Analysis of the ionic conductivity in lithium salt-containing ionic liquids based on the bond strength-coordination number fluctuation model

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Abstract

The temperature dependence of the ionic conductivity of ionic liquids (ILs) and lithium salts mixtures (Li-ILs) that consist of N-methyl-N-propyl-pyrrolidinium (P_{13}^+) and 1-ethyl-3-methylimidazolium (emim$^+$) as cations, and bis(trifluoromethanesulfonyl)amide (TFSA$^-$) and bis(fluorosulfonyl)amide (FSA$^-$) as anions have been analyzed in terms of the fractional Stokes-Einstein (FSE) law and the bond strength-coordination number fluctuation (BSCNF) model of viscosity. In the present paper a new expression for the ionic conductivity is introduced to describe the temperature dependence of the ionic conductivity. It is shown that the derived relation of the ionic conductivity is in good agreement with the experimental values for the TFSA$^-$-based ILs and Li-ILs. Meanwhile, a noticeable change in the FSE behavior is confirmed for the case of FSA$^-$-based system. The relation between the molar conductivity Λ and the viscosity η is also discussed based on the fractional form of these quantities, $\Lambda T \propto (T/\eta)^p$, which is in turn, in good agreement with the experimental value for both systems. The present analysis also shows that according to the strong/fragile classification of liquids, the FSA$^-$-based ILs and Li-ILs are stronger than the TFSA$^-$-based ones, implying that the component anions influence qualitatively the difference in electrical and structural relaxations.

Keywords: Ionic Liquids; Lithium Salts; Ionic Conductivity; Fractional Stokes–Einstein Law

1. Introduction

During the last decades, the room temperature ionic liquids, or simply called ionic liquids (ILs) and their mixtures with lithium salts have attracted much interest due to their potential applications to electrochemical devices such as rechargeable lithium ion batteries [1-3]. From the electrochemical point of view, the high ionic conductivity is a key factor for the performance of materials used in devices. In order to explore further the materials properties of ILs, it is important to study the physicochemical properties from various points of views. In particular, it is necessary to know how the transport coefficients (viscosity η, diffusion coefficient D, ionic conductivity σ, etc.) are interrelated mutually [3-5], because such interrelations are useful to understand the mechanism of mass and charge transport [6].

Generally, the transport property of ILs and lithium salt-containing ILs (Li-ILs) is discussed in terms of the Nernst-Einstein (NE) and the Stokes-Einstein (SE) laws, or the fractional Stokes–Einstein (FSE) law, which is expressed as [7-11]

$$\sigma T \propto \left(\frac{T}{\eta} \right)^p , \tag{1}$$

where T is the absolute temperature and p is a parameter that describes the deviation from the original SE law ($0 < p \leq 1$). Eq. (1) has been used to describe the relation between the conductivity σ and the viscosity η [7,8]. For many kinds of viscous liquids, p takes a value less than unity. For instance, the values $p \approx 0.88$ for ionic glass-forming melt $Ca_2K_3(NO_3)_7$ [7] and $p \approx 0.66$ for neopentylimidazolium ILs with BF_4^- [9] have been reported. Note that there are different expressions for the FSE law [10,11]. One of these is given without the factor T, that is, $D \propto (\eta^{-1})^t$ [10], where D is the diffusion coefficient. Even for such a case, the value of the exponent t does not differ appreciably from that of p denoted in Eq. (1).

In an attempt to utilize the Li-ILs as electrolytes in batteries, the fundamental properties of Li-ILs where ILs are compounds such as bis(trifluoromethanesulfonyl)amide anion ($[(CF_3SO_2)_2N]^-$, or TFSA$^-$) have been studied extensively [1-3,12-14]. However, the ionic conductivity of such type of Li-ILs with TFSA$^-$ is lower than those of conventional organic solvents. This shortcoming of TFSA$^-$-based Li-ILs is related with their high viscosity [2,13]. On the other hand, it has been reported [3, 15, 16] that Li-ILs based on bis(fluorosulfonyl)amide anion ($[(FSO_2)_2N]^-$, or FSA$^-$) shows a lower value of viscosity than that based on TFSA$^-$. The difference in viscosity is ascribed to be due to the difference in the strength of the interaction between Li$^+$ and anionic species [15].

In our previous studies, we have discussed the materials properties of various glass-forming liquids based on the bond strength-coordination number fluctuation (BSCFN) model developed in our group [17-19]. Recently, it was found [20] that under a certain condition, the BSCNF model reduces to an expression very similar to the Vogel-Fulcher-Tammann (VFT) equation of viscosity. Thanks to this finding, new physical implication of the parameters that describe the VFT behavior is obtained. In the present study, to gain further understanding on transport property of Li-ILs, the temperature dependence of the ionic conductivity of TFSA$^-$- and FSA$^-$-based Li-ILs are analyzed based on the BSCNF model. The systems investigated in the present study are listed in Table 1 together with the material parameters and model parameters. The relation between the molar conductivity Λ and the viscosity η is also discussed based on the fractional form of these quantities, which is given as $\Lambda T \propto (T/\eta)^p$ [5, 21]. The experimental data of σ and η as well as Λ are taken from the literature [12,15].

2. Expression of ionic conductivity in terms of the BSCNF model

In most of the studies, the temperature dependence of the transport coefficients are examined using the VFT equation [3-5, 8, 9, 22, 23], which is a well-known relation that describes the non-Arrhenius temperature dependence. In the analysis of the ionic conductivity, the VFT-type expression which is given by

$$\sigma(T) = \sigma_0 T^{-1/2} \exp\left(-\frac{B_{\mathrm{VFT}}^{(\sigma)}}{T - T_0^{(\sigma)}}\right) \tag{2}$$

has been used widely [4,12,24-26,30]. The above expression has three free parameters, σ_0, $B_{\mathrm{VFT}}^{(\sigma)}$ and $T_0^{(\sigma)}$. In the case of viscosity, the VFT equation is given by

$$\eta(T) = \eta_0 \exp\left(\frac{B_{\mathrm{VFT}}^{(\eta)}}{T - T_0^{(\eta)}}\right) \tag{3}$$

This expression has been also used very widely and is known to reproduce well the experimental data with three adjustable parameters, η_0, $B_{\mathrm{VFT}}^{(\eta)}$ and $T_0^{(\eta)}$. In Eqs. (2) and (3), the pre-exponential factors, σ_0 and η_0, are the values of σ and η at high temperature limits, respectively. The physical meanings of the parameters B_{VFT} and T_0, as well as the correlations between these parameters and other transport coefficients, have been discussed by other groups [4-8,22,27]. The parameters of the VFT equation, B_{VFT} and T_0, are thought to be related with the effective activation energy barrier [8] and the ideal glass transition temperature. However, the origin of the VFT behaviors is still debated heatedly even nowadays [20,22,27].

Recently, we have reported [20] that under the condition of $\gamma = (|\Delta E|/E_0)/(|\Delta Z|/Z_0) = 1$, the BSCNF model of viscosity reduces to the following expression

$$\eta = \frac{\eta_0 T}{\sqrt{T^2 - T_{\mathrm{F}}^2}} \exp\left(\frac{T_{\mathrm{D}}}{T - T_{\mathrm{F}}}\right) \tag{4}$$

where

$$T_{\mathrm{D}} = \frac{E_0 \, Z_0}{R} \qquad \text{and} \qquad T_{\mathrm{F}} = \frac{|\Delta E| \, |\Delta Z|}{R}. \qquad (5)$$

Here, E_0 and Z_0 are the mean values of the bond strength and the coordination number of the structural units that form the liquid, and ΔE and ΔZ are their fluctuations, and R is the gas constant. When the BSCNF model is applied to the viscosity of ILs, the component ions of the liquid system (i.e., cations and anions) are regarded as the structural units. The viscous flow of the liquid occurs by disrupting the interactive binding forces between the correlated units through the thermal activation process [28]. According to the BSCNF model, the structural unit is surrounded by Z structural units. For the movement of a structural unit from one position to another, it necessitates to surmount an energy EZ. In the model, the bond energy and the coordination number are described as distributions [17]. For structurally disordered systems including liquid, the introduction of such distribution seems to be reasonable. The basic concept incorporated in our model, that is, the movement of the structural units by fleeing the interactive forces due to the thermal activation process, is in harmony with that of the interstice model [29] which has been applied to ionic liquids.

Turning back again to Eq. (4), it is interesting to note that it is a similar expression to the VFT equation given in Eq. (3), except for their pre-exponential parts. Despite this difference, Eq. (4) exhibits a behavior that follows very closely the behavior of Eq. (3). Indeed, the parameters T_{D} and T_{F} take almost the same values of $B_{\mathrm{VFT}}^{(\eta)}$ and $T_0^{(\eta)}$, respectively. Namely, we have found $T_{\mathrm{D}} \cong B_{\mathrm{VFT}}^{(\eta)}$ and $T_{\mathrm{F}} \cong T_0^{(\eta)}$ [20]. Fig. 1 shows that the VFT-like expression given in Eq. (4) reproduces well the experimental data of the viscosity of ILs and Li-ILs investigated in the present study. Thus, we can use Eq. (4) as an alternative relation to analyze the experimental data in place of the VFT equation that has been used so far. Moreover, the physical meanings of the parameters given in Eq. (5) are clearer than those of the VFT

equation. For instance, from Eq. (5), the strength parameter D (or also called the fragility parameter) given by $D=B_{VFT}/T_0$ [30,31] can be approximated as $D \cong D_F=(E_0 Z_0)/(|\Delta E||\Delta Z|)$. The values of D_F for the materials investigated are given in Table 1.

The application of Eq. (4) to the analysis of the conductivity is more informative than that with the case of VFT equation. For instance, Voronel et al. [7] have employed the Arrhenius-type expression given as $\eta/T=A_\eta \exp(E_a/kT)$ to discuss the FSE law. Here, A_η is the pre-exponential factor, E_a is the activation energy defined in this expression, and k is the Boltzmann's constant. Meanwhile, Eq. (4) enables one to relate η/T directly to σT through the FSE law. Thus we have from Eqs. (1) and (4)

$$\sigma \propto \eta_0^{-p} T^{p-1} \exp\left(-\frac{p\beta(T)}{T-T_F}\right) \tag{6}$$

where

$$\beta(T) = T_D - \frac{T-T_F}{2}\ln\left\{1-\left(\frac{T_F}{T}\right)^2\right\}. \tag{7}$$

It has been already shown [20] that the value of β depends only weakly on temperature and takes almost the same value of $B_{VFT}^{(\eta)}$. That is, $\beta \cong T_D \cong B_{VFT}^{(\eta)}$ over a wide range of temperature. By taking it into consideration, Eq. (6) reduces to

$$\sigma(T) \propto \frac{1}{T^{1-p}}\exp\left(-\frac{pT_D}{T-T_F}\right) \tag{8}$$

This relation suggests that the temperature dependence of the ionic conductivity σ can be understood using the material parameters of the BSCNF model of viscosity. It is also interesting to note that Eq. (8) is similar to the expression given in Eq. (2). It implies that the fractional exponent p is related directly to the parameters of Eq. (2). In other words, the effective activation barrier for the ionic conduction is reduced by a factor p from the activation

energy for the viscous flow (remember that $0 < p \leq 1$). This observation is corroborated with the lower activation energy for σ than that for η reported experimentally [4]. It also suggests the possibility to discuss the activation energy profiles of viscosity and conductivity from a unified point of view. In the next chapter, we will discuss the application of Eq. (8) to the ionic conductivity of TFSA$^-$- and FSA$^-$-based ILs and Li-ILs.

3. Result and discussion

Figure 2 (a) shows the temperature dependence of the ionic conductivity σ of [P$_{13}$][TFSA], [emim][TFSA], and their mixtures with lithium salts, [P$_{13}$][TFSA][Li] and [emim][TFSA][Li]. Here, the experimental data of σ are fitted using

$$\ln(\sigma \ /\text{Scm}^{-1}) = -\frac{pT_\text{D}}{T - T_\text{F}} - (1 - p)\ln(T \ /\text{K}) + \text{const.} \tag{9}$$

This equation is obtained based on Eq. (8). The values of T_D and T_F are determined from the viscosity analysis indicated in Fig. 1, and their specific values are given in Table 1. As shown in Fig. 2 (b) and (c), the values of p are determined from the $\ln(\sigma T)$ vs. $\ln(T/\eta)$ plots. The values obtained here are: p=0.81 ([P$_{13}$][TFSA]), p=0.85 ([P$_{13}$][TFSA][Li]), p=0.87 ([emim][TFSA]) and p=0.87 ([emim][TFSA][Li]), respectively. In Fig. 2 (b) and (c), the dashed lines indicate the SE law (i.e., p=1). In these figures, it is noted that the viscosity data in the lower temperature region are estimated by extrapolation, because no experimental data of η are provided in ref. [12,15]. From Fig. 2 (b) and (c), we can see that the TFSA$^-$-based systems follow the FSE law, which ensures the validity of Eq. (8) in the analysis of the temperature dependence of the ionic conductivity. Indeed, from Fig. 2 (a), it is observed that the newly derived expression Eq. (9) describes well the experimental data of the ionic conductivity of TFSA$^-$-based systems.

On the other hand, as shown in Fig. 3 and 4, a single use of Eq. (9) does not fit the measured ionic conductivity data of FSA$^-$-based ILs and Li-ILs over a wide temperature range. Fig. 3 shows the result of the analysis for [P$_{13}$][FSA] and [P$_{13}$][FSA][Li], while Fig. 4 shows the case for [emim][FSA] and [emim][FSA][Li]. In particular, Fig. 3 (a) and Fig. 4 (a) show that the theoretical curves given by Eq. (9) deviate from the experimental data, noticeably in the lower temperature region. In the high temperature region, the values of p are: p=0.80 for [P$_{13}$][FSA], p=0.83 for [P$_{13}$][FSA][Li], p=0.81 for [emim][FSA], and p=0.75 for [emim][FSA][Li], respectively. Analogously to Fig. 2 (b) and (c), these values of p are determined from the ln(σT) vs. ln(T/η) plots as shown in Figs. 3 (b), (c), 4 (b) and (c). In order to reproduce the experimental data in the low temperature region, another curve given by Eq. (9) with a different value of p is added to the first one. The values of p for those curves are: p=0.96 for [P$_{13}$][FSA], p=0.95 for [P$_{13}$][FSA][Li], p=0.96 for [emim][FSA], and p=0.91 for [emim][FSA][Li], respectively. From Figs. 3 (b), (c), 4 (b) and (c), it is seen that the FSE law for the FSA$^-$-based systems changes in the lower temperature regions. On the other hand, as already shown in Fig. 2, the FSE law for the TFSA$^-$-based ILs and Li-ILs do not show such changes. It should be noted that the characteristics of the material properties of TFSA$^-$ and FSA$^-$-based systems are seen in the viscosity behaviors. Namely, from Fig. 1, we can see that ILs and Li-ILs composed of FSA$^-$ are stronger than that of TFSA$^-$, according to the strong/fragile classification proposed by Angell [32]. From the result, it is implied that the anion component in Li-ILs influences qualitatively the difference between the electrical and structural relaxations. Concerning this point, we will discuss later again.

Kanakubo et al. [21] have pointed out that the fractional expression written as

$$\Lambda T \propto \left(\frac{T}{\eta}\right)^p, \tag{10}$$

where Λ is the molar conductivity, describes better the relation between the conductivity and the viscosity than Eq. (1). The validity of Eq. (10) is confirmed in Fig. 5. In particular, Fig. 5 (a) shows the temperature dependence of Λ for the P_{13}^+-based ILs and Li-ILs with both TFSA$^-$ and FSA$^-$. The solid lines in Fig. 5 (a) are reproduced using Eq. (9) by replacing σ by Λ. This conversion is based on Eq. (10) [21]. We can see that such reproduction follows the data of Λ reasonably. It should be noted that the temperature range of Λ shown in ref. [12] is narrower than that of σ. Fig. 5 (b) shows the relation between $\ln(\Lambda T)$ and $\ln(T/\eta)$ based on the fractional form given in Eq. (10). It permits the determination of the slope or the value of p. It is noted that except for the value of b (= const.), all the parameters such as T_D, T_F and p are the same to those used in Fig. 2 and Fig. 3. From the result, it is suggested that the viscous flow in ILs and Li-ILs with FSA$^-$ influences largely the ionic conduction as compared with the case of ILs and Li-ILs with TFSA$^-$. This indicates that the viscosity plays an important role in the ionic conduction of ILs systems [26].

Tsuzuki et al. [15] have discussed the origin of the low viscosity of FSA$^-$-based Li-ILs with emim$^+$ by means of ab initio numerical calculations and experiments. According to their study, the lower viscosity of FSA$^-$ complexes result from the smaller interaction energy for the FSA$^-$ complexes when compared with that for the corresponding TFSA$^-$ systems. Meanwhile, in the framework of the BSCNF model, some quantities related with transport property of viscous liquids can be calculated [18-20]. Among these, we can mention the mean interaction energy $\varepsilon = E_0 Z_0$ and the number of correlated molecular units (or the structural units, N_B [18,33]) involved in the thermal activation process. Here, N_B is a quantity closely related with the cooperativity within the liquids, whose expression of the temperature dependence is given by

$$N_{\text{B}}(T) = \frac{1}{T_{\text{D}}} \frac{d}{d(1/T)} \ln \eta(T_{\text{D}}, T_{\text{F}}, T). \tag{11}$$

According to the BSCNF model, the activation energy for viscous flow E_η can be expressed as $E_\eta = N_{\text{B}}\varepsilon$ [33], which is related with both, the number of correlated units involved in the viscous flow and the mean bond strength between the structural units or attractive forces operating in the liquid considered. For the case of ILs, the molecular units that compose the cations and anions are regarded as the structural units. Although it is not trivial to compare directly, for instance, ε with the stabilization energies calculated by Tsuzuki et al. [15], the physical quantities evaluated in terms of the BSCNF model are expected to give insights to discuss quantitatively the transport property of Li-ILs.

For instance, the values of N_{B} and E_η evaluated at room temperature ($T=300$ K) are shown in Table 1. For P_{13}^+-based ILs, the values of E_η are: $E_\eta=24.7$ kJ·mol^{-1} for [P_{13}][FSA], $E_\eta=38.2$ kJ·mol^{-1} for [P_{13}][FSA][Li], $E_\eta=31.7$ kJ·mol^{-1} for [P_{13}][TFSA], and $E_\eta=42.0$ kJ·mol^{-1} for [P_{13}][TFSA][Li], respectively. We notice that the addition of lithium salt induces an increase of the activation energy. This suggests that the attractive force between the structural units increases by adding lithium salts. We also notice that E_η of the systems with FSA$^-$ is smaller than that with TFSA$^-$. These observations are in accord with the discussion given in ref. [15]. On the other hand, for the emim$^+$-based ILs, the values of E_η are, $E_\eta=39.8$ kJ·mol^{-1} for [emim][FSA], $E_\eta=22.6$ kJ·mol^{-1} for [emim][FSA][Li], $E_\eta=26.6$ kJ·mol^{-1} for [emim][TFSA], and $E_\eta=31.2$ kJ·mol^{-1} for [emim][TFSA][Li], respectively. There, a clear material trend is not found as in the case of P_{13}^+-based ILs. This may be due to the difference of interactions between cationic and anionic species.

The fragility of a liquid can be characterized, for instance, through the strength parameter D. According to the strong/fragile scheme proposed by Angell [32], liquids with large and

small values of D are classified as strong and fragile systems [17,32-34]. As mentioned in the previous section, the value of D_F corresponds almost exactly to the strength parameter D [20]. From Table 1, we note that the calculated values of D_F for FSA⁻-based system are larger than that for TFSA⁻-based ones. That is, in terms of the BSCNF model, the average strength of the interaction in FSA⁻-based system is stronger than that in TFSA⁻-based ones, because according to this model, strong systems have large value of mean binding energy and small degree of energy fluctuations [17,19,33]. However, this picture seems to contradict intuitively the interpretation given in ref. [15]. There, it is discussed that the cause of the smaller viscosity of FSA⁻-based system compared with that of the TFSA⁻-based ones is due to the weak interaction between FSA⁻ and the cationic species such as emim⁺ and Li⁺. It suggests that the microscopic interaction between the cationic and anionic species is not as simple as expected. It is also important to understand the mechanism of aggregation or ion-pairing in the solutions, since it is closely related with the charge transport mechanism [6,35].

For typical binary ILs, it has been discussed [18] that the temperature dependence of N_B can be correlated with that of the self-diffusion coefficients of cations and anions. The picture obtained there implies that the diffusion process occurs highly cooperatively, and the diffusion process is driven by the bond-breaking between the structural units. The obtained picture is in harmony with the result of MD simulation [36].

4. Conclusion

In the present study, the temperature dependence of the ionic conductivity of the ILs, [P$_{13}$][TFSA], [emim][TFSA], [P$_{13}$][FSA] and [emim][FSA], and their mixtures with lithium salts, [P$_{13}$][TFSA][Li], [emim][TFSA][Li], [P$_{13}$][FSA][Li] and [emim][FSA][Li], were investigated in terms of the FSE law given in Eq. (1) and the BSCNF model of the viscosity. It

was shown that the newly introduced expression for the ionic conductivity is written in terms of the exponent p of the FSE law and the parameters of the BSCNF model, which gives a clue to understand the interrelation between the activation energies for conductivity and viscosity from a unified point of view. The present analysis revealed that the expression of σ given by Eq. (8) describes well the experimental data of the ionic conductivity of TFSA⁻-based ILs and Li-ILs. In contrast, for the FSA⁻-based systems, it does not reproduce the behavior over a wide temperature range. For the FSA⁻-based systems, it was seen that the FSE law changes noticeably in the low temperature region. This difference may ascribe to the influence of the viscosity to the ionic conduction as shown in Fig. 1. The relation between the molar conductivity Λ and the viscosity η was also discussed based on the fractional form of these quantities, $\Lambda T \propto (T/\eta)^p$, which is in turn, in good agreement with the experimental values for both systems. It was also discussed that from the outcome of the calculated values of D_F, the FSA⁻-based ILs and Li-ILs are stronger than the TFSA⁻-based ones, implying that the component anionic species influence qualitatively the difference in the electrical and structural relaxations.

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Figure Captions

Fig. 1. Temperature dependence of the viscosity of ILs and Li-ILs investigated in the present study. The parameters of the BSCNF model used to reproduce the experimental data are listed in Table 1.

Fig. 2. (a): Temperature dependence of the ionic conductivity of ILs and Li-ILs, [P$_{13}$][TFSA], [P$_{13}$][TFSA][Li], [emim][TFSA] and [emim][TFSA][Li]. (b): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ in [P$_{13}$][TFSA] and [emim][TFSA]. (c): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ in [P$_{13}$][TFSA][Li] and [emim][TFSA][Li].

Fig. 3. (a): Temperature dependence of the ionic conductivity of ILs and Li-ILs, [P$_{13}$][FSA] and [P$_{13}$][FSA][Li]. (b): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ in [P$_{13}$][FSA]. (c): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ for [P$_{13}$][FSA][Li]. In the figures (b) and (c), the arrows indicate the points where the values of p change. The estimated values of the viscosity were supplemented to compare with the measured ionic conductivity data in the lower temperature region. The same holds for Fig. 4.

Fig. 4. (a): Temperature dependence of the ionic conductivity of ILs and Li-ILs, [emim][FSA] and [emim][FSA][Li]. (b): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ in [emim][FSA]. (c): Relation between $\ln(\sigma T)$ and $\ln(T/\eta)$ in [emim][FSA][Li]. In the figures (b) and (c), the arrows indicate the points where the values of p change.

Fig. 5. (a): Temperature dependence of the molar conductivity of P$_{13}^{+}$–based ILs and Li-ILs. The curve fitting was done by replacing σ in Eq. (9) with Λ, based on Eq. (10). (b): Relation between $\ln(\Lambda T)$ and $\ln(T/\eta)$. The symbols and the parameters T_{D}, T_{F}, and p, are the same to those used in Figs. 2 and 3.

Table Caption

Table 1. BSCNF parameters determined by the viscosity analysis (η_0, T_D, T_F), the exponent p of the FSE law, the constant b in Eq. (9), the strength parameter D_F, the quantity N_B (T=300 K) defined in the text, and the activation energy for the viscous flow E_η (T=300 K). In the columns of p and b, two values determined at high (left column) and low (right column) temperatures are indicated.
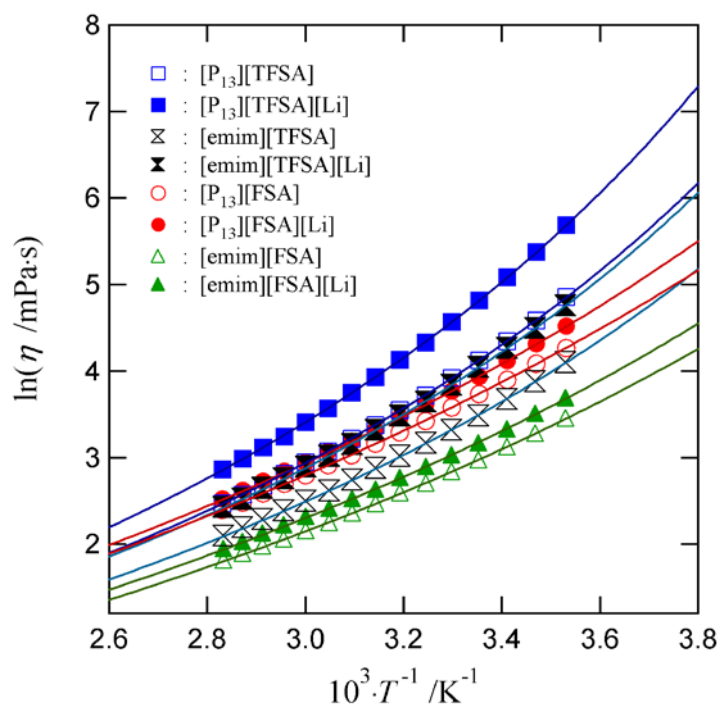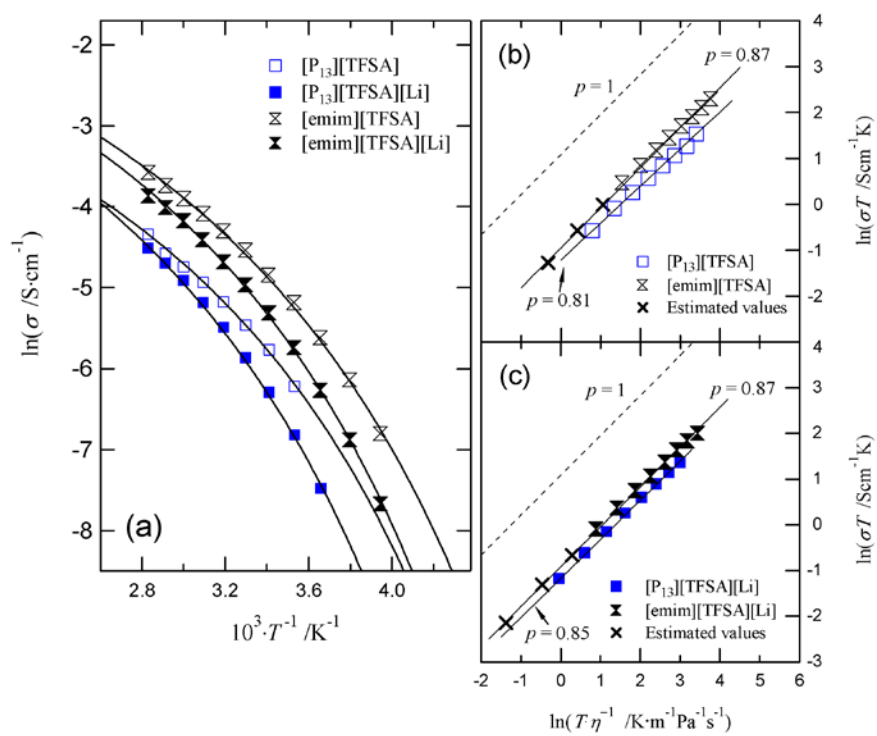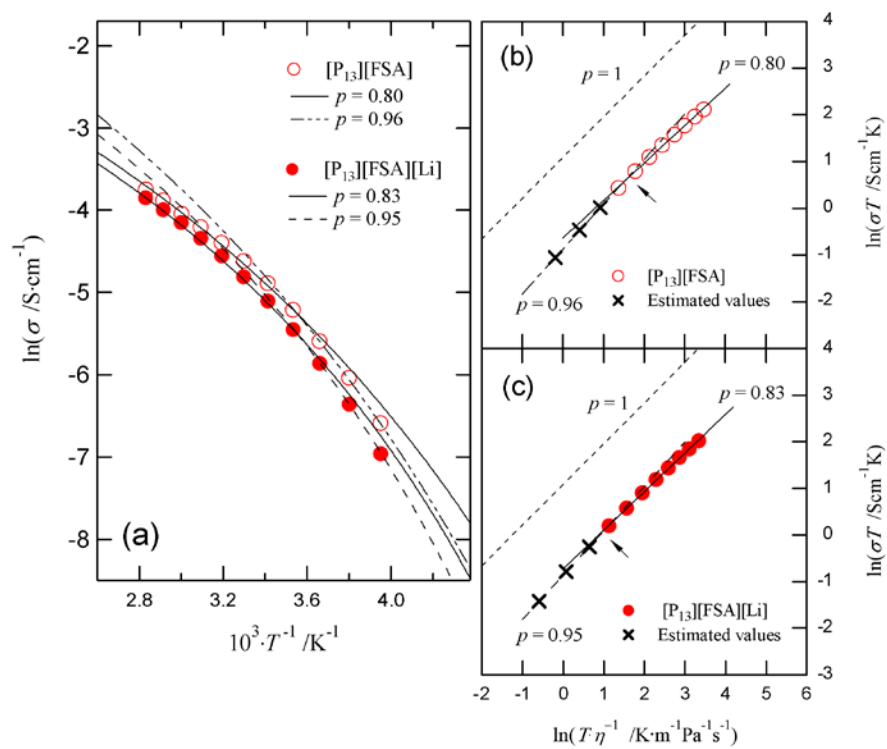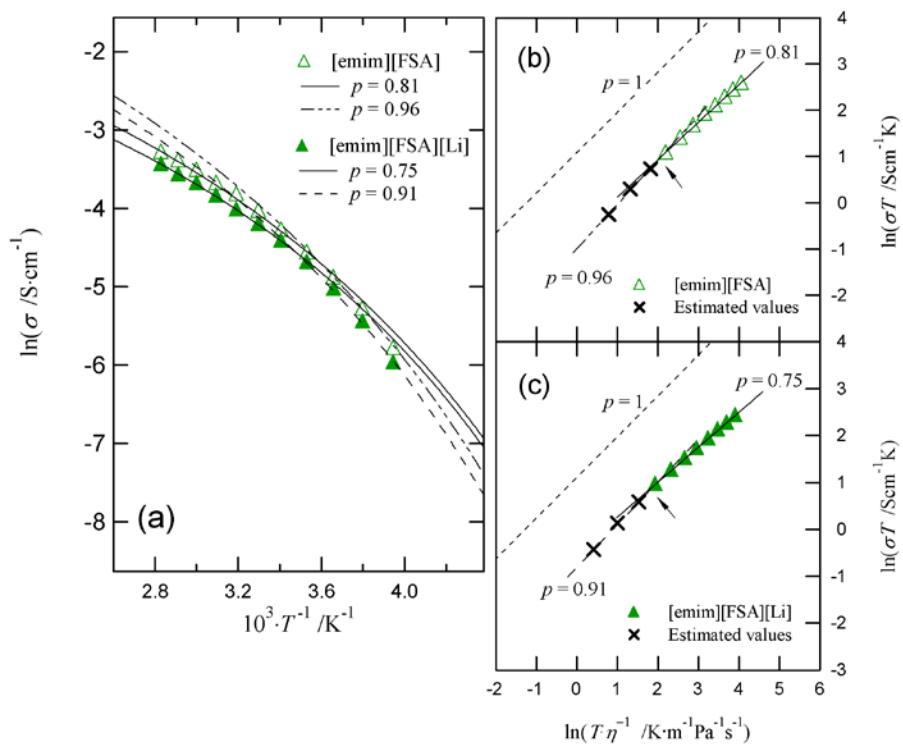
Fig. 1

Fig. 2

Fig. 3

Fig. 4
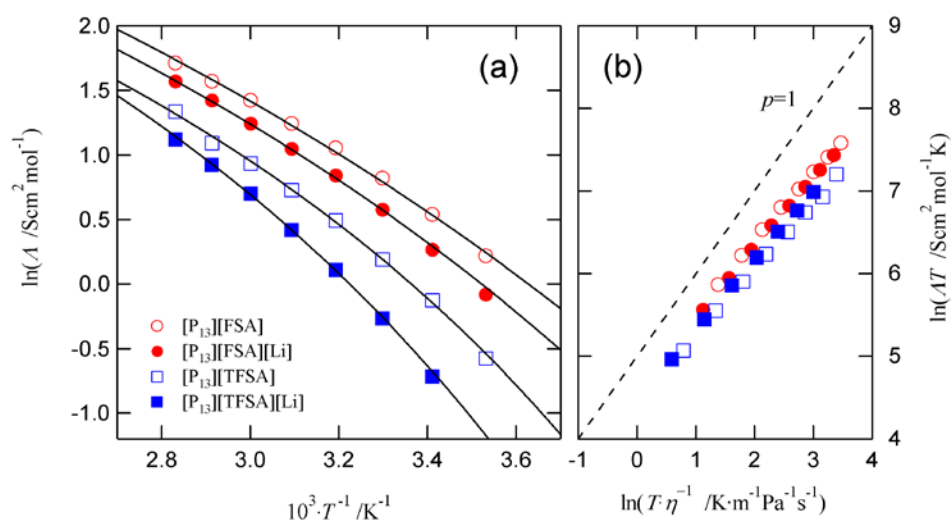
Fig. 5

System	η_0 /10^{-1} mPa·s	T_D /K	T_F /K	p		b /10^{-2}		D_F	N_B (300K)	E_η(300K) /kJ·mol^{-1}
[P$_{13}$][TFSA]	2.11	715	168	0.81,	–	-9.67,	–	4.3	5.3	31.7
[P$_{13}$][TFSA][Li]	1.81	796	172	0.85,	–	12.3,	–	4.6	6.4	42.0
[emim][TFSA]	2.22	667	161	0.87,	–	21.9,	–	4.1	4.8	26.6
[emim][TFSA][Li]	2.15	698	168	0.87,	–	24.9,	–	4.1	5.4	31.2
[P$_{13}$][FSA]	1.18	1013	123	0.80,	0.96	98.6,	111	8.2	2.9	24.7
[P$_{13}$][FSA][Li]	1.93	866	139	0.83,	0.95	51.9,	57.7	6.2	5.3	38.2
[emim][FSA]	1.72	754	135	0.81,	0.96	63.5,	57.8	5.6	6.4	39.8
[emim][FSA][Li]	1.80	756	140	0.75,	0.91	68.8,	59.6	5.4	3.6	22.6

Table 1