$N_B(B,C) = \frac{B - C + 2\left[ \ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right]}{C(1-B)}. \tag{5}$$

The concept of $N_B$ described by Eq. (5) can be extended to any other temperature as follows. According to the BSCNF model, the fragility index $m$ is given by [4, 6]

$$m = \frac{1}{\ln(10)} \left\{ \frac{B - C + 2\left[ \ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right]}{(1-B)} \right\}. \tag{6}$$

By using Eq. (6), Eq. (5) is expressed as $N_B = \ln(10)m/C$. The fragility index $m$ is defined as the derivative of the logarithm of the viscosity at $T_g$. That is, $m = \mathrm{d}\log\eta/\mathrm{d}(T_g/T)|_{T=T_g}$ [12]. Therefore, we can obtain an analytical expression for $N_B(B, C, T)$ at any temperature $T$,

$$N_B(B,C,T) = \frac{\ln(10)m(x)}{C}, \tag{7}$$

Table II. Materials parameters used in the present work. Data of $\eta_0$, $T_g$, and the VFT parameters are from refs 8, and 9. $\ln \eta_{Tg}$ is one of the fitting parameters in our model. The value of $\ln \eta_{Tg}$ is determined from the VFT equation; $\eta = \eta_0 \exp\{B_{VFT}{}^{(\eta)}/(T - T_0{}^{(\eta)})\}$.

| No. | $T_g$ [K] | ($B^*$, $C^*$) | $\ln(\eta_{Tg}/\eta_0)$ | $B_{VFT}{}^{(\eta)}$ | $T_0{}^{(\eta)}$ |
|---|---|---|---|---|---|
| (1) | 202 | (0.81, 3.45) | 34.831 | 721 | 181 |
| (2) | 184 | (0.69, 3.95) | 24.226 | 751 | 153 |
| (3) | 186 | (0.57, 4.39) | 18.261 | 840 | 140 |
| (4) | 186 | (0.94, 3.29) | 104.064 | 625 | 180 |
| (5) | 192 | (0.81, 3.82) | 39.824 | 757 | 173 |
| (6) | 193 | (0.82, 4.08) | 44.533 | 802 | 173 |

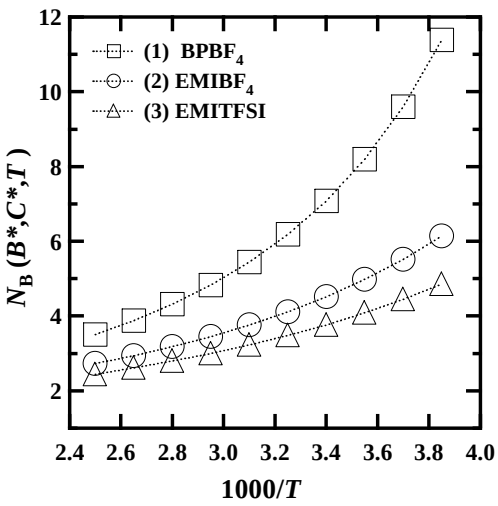


Fig. 2. Temperature dependence of the cooperativity described by $N_B(B^*, C^*, T)$ given by Eq. (7) - Eq. (9).

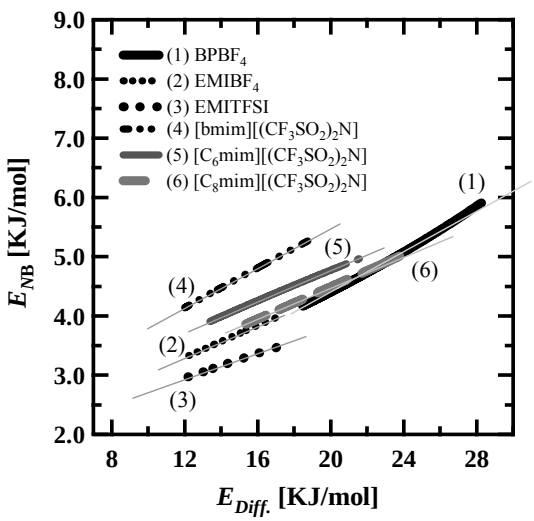


Fig. 3. Relation between the activation energies, $E_{NB}(T)$ and $E_{Diff.}(T)$. The temperature range shown in this figure is $2.4 \leq 1000/T \leq 4.0$. The behaviors at the same temperature range are shown in Fig. 4 and Fig. 5.

where $x=T_g/T$. $m(x)$ is expressed in terms of the BSCNF model as

$$m(x) = \frac{\mathrm{d}\log\eta}{\mathrm{d}x}$$

$$= \frac{1}{\ln(10)}\left[\frac{C(1-Bx^2)(1+2xH)+2BCx^2(1+xH)}{(1-Bx^2)^2} + \frac{Bx}{1-Bx^2}\right], \quad (8)$$

where

$$H \equiv \left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right\}\frac{(1-B)}{C} - 1. \quad (9)$$

It should be noted that in the case of $x$=1, Eq. (8) reduces to the fragility index $m$ given in Eq. (6).

Fig. 2 shows the temperature dependences of $N_B$ for the ionic liquids, (1) $BPBF_4$, (2) $EMIBF_4$, and (3) EMITFSI. From this figure, we can see that the value of $N_B$ for (1) $BPBF_4$ is the largest among these three ionic liquids. The temperature dependence of $N_B$ described by Eq. (7) is expected to have several significances from the physical point of view. For instance, the quantity $N_B$ which gives the number of structural units involved in the thermally activated viscous flow provides information on the degree of the fluidity. Namely, it gives the degree of cooperativity of ionic motions within the ionic liquids. The analytical expression $N_B(B, C, T)$ given in Eq. (7) also provides an additional information to the conventional transport coefficients.

*2.3 Activation energies for diffusion coefficient and $N_B$*

As shown in Fig. 2, $N_B$ can be described as $N_B(B^*, C^*, T)$, where $B^*$ and $C^*$ are the best fitted parameters of the BSCNF model that reproduces exactly the behavior of the VFT equation. In this subsection, the temperature dependence of $N_B$ is discussed along with the viscosity $\eta$ and the diffusion coefficients $D$. Concerning the diffusion coefficient $D$, we adopted a simple sum of the self-diffusion coefficients for cations and anions measured by the pulsed-field-gradient spin-echo (PGSE) NMR technique [8,9].

To compare the quantities, $\eta$, $D$, and $N_B$ within the same scale, we investigated the temperature dependences of the activation energies for each transport coefficients through

$$E_a(T) = \pm RT\ln\left(\frac{A_{VFT}(T)}{A_0}\right), \quad (10)$$

where $A_{VFT}$ is the transport coefficient described by the VFT law, $\ln(A_{VFT}/A_0) = \pm B_{VFT}/(T-T_0)$. Therefore, the temperature dependences of the activation energy for the viscosity $E_\eta$, and for the diffusion coefficient $E_{Diff.}$, are calculated from $E_\eta(T)=RT\{B_{VFT}^{(\eta)}/(T-T_0^{(\eta)})\}$, and $E_{Diff.}(T)=RT\{B_{VFT}^{(Diff.)}/(T-T_0^{(Diff.)})\}$. The VFT parameters used in the analysis of the diffusion coefficient are determined from the experimental data [8, 9]. On the other hand, regarding the temperature dependence of the activation energy for $N_B$, the following relation is used instead of Eq. (10),

$$E_{N_B}(T) = RT\ln\left(\frac{N_B(B^*, C^*, T)}{N_{B0}}\right), \quad (11)$$

where $N_B(B^*, C^*, T)$ is calculated through Eq. (7). Here, we want to emphasize once again that in our model, $B^*$ and $C^*$ are the set of parameters that the viscosity behavior described by the BSCNF model reproduces exactly that described by the VFT equation. This is one of the advantages of the BSCNF model compared with the VFT equation, because the fitting parameters can be utilized to extract microscopic information concerning the viscous flow. In Eq. (11), $N_{B0}$ is the value of $N_B$ at the high temperature limit. Note that when $x$=0, $N_B$ described by Eq. (7) reduces to unity. Thus, through this analysis, $N_{B0}$=1 is adopted. This adoption is probable, because according to the concept of CRR in glass-forming liquids, the cooperativity increases with the decrease in temperature [13]. Therefore, in the high temperature region, the degree of the CRR is expected to be

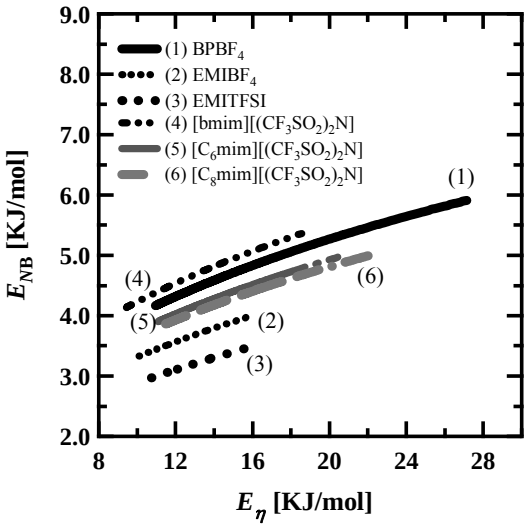


Fig. 4. Relation between the activation energies, $E_{NB}(T)$ and $E_{\eta}(T)$.

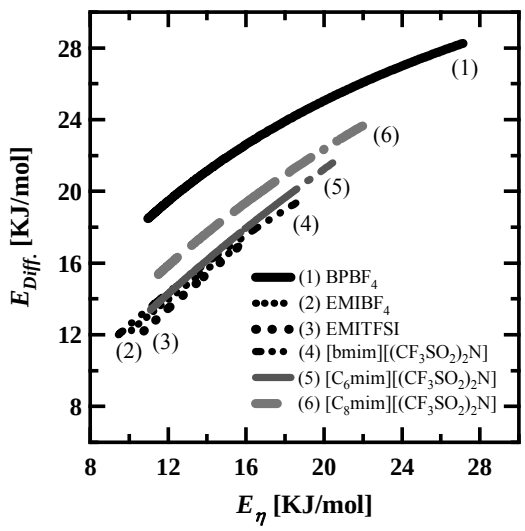


Fig. 5. Relation between the activation energies, $E_{Diff.}(T)$ and $E_{\eta}(T)$.

smaller and each structural units of the melt are considered to move and relax independently.

## 3. Discussion

Fig. 3 shows the relation between the activation energies, $E_{NB}$ and $E_{Diff.}$ for six different ionic liquids. The temperature range shown in Fig. 3 is $250 \leq T\,[\mathrm{K}] \leq 417$. Note that the actual data are measured approximately in the range of $270 \leq T\,[\mathrm{K}] \leq 360$ [8, 9]. From Fig. 3, we note an interesting feature. That is, for all the six ionic liquids analyzed in the present work, the behaviors of $E_{NB}$ are almost proportional to the behaviors of $E_{Diff.}$. On the other hand, Fig. 4 and Fig. 5 show the relations between $E_{NB}$ and $E_{\eta}$, and between $E_{Diff.}$ and $E_{\eta}$, respectively. From Fig. 4 or Fig. 5, we also note that some ionic liquids exhibit a slight curvature, and some ionic liquids show a nearly straight line between the activation energies. Thus, it indicates that for the ionic liquids analyzed in the present study, $E_{\eta}$ is not necessarily proportional to $E_{NB}$ and $E_{Diff.}$. From a physical point of view, Fig. 3 suggests that the behavior of the diffusional motion among the cations and anions within the ionic liquid are highly cooperative. This is an interesting result, because one usually expects that $E_{NB}(T)$ is proportional to $E_{\eta}(T)$. In addition, as discussed in section 2.2, the value of $N_B$ is obtained from the viscosity analysis. From this finding, it is also suggested that further microscopic information on the ionic diffusion within the ionic liquids can be extracted through the cooperativity described by $N_B$. In our next work, we will extend this analysis and discuss more deeply the transport properties of ionic liquids from the point of view of cooperativity.

## 3. Conclusion

In this work, it was shown that the quantity $N_B$ derived from the Bond Strength – Coordination Number Fluctuation (BSCNF) model provides a new physical information on the cooperativity of ionic motions in addition to the conventional transport properties such as the viscosity and the diffusion coefficient. More specifically, it was shown that for the six kinds of ionic liquids investigated in the present work, the temperature dependence of the activation energy for the diffusion coefficient $E_{Diff.}$ is proportional to $E_{NB}$ given by Eq. (11). It is necessary to check whether the proportionality relation found between these activation energies are satisfied for other kinds of ionic liquids.


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