A relationship between diffusivity and cooperativity of supercooled liquids in the proximity of glass transition

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Abstract

In structurally disordered glass-forming liquids, the Stokes-Einstein (SE) law for translational diffusivity is violated, in particular, in the proximity of the glass transition temperature. Usually, the violation of the SE law is explained as due to the decoupling of the diffusivity from the viscous flow. Meanwhile, one of the prominent features observed in the supercooled liquids is the drastic increase of the viscosity with the decrease of temperature. The origin of the increase of the viscosity is attributed to the increase of the molecular motion cooperativity. In the present study, it is shown that the translational diffusivity of glass-forming liquids can be correlated with the cooperativity involved in the thermally activated viscous flow. In the present analysis, the cooperativity is defined in the framework of the bond strength-coordination number fluctuation (BSCNF) model of the viscosity. The result of the analysis suggests that the translational diffusivity is driven by the bond-breaking and bond-switching between the structural units that compose the network structure.

Keywords: diffusivity; viscous flow; fractional Stokes-Einstein law; cooperativity

1. Introduction

The understanding of the diffusion mechanisms in structurally disordered substances near the melting temperature T_m and the glass transition temperature T_g is of crucial importance for practical applications such as the suppression of devitrification in silicate glasses [1], in phase change materials [2], in pharmaceutical science [3], etc. From a fundamental point of view, the microscopic transport properties of the melts and glasses have been investigated directly through the measurements of the diffusion coefficients by means of NMR [4,5], radiotracer [6], electrochemical methods [7,8], molecular dynamic (MD) simulations [9-11], and other techniques [12,13]. Concerning the relation between the diffusion coefficient and the viscosity, the validity of the Stokes-Einstein (SE) relation [14,15] remains a subject of intensive debates [3,6-10]. The SE relation for translational diffusivity is given by $D=k_BT/6\pi r_s\eta$ [3,6,7,16] in the case of "stick" boundary condition, where D is the self-diffusion coefficient, k_B is the Boltzmann's constant, T is the absolute temperature, r_s is the spherical radius of the diffusive species and η is the viscosity, respectively. The SE relation has been used widely in the discussion of atomic transport in liquids [17]. However, it has been revealed that the SE relation is violated, in particular, in the proximity of the glass transition temperature [6,7,12, 18-21]. In these cases, the fractional Stokes-Einstein (FSE) law which is given by

$$D \propto \left(\frac{T}{\eta}\right)^p \quad (0 < p \leq 1), \tag{1}$$

describes the relation between the translational diffusivity and the viscosity. Here p gives the degree of deviation from the original SE law. As has been reported in many studies, p takes a value of less than unity for various glass-formers [10,12,16]. The FSE law given by Eq. (1) indicates the "decoupling" of the diffusive motions from the viscous flow. The FSE law is

observed especially in fragile liquids in the temperature range lower than the crossover temperature [16,18]. It has been discussed that the origin of the FSE law could be attributed to the spatial heterogeneity of the liquids under supercooling [22]. On the other hand, other authors have cast doubt on the general validity of the fractional Stokes-Einstein law [23].

It should be also noted that one of the prominent features observed in supercooled liquids is the drastic increase of viscosity or relaxation time with the decrease of temperature [24]. This process is accompanied by the increase of the molecular motion cooperativity among the constituent elements of the supercooled liquid. In our previous study [25], it was discussed that the self-diffusion coefficients of cations and anions in room temperature ionic liquids (RTILs) can be correlated with the cooperativity involved in the thermally activated viscous flow. There, the cooperativity of the RTILs was evaluated by the quantity N_B which was defined in the framework of the bond strength-coordination number fluctuation (BSCNF) model of the viscosity [26]. The result suggested that the diffusivity of cations and anions in the RTILs are driven by the bond-breaking and bond-switching between the constituent elements of the liquids, which leads to the cooperative motion of the diffusivity [27].

The main objective of the present work is to investigate if the above picture of the correlation between the diffusivity and the cooperativity is common in other glass-forming liquids as well. In Fig. 1, the temperature dependence of the diffusion coefficient is shown for the materials investigated in the present study. It includes various materials as indicated in Table 1. The experimental data of the diffusion coefficient D are taken from the literatures [12, 16,18-20]. As mentioned in the beginning, understanding the mechanism of viscous flow near T_g is of fundamental importance for the clarification of the mechanisms of glass transition [22], as well as the crystallization process in glassy state and melts [1-3, 21, 22]. In the

following, the validity of the relation mentioned above, as well as the implications of the results to the exponent p of the FSE law will be discussed.

2. Evaluation of the cooperativity of the melt

The viscous flow of a liquid occurs by involving a large number of molecules or structural units that form the liquid. In such flow process, the connectivity of the structural units depends on the nature of the chemical bonds and affects greatly the behavior of the structural relaxation [24]. In one of our previous studies, with the objective to understand the viscous flow of the melt, a model for the temperature dependence of the viscosity has been proposed by one of the authors [26]. The model has been called bond strength-coordination number fluctuation (BSCNF) model and describes the viscosity behaviors in terms of the mean bond strength E_0, the coordination number Z_0, and the fluctuations, ΔE, ΔZ, of the structural units that form the melt. The BSCNF model of the viscosity is given by [26,28]

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

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} \quad \text{and} \quad C = \frac{E_0 Z_0}{R T_g}. \tag{3}$$

Here, x is the inverse temperature normalized by T_g, $x = T_g/T$. η_0 and η_{T_g} are the viscosity at the high temperature limit and at T_g, respectively. R is the gas constant. In the BSCNF model, the glass-forming liquids are characterized with the parameters B and C, whose numerical values

are determined from the viscosity analysis. Intuitively, B gives the degree of the fluctuation, and C gives the degree of the mean binding energy between the structural units against the thermal disturbance at T_g. The explanations of the model have been given in detail elsewhere [25-29].

The atomic and molecular cooperative rearrangement involved in the viscous flow plays an important role in the agglomeration process of the melt [21,30,31]. In our previous study [29], a quantity N_B which gives the number of structural units involved in the thermally activated viscous flow has been introduced in the light of the BSCNF model. This quantity is defined as $N_B = E_\eta/(E_0 Z_0)$, 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 other words, N_B gives the ratio between the thermally activated energy (or enthalpy) and the average binding energy that depends on the materials. From the theoretical point of view, it has been also shown [32] that N_B is closely related with the notion of cooperatively rearranging region (CRR) in the theory of Adam and Gibbs [33]. In the present analysis, the temperature dependence of the cooperativity in glass-forming liquids is evaluated by the relation

$$N_{\mathrm{B}}(T) = \frac{\ln(10)}{C} \frac{\mathrm{d}}{\mathrm{d}(T_{\mathrm{g}}/T)} \log \eta(B,C,T). \tag{4}$$

Here, the viscosity η is given by Eq. (2). Note that at T_g, the term $\mathrm{d}\log\eta/\mathrm{d}(T_g/T)$ reduces to the fragility index m [34]. Eq. (4) is obtained by extending the original definition of N_B. The quantity N_B which is given by Eq. (4) increases with the decrease of temperature. The growth behavior of the cooperativity described by this equation is consistent with the results by other studies [30, 31]. However, concerning the number of correlated units involved in glass-forming liquids, i.e., the number of molecules or structural units that are involved during supercooling depends on theoretical models [31,35]. It would be interesting to perform a

detailed comparative study on the temperature dependence of cooperativity based on different models. In the present analysis, we have focused on the rate of increment of the cooperativity described by N_B in the range of temperature close to T_g, since it is closely related with the activation energy.

3. Result and discussion

Figure 2 shows the relation between the diffusivity and the viscosity. Here, the experimental data of the diffusion coefficient and the viscosity in the proximity of the glass transition temperature are plotted in logarithmic scales. The straight lines shown in the figure are described by

$$\log(D \ /\mathrm{m}^2\mathrm{s}^{-1}) = p\log\!\left(T \cdot \eta^{-1} \ /\mathrm{K} \cdot \mathrm{Pa}^{-1}\mathrm{s}^{-1}\right) + \mathrm{const.} \tag{5}$$

The broken line in Fig. 2 indicates the SE law ($p=1$). We can see that the glass-forming liquids investigated are characterized by the exponent p which is determined from the slope of the straight line described by Eq. (5). The values of p obtained in the present study are listed in Table 1. In Fig. 2, it is also seen that the value of p takes a value less than unity. Namely, the relation between the diffusion coefficient and the viscosity shows clearly the violation of the SE law. This indicates that the translational diffusivity takes a value larger than that predicted by the SE law as observed in other studies [16,18,19]. It has been also discussed that the FSE law is related with the electrical conductivity [36,37]. Thus, the value of p is expected to contain information on the transport mechanism operating in the system.

The main results of the present study are shown in Figs. 3 and 4. In particular, Fig. 3 shows the relation between $\log D$ and $\log(N_B^{-1})$. Note that the value of N_B is calculated by Eq. (4). On the other hand, Fig. 4 shows the relation between $\log(N_B^{-1})$ and $\log(T/\eta)$. From both

figures, it is observed that each glass-forming liquid investigated, the slopes of the straight lines are almost constant. This implies that the slopes in these figures do not depend, or depends only slightly on temperature. In particular, we note from Fig. 3 that the translational diffusion coefficient D can be correlated with a single parameter N_B. This indicates that the slope in the relation between $\log D$ and $\log(N_B^{-1})$ gives the ratio of the activation energies between the diffusion coefficient D and the cooperativity N_B. That is, as shown in the figure, the ratio between these activation energies is almost temperature-independent. This observation suggests that N_B can be used as an indicator to discuss the transport properties of viscous liquids.

The relation between the diffusivity and the cooperativity can be rationalized as follows. Based on Figs. 3 and 4, the following linear relationship are derived,

$$D \propto \left(\frac{T}{\eta}\right)^p \propto (N_B^{-1})^{\varsigma}, \tag{6}$$

where

$$\varsigma = \frac{E_D}{E_{N_B}}. \tag{7}$$

Here E_D and E_{N_B} are the activation energies for D and N_B. These activation energies are introduced through the Arrhenius equations, $D = D_0 \exp(-E_D/RT)$ and $N_B = N_{B0}\exp(E_{N_B}/RT)$, respectively. The expression for N_B is introduced based on the physical picture that the cooperativity of the melt increases with the decrease of temperature accompanying the increase of the viscosity. Here, the activation energy E_{N_B} varies with temperature, because N_B is given by $N_B = E_\eta/(E_0 Z_0)$. In particular, for fragile glass-formers the activation energy for viscosity E_η increases markedly with the decrease of temperature, which leads to a VFT-like

behavior. Therefore, the behavior of $N_\mathrm{B} = N_\mathrm{B0}\exp(E_{N_\mathrm{B}}(T)/RT)$, as well as the behavior of the viscosity $\eta = \eta_0\exp(E_\eta(T)/RT)$, exhibit the VFT-like temperature dependence [30]. It should be also noted that in the BSCNF model, the relation for the pre-exponential factor, $N_\mathrm{B0} = 1$ holds [25], which physically indicates that in the high temperature limit, each structural units relaxes non-cooperatively.

The straight lines shown in Figs. 3 and 4 are described as

$$\log(D\ /\mathrm{m^2 s^{-1}}) = a\ \log(N_\mathrm{B}^{-1}) + \mathrm{const..}, \tag{8}$$

and

$$\log(N_\mathrm{B}^{-1}) = a'\ \log\!\left(T\cdot\eta^{-1}\ /\mathrm{K\cdot Pa^{-1}s^{-1}}\right) + \mathrm{const.} \tag{9}$$

Here, a and a' are the slopes of the straight lines. In terms of the symbols used in Eq. (6), these are written as $a = \varsigma$ and $a' = p/\varsigma$. It is interesting to note in Fig. 3 that the slope $a = \varsigma = E_D\,/\,E_{N_\mathrm{B}}$ is temperature independent. The physical implications of this ratio are discussed later. In addition, it is also noted that the value of p satisfies $p=aa'$. For instance, the value of p for the metallic system $Pd_{43}Cu_{27}Ni_{10}P_{20}$ is reported as $p\approx0.75$ in ref. [16]. This is in good agreement with the value obtained from the above relation (i.e., $p=aa' \approx 0.74$). Voronel et al. [36] have discussed that the fractional exponent of the FSE law for ionic melts can be characterized by the ratio E_ρ/E_η (≈0.8), where E_ρ and E_η are the activation energy for the resistivity ρ and the viscosity η, respectively, which is similar to the ratio of activation energies used in the present study. It should be noted however, that the Arrhenius equation used in their study is slightly different from ours. The expression for the viscosity used there is given by $\eta/T=A_\eta\exp(E_\eta/k_\mathrm{B}T)$ [36].

According to the BSCNF model, the viscous flow occurs involving the movement of large number of structural units. In such flow process the atoms composing the structural units are bonded strongly. The viscous flow occurs when the weak bonds connecting the structural units are disrupted by the thermal activation. The proportion of these weak interconnections increases with the increase of temperature. In other word, the number of structural units involved in the flow process decreases with the increases of temperature. The quantity $N_B(T)$ describes this behavior. The relation between $\log D$ and $\log(N_B^{-1})$ found above implies that the translational diffusivity is cooperative. This can be understood as follows. When an atom diffuses, it breaks and twists the bonds that surround it. These events occur preferentially at the sites where the interconnections between the structural units are weakly bonded. The diffusing atom is arrested temporally by the structural unit and diffuses by breaking the bonds. This eventually contributes to the appearance of viscous flow. The relation between D and N_B reflects this situation. Meanwhile, since the diffusion event distorts the bonds surrounding the diffusing atom, it also triggers the diffusion of other atoms. That is, the dynamics of the cooperativity among the structural units is involved in the correlated motions of diffusing atoms. When the temperature is lowered, or when the viscosity of the system is increased, the number of structural units bonded strongly increases. The rapid relaxation among the structural units becomes difficult to occur. This situation is reflected in the behavior of Eq. (4). However, since the diffusion process is a local event involving local breaking and twisting of bonds, the decoupling of diffusion and structural relaxation processes appear when the system in consideration is sufficiently viscous. This picture results in the deviation from the SE relation. The above explanation is also consistent with other studies that aim to explain the FSE behavior. Indeed, many authors have suggested that close to T_g, a decoupling between diffusion and structural relaxation takes place. Concerning diffusion, there is a suggestion that

the jump diffusion process via vacancy-like sites occurs at temperatures close to T_g [21,37]. There are also results of MD simulations studied for high density hard sphere fluids [9] and ionic liquids with lithium salts [11], which revealed the occurrence of hopping process among the constituent elements of the liquids. These results support our interpretation given above.

4. Conclusions

In the present study, the relationship between the diffusivity and the cooperativity of glass-forming liquids was discussed based on the FSE law and the BSCNF model. Specifically it was shown that the cooperativity N_B which is defined in the framework of the BSCNF model is related with the translational diffusivity of glass-forming liquids. The quantity N_B gives the degree of molecular motion cooperativity involved in the thermally activated viscous flow. In addition, the expression for the temperature dependence of the cooperativity N_B was given. The results of the present analysis suggested that the diffusive motion of mobile species is cooperative and is driven by the bond-breaking and bond-switching between the constituent elements of glass-forming materials. A theoretical relation that connects the cooperativity N_B with the FSE law was also presented. The present analysis suggests that N_B can be used as an indicator to discuss the transport property of viscous liquids.

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Figure Captions

Fig. 1. Temperature dependence of diffusion coefficients for the materials investigated in the present study. The methods used in the measurements of the diffusion coefficient and the references where the experimental data are taken are listed in Table 1.

Fig. 2. Relation between $\log D$ and $\log(T/\eta)$ close to T_g. The straight lines that fit the data are described by Eq. (5). The slope described by the value of p gives the exponent of the FSE law. Their values are given in Table1.

Fig. 3. Relation between $\log D$ and $\log(N_B^{-1})$. The straight lines shown in the figure are described by Eq. (8). The slope of the line gives the ratio between the activation energies for D and N_B; $a = \varsigma = E_D / E_{N_B}$.

Fig. 4. Relation between $\log(N_B^{-1})$ and $\log(T/\eta)$. The straight lines in the figure are described by Eq. (9). The slopes of the lines are given by $a' = p/\varsigma$.

Table Caption

Table 1. Materials, glass transition temperature T_g, values of the parameters B and C used in this study, shift factor $a_T = \ln(\eta_{Tg}/\eta_0)$ or $a^*_T = \ln(\tau_{Tg}/\tau_0)$, exponent p of the FSE law, methods used in the measurements of the diffusion coefficients D and the references where the data of the viscosity η or the relaxation time τ are provided. The acronyms used in the list stand for, MS (mass spectrometry), IS (isothermal desorption), FRAP (fluorescence recovery after photobleaching), respectively.
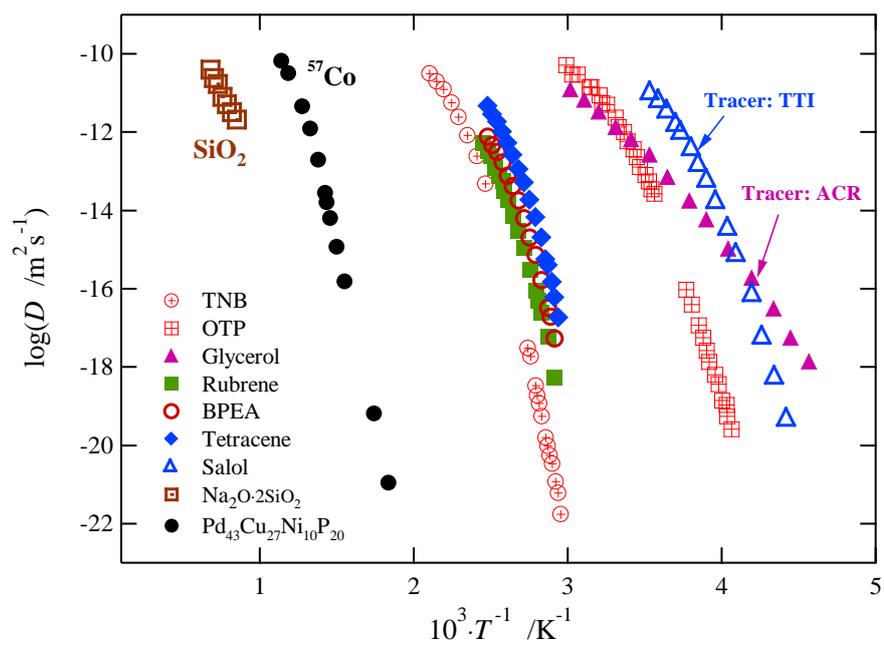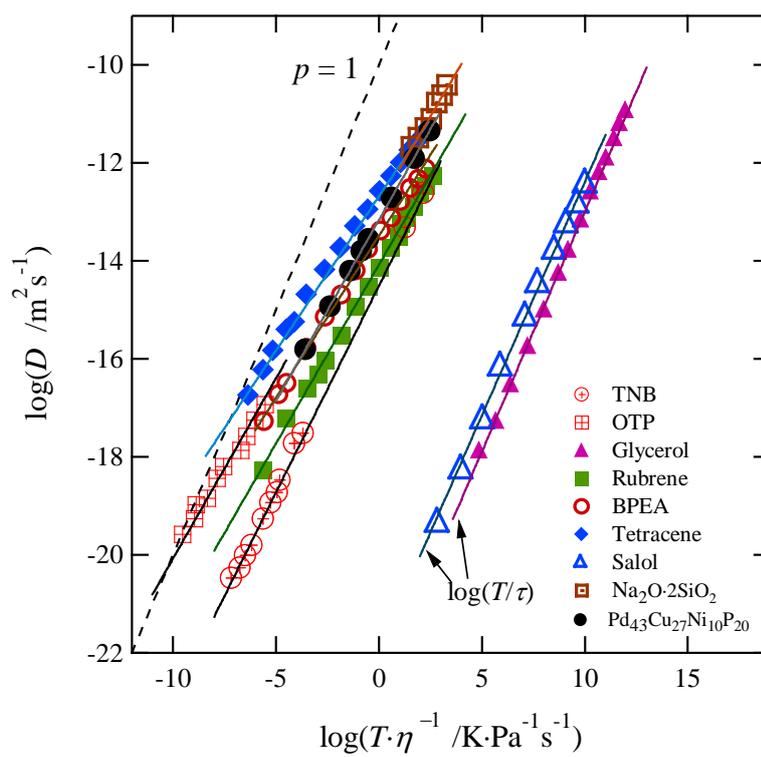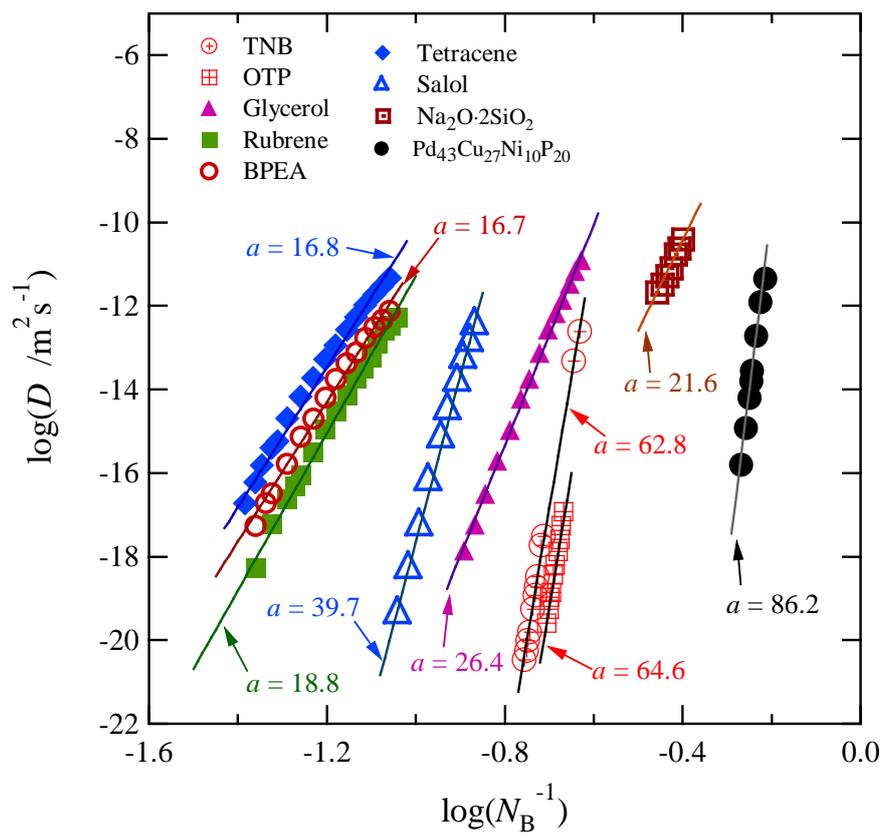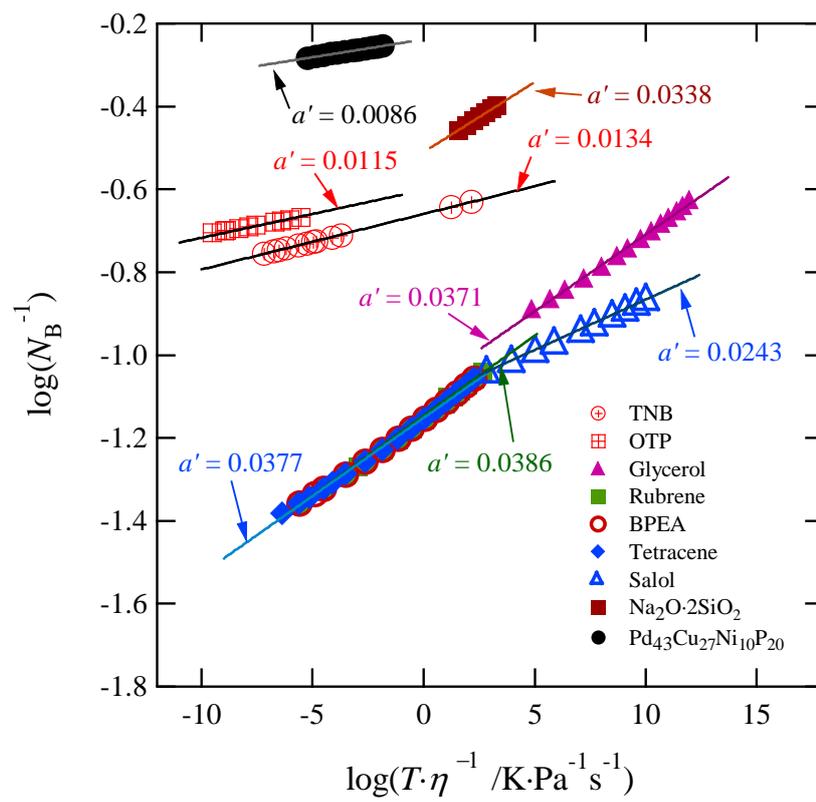
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Materials	T_g [K]	B	C	a_T	p	Method or the diffusive species (D)	η or τ(*)
Tris-naphthylbenzene (TNB)	343	0.34	27.6	66.3	0.84	MS [18]	[38]
o-terphenyl (OTP)	243	0.31	37.4	85.3	0.74	NMR, IS [16, 39,40]	[16,41]
Rubrene	337	0.64	8.5	43.5	0.73	FRAP [12]	[12]
9,10-bis(phenylethynyl)anthracene (BPEA)	337	0.64	8.5	43.5	0.66	FRAP [12]	[12]
Tetracene	337	0.64	8.5	43.5	0.63	FRAP [12]	[12]
$Na_2O \cdot 2SiO_2$	728	0.29	17.5	35.9	0.71	SiO_2 in $Na_2O \cdot 2SiO_2$ [20]	[20]
$Pd_{43}Cu_{27}Ni_{10}P_{20}$	582	0.09	50.8	72.1	0.74	Tracer (^{57}Co) [16,6]	[16,42]
Glycerol	185	0.52	11.2	40.3*	0.98	Tracer (ACR) [19]	[43]*
Salol	218	0.51	15.2	53.6*	0.95	Tracer (TTI) [19]	[43]*

Table 1