Temperature dependence of transport coefficients and cooperativity in ionic liquids

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Abstract:

The temperature dependence of the molecular motion cooperativity in imidazolium-based room temperature ionic liquids with bis(trifluoromethane sulfonyl)amide anion, [Rmim][(CF$_3$SO$_2$)$_2$N], where, R=e (ethyl), b (butyl), C$_6$ (hexyl) and C$_8$ (octyl), respectively, were evaluated by using a relation defined in the framework of the Bond Strength-Coordination Number Fluctuation (BSCNF) model. The degree of the cooperativity in ionic liquids was reflected in the quantity N_B, which gave the number of structural units involved in the thermally activated viscous flow. It was shown that by using the BSCNF model together with both, the Nernst-Einstein and the Stokes-Einstein relations, N_B was mutually related with the transport coefficients, i.e., viscosity, diffusion coefficient and ionic conductivity.

Keywords: transport coefficients; cooperativity; ionic liquids

In recent years, room-temperature ionic liquids, or simply called ionic liquids, have gained considerable interest in the area of environmental and materials science[1-4]. Ionic liquids are composed of cations and anions. Therefore, by changing the combination of the composition, a wide variety of ionic liquids with unique and excellent material properties such as negligible vapor pressure, thermal and chemical stability, high ionic conductivity, etc., can be synthesized[1,2,5,6]. Usually, to understand the microscopic mechanism occurring within the liquid state including the molten salts[7], the temperature and composition dependence of the

diffusion coefficients are examined [6], along with other properties such as viscosity, conductivity, density, surface tension, etc [5-8]. In the present study, to generalize the knowledge accumulated till now and to gain further insights on the properties of ionic liquids, an analytical method of analysis based on our model of viscosity, the Bond Strength – Coordination Number Fluctuation (BSCNF) model[9,10] was presented. Specifically, the temperature dependence of the cooperativity for the ionic liquids, 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide, [Rmim][(CF$_3$SO$_2$)$_2$N], where R is the alkly group, R=e (ethyl), b (butyl), C$_6$ (hexyl), and C$_8$ (octyl), respectively[6], are evaluated in terms of the quantity N_B, which is defined in the framework of the BSCNF model [11]. As will be shown below, N_B quantifies the number of structural units involved in the thermally activated viscous flow[11,12]. In this study, it was also shown that by relating the BSCNF model with the Nernst-Einstein and the Stokes-Einstein relations, simple linear functions that connect N_B to diffusivity and ionic conductivity were obtained.

1. Analytical method of analysis based on the BSCNF model

1.1 BSCNF model of viscosity

Many experiments have shown that for various ionic liquids, the transport coefficients such as viscosity η, diffusion coefficient D, and ionic conductivity σ, exhibit a super-Arrhenius behavior in their temperature dependence. Such a behavior is well reproduced by the Vogel-Fulcher-Tammann (VFT) equation. On the other hand, with the objective to understand the microscopic behavior of viscous liquids, a model for the viscosity has been proposed by one of the authors[9]. The model which is called 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, ΔE, ΔZ, of the structural units that form the melt. The BSCNF model is given by[9]

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

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, T_g is the glass transition tempearture. R is the gas constant. η_{Tg} and η_0 are the viscosities at T_g and at the high temperature limit, respectively. According to the BSCNF model, the experimental viscosity behaviors are systematized in terms of the parameters, B and C, which contains microscopic information on bonding connectivity among the structural units that form the melt[9-11]. Fig. 1 shows that the BSCNF model reproduces well the experimental viscosity data of ionic liquids investigated in the present study. The parameters used in the analysis are given in Table 1. The experimental data used in this study were taken from the work by Tokuda et al.[6] In their study, the viscosity behavior was analyzed by using the VFT equation. The advantages gained through the analysis by the BSCNF model, and some theoretical considerations on the relationship between the BSCNF model and the VFT equation are discussed in detail elsewhere[10].

1.2 Temperature dependence of the cooperativity

The thermally activated viscous flow occurs through the involvement of many components in the liquid. When the viscous flow occurs, the bond-breaking or bond-twisting between the structural units triggers a series of flow processes. Based on this picture, a quantity N_B defined as $N_B = E_\eta/(E_0Z_0)$ was proposed[11]. Here, E_η is the activation energy for viscous flow and E_0Z_0 is the mean binding energy per structural unit, respectively. In the present analysis, the temperature dependence of the cooperativity in ionic liquids is evaluated by,

$$N_B(x) = \frac{1}{C}\frac{d}{dx}\ln\eta(B,C,x).$$ (3)

This expression is obtained by extending the original definition given above by including the temperature dependence. Fig. 2 shows the temperature dependence of N_B for the same ionic liquids as those shown in Fig. 1. From Fig. 2, we can see that the value of N_B increases with the decrease in temperature. In this regard, it has been shown that N_B is closely related with the concept of cooperatively rearranging region (CRR) of glass-forming liquids[10]. This indicates that as the temperature of the system decreases, larger numbers of elements are involved in the structural relaxation[13]. Thus, N_B provides additional information on the cooperativity that is behind the relaxation of viscous melt. In view of these backgrounds, it will be interesting to know how the behaviour of N_B can be related with that of ionic diffusion and conductivity in ionic liquids.

2.   Relation between the transport coefficients and N_B

2.1   Activation energy for transport coefficients and cooperativity

In this section, the temperature dependence of N_B was discussed along with other transport coefficients. To compare these quantities, namely, η, D, and σ, with N_B, within the same scale, we compare the temperature dependence of the activation energies for these transport coefficients as well as that of N_B, by using the Arrhenius relation,

$$E_a(T) = \pm RT \ln\left(\frac{A(T)}{A_0}\right),\tag{4}$$

where A is the transport coefficient and A_0 is the pre-exponential factor. The activation energies for the viscosity E_η, the diffusion coefficient E_{Diff}, the ionic conductivity E_σ, and the cooperativity E_{NB} are calculated using Eq. (4). It must be noted however that, in the analysis of the experimental data of D and σ, the VFT expression, $A = A_0 \exp\{\pm B_{VFT}^{(A)}/(T - T_0^{(A)})\}$ were used[6]. Consequently, E_{Diff} and E_σ are computed by using $E_{Diff}(T) = RT\{B_{VFT}^{(Diff.)}/(T - T_0^{(Diff.)})\}$, and $E_\sigma(T) = RT\{B_{VFT}^{(\sigma)}/(T - T_0^{(\sigma)})\}$, respectively. In Table 2, the parameters of the VFT equation of D and σ are given. On the other hand, concerning E_η and E_{NB}, $A(T)$ in Eq. (4) are calculated through Eq. (1) and Eq. (3), respectively. In the calculation of N_B, it must be also noted that at the high temperature limit, the value of N_B reduces to unity[12]. So, we adopted the pre-exponential factor of N_B as $N_{B0} = 1$. According to reference[6], for the diffusion coefficients of cations and anions, the values determined by means of the pulsed-field-gradient spin-echo (PGSE) NMR technique are employed. In the present study, a simple sum of the self-diffusion coefficients for cations and anions is adopted.

2.2   Relation between the Nernst-Einstein, the Stokes-Einstein laws and N_B

The Nernst-Einstein (NE) and the Stokes-Einstein (SE) relations have been widely used in the analysis of transport property in the liquid state[5,6]. Using both relations, the following linear relation is obtained[14,15],

$$\sigma T \propto D \propto \left(\frac{T}{\eta}\right)^m,\tag{5}$$

where m is the fractional exponent that gives the degree of deviation from the SE law.

In one of our recent works, it was shown that for several ionic liquids, $E_{Diff.}$ and E_{NB} are highly correlated[12]. Based on this result, two simple liner functions, one between D and N_B, and another between σT and N_B, are derived. By expressing the diffusion coefficient D and N_B as $D=D_0\exp(-E_{Diff.}/RT)$ and $N_B=N_{B0}\exp(E_{NB}/RT)$, and by connecting them, the following linear function is obtained,

$$\ln D = \varsigma \, \ln(N_B^{-1}) + b, \tag{6}$$

where

$$\varsigma = \frac{E_{Diff.}}{E_{NB}}. \tag{7}$$

Here, ζ gives the ratio of the activation energy for diffusivity to that of the cooperativity. In Eq. (6), b is a constant. Fig. 3 (a) shows the relation between D and N_B. The materials and symbols used in Fig. 3 are the same to those used in previous figures. In Fig. 3 (a), we note that the slopes of the straight lines are given by ζ, and that the straight lines obey Eq. (6). This linear function reproduces well the relations between D and N_B for the four ionic liquids investigated in the present analysis. Strictly speaking, however, we can observe that for some ionic liquids, the ratio ζ does not depend, or depends only slightly on temperature. In our recent work[12], it has been shown that the other ratios such as E_{NB}/E_η or E_{Diff}/E_η, depend apparently on temperature. Therefore, the invariance of ζ on temperature suggests that the diffusion motions of cations and anions in ionic liquids are strongly reflected in the behavior of cooperativity N_B which is obtained from the viscosity analysis.

On the other hand, Fig. 3 (b) shows the relation between ionic conductivity σ, temperature T, and N_B. In Fig. 3 (b), it is noteworthy that the slopes of the straight lines are also determined by ζ, whose values are the same to those used in Fig. 3 (a). Analogous to the derivation of Eq. (6), the following linear function between σT and N_B is obtained,

$$\ln \sigma T = \varsigma \, \ln(N_B^{-1}) + b', \tag{8}$$

where b' is a constant as well as b in Eq. (6). We can see that all the straight lines in Fig. 3 (b) are reproduced by Eq. (8). The application of Eq. (8) to other species is interesting, because, it is possible to predict the temperature dependence of the ionic conductivity σ with good precision, if we have the temperature dependence of the diffusion coefficient D and N_B.

Finally, a brief comment on the SE relation was given. It has been reported that for certain kinds of ionic liquids, the SE relation does not reproduce the experimental data. For such

systems, the fractional Stokes-Einstein relation, $D \propto (T/\eta)^m$, has been applied[16]. For instance, in the ionic liquid neopentylimidazolium with anion BF^{4-}, the fractional exponent takes the value $m \approx 0.66$[16]. By using the method presented in this article, it is possible to give a physical explanation to the derivation from the usual SE law ($m = 1$) in terms of the cooperativity of molecular agglomeration. Concerning this point, it will be discussed in our next work.

3.   Conclusions

The temperature dependence of transport coefficients and N_B of ionic liquids, 1-alkyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide were investigated. By applying the BSCNF model to ionic liquids, it was discussed that the cooperativity evaluated by N_B can be related with the diffusivity and ionic conductivity. Furthermore, to compare the transport coefficients with N_B within the same scale, the temperature dependence of the activation energies for the transport coefficients were investigated. According to our analysis, the value of ζ does not depend or depends only slightly on temperature. From the result, two simple linear functions, one between D and N_B, and another between σT and N_B, were derived. These relations show excellent agreement with the relations between the transport coefficients and N_B of ionic liquids investigated in the present study.

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Figure Captions

Fig. 1 Temperature dependence of the viscosity reproduced by the BSCNF model

Fig. 2 Temperature dependence of the cooperativity N_B described by Eq. (3)

Fig. 3 (a) Relation between $\ln D$ and $\ln(N_B^{-1})$. (b): Relation between $\ln \sigma T$ and $\ln(N_B^{-1})$

Table Captions

Table 1 Materials and fitting parameters in the viscosity analysis

Table 2 Parameters of the VFT equation of diffusivity and ionic conductivity
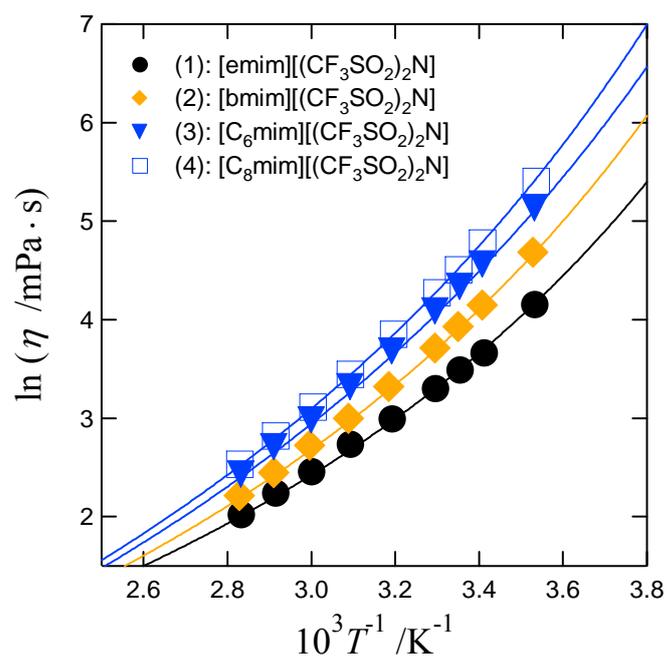
Fig. 1
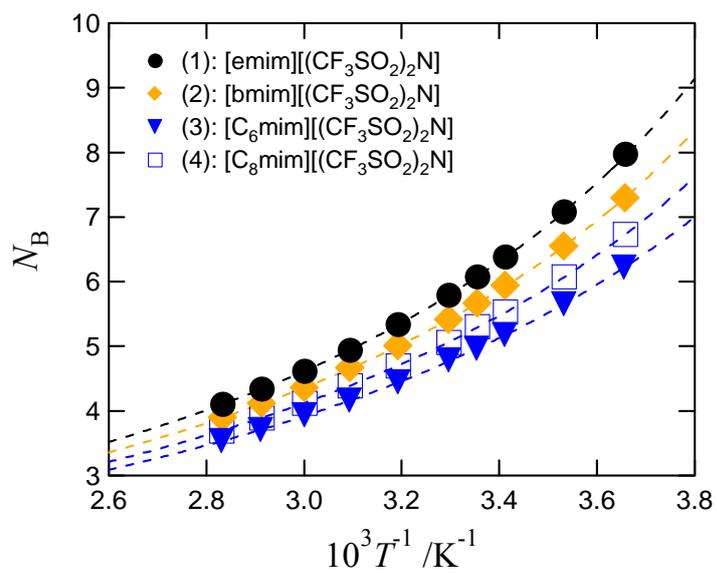
Fig. 2
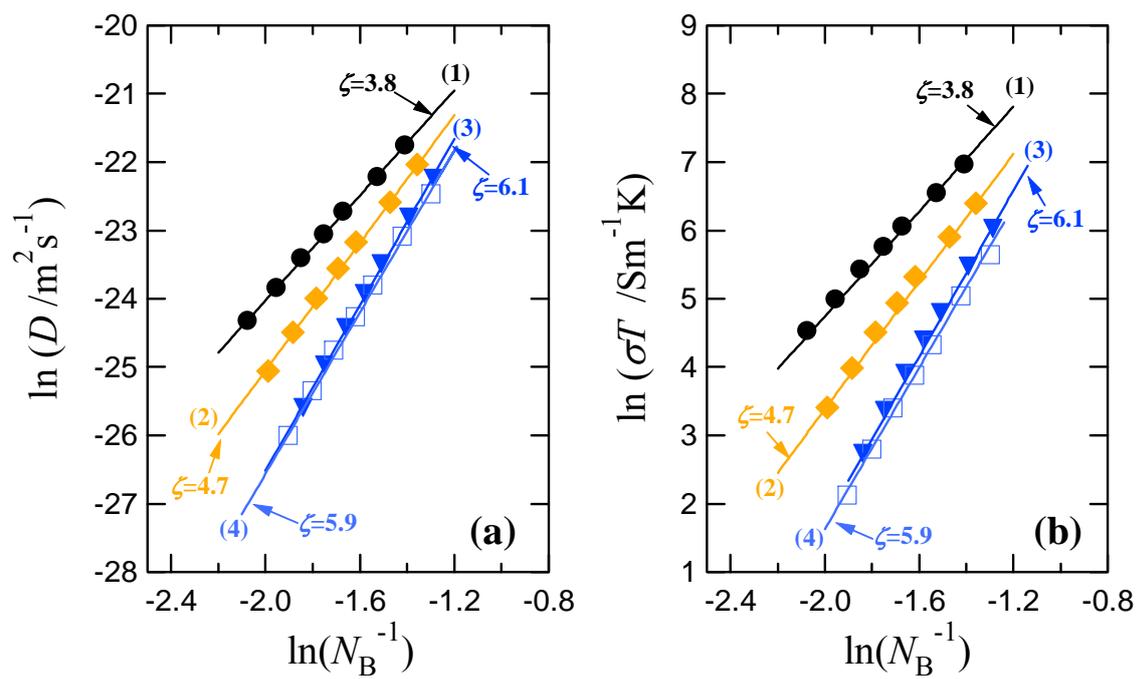
Fig. 3

Table 1

No.	T_g/(K)[6]	B	C	$\ln(\eta_{Tg}/\eta_0)$
(1)	186	0.879	3.08	50.3
(2)	186	0.840	3.78	46.2
(3)	192	0.715	4.51	29.8
(4)	193	0.744	4.50	33.5

Table 2

No.	$\ln(D_0/\text{m}^2\,\text{s}^{-1})$	$B_{\text{VFT}}^{(Diff.)}$/(K)	$T_0^{(Diff.)}$/(K)	$\ln(\sigma_0/\text{S}\,\text{m}^{-1})$	$B_{\text{VFT}}^{(\sigma)}$/(K)	$T_0^{(\sigma)}$/(K)
(1)	-17.8	807	150	3.84	492	173
(2)	-17.4	939	152	3.82	587	176
(3)	-17.3	970	156	4.24	774	164
(4)	-16.8	1168	146	4.07	796	168