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1-丁腈-3-甲基咪唑双三氟甲基磺酸亚胺的性质

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摘要: 制备了功能化离子液体 1-丁腈-3-甲基咪唑双三氟甲基磺酸亚胺。在 T 为 283.15–353.15 K 温度范围内, 测定了该功能化离子液体的密度、动力粘度、电导率及折光率。讨论了亚甲基的增减对该类功能化离子液体的密度、动力粘度、电导率及折光率等性质的影响, 并与传统咪唑类、吡啶类离子液体物理化学性质的变化趋势进行了对比。通过经验方程计算了该功能化离子液体的热膨胀系数、分子体积、标准摩尔熵及晶格能等热力学性质参数。讨论了 Vogel-Fulcher-Tamman (VFT) 方程和 Arrhenius 方程的适用性, 得出 VFT 方程适用于该功能化离子液体, 而 Arrhenius 方程并不适用。有关研究对新型离子液体的合成及其工业化的应用具有十分重要的意义。

关键词: 功能化离子液体; 密度; 动力粘度; 电导率; 折光率

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Properties of 1-(Cyanopropyl)-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide

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Abstract: The functional ionic liquid (FIL) 1-(cyanopropyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [PCNMIM][NTf₂] was synthesized using an ion-exchange method. Density, dynamic viscosity, electrical conductivity, and refractive index were determined in the temperature range 283.15–353.15 K. The effect of methylene group introduction is discussed for the FILs and imidazolium ionic liquids (ILs). The thermal expansion coefficient, molecular volume, standard molar entropy, and lattice energy were determined by the empirical equations from the measurement values. The temperature dependence on electrical conductivity and dynamic viscosity of the FILs were fitted by the Vogel-Fulcher-Tammann (VFT) equation. The adaptability of the Arrhenius equation was also discussed for the electrical conductivity and dynamic viscosity. The study of the thermodynamic properties of the FIL is important for synthesis of new ILs and their application.

Key Words: Functional ionic liquid; Density; Dynamic viscosity; Electrical conductivity; Refractive index

1 Introduction

Ionic liquids (ILs) have exhibited outstanding physico-chemical

properties^{1–5}, like good solvation, negligible vapor pressure, good thermal stability, and designability etc. ILs have been applied for

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industrial and scientific area as the green solvents. The functional ionic liquids (FILs) have been paid much more attention because of the designability^{6–15}. The physical chemical properties can be designed according to the introduction of the functional groups, like $-\text{CN}$, $-\text{OH}$, $-\text{CH}_2-\text{O}-\text{CH}_3$, etc.

Egashira *et al.*^{6–8} have introduced the cyano group on the imidazolium FILs and quaternary ammonium FILs, respectively. The FILs have been applied in the lithium batteries as electrolyte components. The FILs have showed an improved cycle behavior compared with the electrolyte based on a tetraalkylammonium ionic liquid without a cyano group. The quaternary ammonium-based FILs containing a cyano group showed the better stability of the cathodic than the imidazolium-based FILs. Hardacre *et al.*^{9,10} have synthesized two series of pyridinium-based FILs in order to compare the effects of different electron-withdrawing functional groups on their ability to form ionic liquids. The presence of the electron-withdrawing functional groups nitrile or trifluoromethyl substituent on the pyridinium ring leads to salts with higher melting temperature than traditional ILs. On the basis, the authors have observed the liquid charge-transfer complex form on contacting electron-rich aromatics with electron withdrawing group appended 1-alkyl-4-cyanopyridinium ionic liquids. Zhang *et al.*¹¹ have studied the solubilities of C_2H_4 and CO_2 in the cyano type imidazolium FILs through the gas chromatography. Compared with the 1,3-dialkylimidazolium type ILs, the cyano type FILs result in a remarkable decrease of the interactions of hydrocarbons. The cyano type ILs have exhibited the advantageous properties. As the solvent, it can be applied as suitable reaction media and ligands in catalytic reaction, as electrolyte in lithium battery, as solvent for extraction of metals and dissolution of cellulose.

Although the cyano type FILs have been applied in some area, the physico-chemical properties are not enough for the application. Recently, the 1-(cyanomethyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [PCNMIM][NTf₂] has been synthesized in our group¹². The density, dynamic viscosity, electrical conductivity were determined by the traditional methods. In order to study the effect of the methylene on the properties for the series ILs, the 1-(cyanopropyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide [PCNMIM][NTf₂] was synthesized and the properties were determined. The comparison of the properties was also discussed with the non-functional traditional ILs. The traditional ILs are 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([EMIM][NTf₂]), 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([BMIM][NTf₂]), 1-ethyl-2,3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([EMMIM][NTf₂]), 1-butyl-2,3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([BMMIM][NTf₂]). Some of the thermodynamic properties were estimated from the measurement data by the empirical equations. The studies of the above FIL properties are important for the novel IL synthesis and industrial application.

2 Experimental

2.1 Materials

The putities, molecular weight (MW), and company name (Source) of the 1-(cyanomethyl)-3-methylimidazolium chloride ([PCNMIM][Cl]) and lithium bis[(trifluoromethyl)sulfonyl]imide ([Li][NTf₂]) are listed in Table S1 of the Supporting Information.

The hydrophobic FIL [PCNMIM][NTf₂] was obtained in the distilled water by the traditional ion exchange reaction according to the literature¹². The [PCNMIM][Cl] was dissolved by distilled water in flask, the equivalent amount of LiNTf₂ salt was added into the flask under stirring. The bottom colorless phase was washed several times with distilled water until no Cl^- (it was determined by $\text{AgNO}_3/\text{HNO}_3$ solution, the content of Cl^- was estimated to lower than 0.005% (in mass fraction). The products were finally dried in high vacuum for 48 h at 353 K. The FIL [PCNMIM][NTf₂] was characterized by ^1H NMR and ^{13}C NMR spectra (See the Figs.S1 and S2 of the Supporting Information). The final mass fraction and molecular weight of the FIL [PCNMIM][NTf₂] were also listed in Table S1 of the Supporting Information.

In order to compare the differences of the structure, the [PCNMIM][NTf₂], [MCNMIM][NTf₂], ([EMIM][NTf₂]), and ([BMIM][NTf₂]) are presented in Fig.1.

2.2 Measurements of the density, electrical conductivity, dynamic viscosity, and refractive index

The weight content of the water was determined by a Cou-Lo Aquamax Karl Fischer moisture meter v.10.06 (Mettler Toledo, Switzerland), and was found to be $< 0.02\%$ (in mass fraction). Recently, Jacquemin *et al.*¹⁶ have studied the effect of the water content on the hydrophobic IL [EMIM][NTf₂] properties (density and dynamic viscosity) from 0.005% to 1.98% (mass fraction). So, the water content can be ignored in this work.

The density, electrical conductivity, dynamic viscosity, and refractive index were determined by a previous method at atmosphere¹². The uncertainties of the experimental values are also estimated according to literature^{17–20}.

The density and dynamic viscosity of the FIL [PCNMIM][NTf₂] was determined by a automated SVM3000 Anton Paar rotational Stabinger viscometer-densimeter (Anton Paar GmbH, Austria) with cylinder geometry at $((288.15\text{--}338.15) \pm 0.01) \text{ K}$ ¹². The principle was based on a modified Couette according to a rapidly rotating outer tube and a relative slowly rotating inner measuring bob. The values were recorded every 5 K after attaining thermal equilibrium 30 min. The electrical conductivity was carried out on a MP522 conductivity instrument (Shanghai San-Xin Instrumentation, P. R. China) with the cell constants of 1 cm^{-1} (the cell was calibrated with the aqueous KCl solution) at $((288.15\text{--}338.15) \pm 0.05) \text{ K}$ ¹². The measurement frequency and voltage of the electrical conductivity were 50 Hz and 9 V, respectively. The refractive index was carried out according to the literature²¹. The data were carried on an Abbe refractometer (Shanghai Shen Guang Instrument Co., P. R. China) and the frequency was 50 Hz. The degassed water refractive index was determined by the instrument at

Fig.1 Structures of [PCNMIM][NTf₂], [BMIM][NTf₂], [MCNMIM][NTf₂], and [EMIM][NTf₂]

(298.15 ± 0.05) K and the value was in good agreement with the literature²². Each value was the average of the three times and the standard uncertainties were ±0.0002 g·cm⁻³ for density at 0.65 confidence level, ±1% for dynamic viscosity at 0.95 confidence level, and ±1% for dynamic viscosity at 0.95 confidence level. The uncertainty values were estimated from the effect of the machine, room temperature and pressure, water and halogen content etc.

The above experimental values are listed in Table 1.

3 Results and discussion

From the Table 1, the value of electrical conductivity is 1.125 mS·cm⁻¹ for FIL [PCNMIM][NTf₂] and the relative deviation is

Table 1 Experimental values of density, ρ , dynamic viscosity, η , electrical conductivity, σ , and refractive index, n_D , of [PCNMIM][NTf₂] from 283.15 to 353.15 K under atmosphere pressure

T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\sigma/(\text{mS}\cdot\text{cm}^{-1})$	n_D
283.15	1529.0	612.68	0.425 ^a	1.4421 ^a
288.15	1523.9	419.66	0.612	1.4412
293.15	1519.1	303.31	0.841	1.4400
298.15	1514.3	222.35	1.125	1.4387
303.15	1509.7	166.86	1.473	1.4373
308.15	1505.1	131.14	1.874	1.4360
313.15	1500.6	99.090	2.33	1.4349
318.15	1496.1	78.438	2.88	1.4339
323.15	1491.6	63.791	3.49	1.4328
328.15	1487.0	55.023	4.17	1.4317
333.15	1482.6	44.728	4.94	1.4306
338.15	1478.1	37.515	5.78	1.4296
343.15	1473.7	29.223	6.66	1.4285
348.15	1469.2	26.418	7.60	1.4275
353.15	1464.8	23.573	8.65 ^a	1.4262 ^a

^a calculated value

6.25% with the literature value of 1.2 mS·cm⁻¹ at 298.15 K⁷.

In order to compare the influence of methylene on IL properties, the values of density, dynamic viscosity, and electrical conductivity for three series ILs are listed in Table 2 at 298.15 K. The ILs are [EMIM][NTf₂], [BMIM][NTf₂], [EMMIM][NTf₂], [BMMIM][NTf₂], [MCNMIM][NTf₂], and [PCNMIM][NTf₂], respectively.

From Table 2, the three series ILs have exhibited the same tendency for density after the introduction of the methylene on alkyl side chain. Usually, for dynamic viscosity and electrical conductivity, the introduction of the methylene leads to the increase of dynamic viscosity and decrease of electrical conductivity. However, for the two FILs, the values have exhibited the contrary tendency with the traditional ILs. Compared with the literature¹², the dynamic viscosity values of FIL [PCNMIM][NTf₂] are lower than FIL [MCNMIM][NTf₂] and the electrical conductivity values of FIL [PCNMIM][NTf₂] are higher than FIL [MCNMIM][NTf₂] in the temperature range. The abnormal results have been also discovered for traditional pyridinium type ILs from our group²³⁻²⁷. For the pyridinium type ILs, the electrical conductivity values increase when the methyl group is introduced on position 4. The dynamic viscosity values decrease when the methyl group is introduced on position 4. We believe that the groups of the electron withdrawing and electron donating play the important role to the effect of the properties. —CN is the electron withdrawing group, —CH₂— and —CH₃ are the electron donating groups. For the two series ILs, the introduction of the —CH₂— and —CH₃ leads to the cation having the relatively symmetry structure. Then, the cation and anion are relatively far away and the force of them becomes weak. So, the ILs exhibit the high fluidity after the introduction of —CH₂— and —CH₃.

Based on the same anion, at 298.15 K, the density follows the order of ILs [C₄mpy][NTf₂] < [BMMIM][NTf₂] < [BMIM]

Table 2 Comparison of density, dynamic viscosity, and electrical conductivity of [EMIM][NTf₂], [BMIM][NTf₂], [EMMIM][NTf₂], [BMMIM][NTf₂], [MCNMIM][NTf₂], and [PCNMIM][NTf₂] at 298.15 K under atmosphere pressure

IL	MW/(g·mol ⁻¹)	$V/(\text{cm}^3\cdot\text{mol}^{-1})$	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\sigma/(\text{mS}\cdot\text{cm}^{-1})$
[EMIM][NTf ₂]	391.31	257.75	1518.2 ^a	32.0 ^a	8.96 ^a
[BMIM][NTf ₂]	419.36	291.91	1436.6 ^a	51.7 ^a	3.98 ^a
[EMMIM][NTf ₂]	405.33	271.48	1493.1 ^a	72.2 ^a	3.89 ^a
[BMMIM][NTf ₂]	433.38	304.70	1422.4 ^a	101.6 ^a	2.12 ^a
[MCNMIM][NTf ₂]	402.29	249.92	1609.7 ^b	315.5 ^b	0.919 ^b
[PCNMIM][NTf ₂]	430.34	284.18	1514.3 ^c	222.35 ^c	1.125 ^c

^a literature²²; ^b literature¹²; ^c this work

[NTf₂] < [C₄py][NTf₂] < [PCNMIM][NTf₂], whereas the experimental density values are 1.5143 g·cm⁻³ for [PCNMIM][NTf₂], 1.4366 g·cm⁻³ for [BMIM][NTf₂]²⁸, 1.4224 g·cm⁻³ for [BMMIM][NTf₂]²⁸, 1.4547 g·cm⁻³ for 1-ethylpyridinium bis[(trifluoromethyl)sulfonyl]imide [C₄py][NTf₂]²⁵, and 1.4187 g·cm⁻³ for 4-methyl-1-butylpyridinium bis[(trifluoromethyl)sulfonyl]imide [C₄mpy][NTf₂]²⁶. The dynamic viscosity follows the order of ILs [BMIM][NTf₂] < [C₄mpy][NTf₂] < [C₄py][NTf₂] < [BMMIM][NTf₂] < [PCNMIM][NTf₂], whereas the values are 222.35 mPa·s for [PCNMIM][NTf₂], 51.7 mPa·s for [BMIM][NTf₂]²⁸, 101.6 mPa·s for [BMMIM][NTf₂]²⁸, 58.3 mPa·s for [C₄py][NTf₂]²⁷, and 55.14 mPa·s for [C₄mpy][NTf₂]²⁶. The electrical conductivity follows the order of ILs [PCNMIM][NTf₂] < [C₄py][NTf₂] < [BMMIM][NTf₂] < [C₄mpy][NTf₂] < [BMIM][NTf₂], whereas the values are 1.125 mS·cm⁻¹ for [PCNMIM][NTf₂], 2.12 mS·cm⁻¹ for [BMMIM][NTf₂]²⁸, 3.98 mS·cm⁻¹ for [BMIM][NTf₂]²⁸, 1.67 mS·cm⁻¹ for [C₄py][NTf₂]²⁷, and 3.41 mS·cm⁻¹ for [C₄mpy][NTf₂]²⁶.

From the above result, the introduction of the —CN functional group on imidazolium ring leads to the density and dynamic viscosity increasing, electrical conductivity decreasing. The reason of the above result may be the increasing of the van der Waals force between the functional group with cation or anion and insufficient side-chain mobility. The effect order of the interaction force is —CN > —CH₃.

The temperatures dependences on density, electrical conductivity, dynamic viscosity, and refractive index of the FIL [PCNMIM][NTf₂] are plotted in Figs.2 and 3. From the Fig.2, it can be seen that the lines of density and refractive index are linear one with the increasing of the temperature. From the Fig.3, the electrical conductivity and dynamic viscosity exhibit non-linear one with temperature increasing.

3.1 Density

From Fig.2, the $\ln\rho$ vs T can be fitted according to the following straight line. The thermal expansion coefficient, α , can be obtained.

$$\ln\rho = b - \alpha T \quad (1)$$

herein, ρ is the density values, b is an empirical constant, α is the thermal expansion coefficient, T is the experimental temperature. The thermal expansion coefficient is $6.09 \times 10^{-4} \text{ K}^{-1}$. The value is in the range of 5×10^{-4} and $7 \times 10^{-4} \text{ K}^{-1}$ which obtained by Jacquemin *et al.*¹⁶.

According to Glasser²⁹, the empirical equations are used for estimation of the molecular volume, V_m , standard molar entropy, S^0 , and lattice energy, U_{POT} from density values.

$$V_m = M/(N \cdot \rho) \quad (2)$$

$$S^0 = 1246.5V_m + 29.5 \quad (3)$$

$$U_{\text{POT}} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (4)$$

herein, M is molar mass, N is Avogadro's constant, The calculated values of the above are 0.4721 nm³ for molecular volume, 617.9 J·K⁻¹·mol⁻¹ for standard molar entropy, and 405 kJ·mol⁻¹ for lattice energy, respectively. According to the literature¹², the value of the molecular volume is 0.4151 nm³. The contribution of the

Fig.2 Density and refractive index vs temperature plots for FIL [PCNMIM][NTf₂]

Fig.3 Dynamic viscosity and electrical conductivity vs temperature plots for [PCNMIM][NTf₂]

methylene to the molecular volume is 0.0285 nm³ for the cyano type FILs. The value is in good agreement with the reported values of 0.0277 nm³ for [C_n3mpy][NTf₂] ($n = 3, 4, 6$)²³, 0.0289 nm³ for [C_nmpy][NTf₂] ($n = 2, 4, 6$)²³, 0.0280 nm³ for ILs [C_npy][NTf₂]^{24,30}, 0.0282 nm³ for [C_nmim][NTf₂]²⁹, and 0.0279 nm³ for Amino acid at 298.15 K³¹⁻³⁴. The lattice energy is much lower than traditional salts, like $U_{\text{POT,CSl}} = 613 \text{ kJ} \cdot \text{mol}^{-1}$ ²². Usually, the ILs exhibit the low lattice energy²³⁻³⁴. And it is the reason that the ILs have the relatively low melting temperature, can exist as liquid state at room temperature.

3.2 Molar electrical conductivity

The molar electrical conductivities can be calculated from density and electrical conductivity by the following equation:

$$\Lambda = \sigma M \rho^{-1} \quad (5)$$

where Λ is the molar electrical conductivity, σ is the electrical conductivity, M is the molar mass, and ρ is the density. The molar electrical conductivity values are listed in Table 3.

3.3 Electrical conductivity

Recently, Vila *et al.*³⁵ have built the relationship of the Vogel-Fulcher-Tamman (VFT) and Arrhenius equations as the modified VFT equation. The electrical conductivity activation energies for the four FILs can be calculated by the modified VFT equation. The VFT equation, Arrhenius equation, and modified VFT equation are below:

Table 3 Calculated values of molar electrical conductivity [PCNMIM][NTf₂] at 288.15–338.15 K under atmospheric pressure

<i>T</i> /K	<i>A</i> /(S·cm ² ·mol ⁻¹)	<i>T</i> /K	<i>A</i> /(S·cm ² ·mol ⁻¹)
283.15	0.119	323.15	1.007
288.15	0.173	328.15	1.207
293.15	0.238	333.15	1.434
298.15	0.320	338.15	1.683
303.15	0.420	343.15	1.945
308.15	0.536	348.15	2.226
313.15	0.668	353.15	2.541
318.15	0.828		

The uncertainties are $\pm 0.001 \text{ mS} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ for molar electrical conductivity and $\pm 0.05 \text{ K}$ for temperature at 0.95 confidence level.

$$\sigma = \sigma_0 \exp(-B/(T - T_0)) \quad (6)$$

$$\sigma = \sigma_\infty \exp(-E_a/(k_B T)) \quad (7)$$

$$\sigma = \sigma_\infty \exp(-E_a/(k_B(T - T_0))) \quad (8)$$

here σ is the electrical conductivity; σ_0 , B are fitting parameters; E_a is the activation energy, which indicates the energy needed for an ion to hop to a free hole; σ_∞ is the maximum electrical conductivity, k_B is the Boltzmann constant, $\sigma_0 = \sigma_\infty$ and $B = E_a/k_B$.

The fitted equation is $\sigma = 491.6 \exp(661.8/(T + 189.3))$ by the equation (6). And the correlation coefficient, R , is 0.99997, which indicates that the VFT equation can be well used for the electrical conductivity fitting. The calculated value of electrical conductivity activation energy is $57.1 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [PCNMIM][NTf₂] according to equation (8). According to literature¹², the electrical conductivity activation energies are $53.6 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [MCNMIM][NTf₂] and $47.6 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [EOHMIM][NTf₂], respectively. The FIL [PCNMIM][NTf₂] exhibits the highest energy than other two FILs [MCNMIM][NTf₂] and [EOHMIM][NTf₂].

By the Arrhenius equation, the $\ln \sigma$ vs $1000/T$ was plotted for the FIL in Fig.4.

3.4 Dynamic viscosity

Like the electrical conductivity, the VFT equation, Arrhenius equation, and modified VFT equation are below:

$$\eta = \eta_0 \exp(B/(T - T_0)) \quad (9)$$

$$\eta = \eta_\infty \exp(E_\eta/(k_B T)) \quad (10)$$

$$\eta = \eta_\infty \exp(E_\eta/(k_B(T - T_0))) \quad (11)$$

where η is the dynamic viscosity; η_0 , B are fitting parameters; E_η is the activation energy for dynamic viscosity; η_∞ is the maximum dynamic viscosity, k_B is the Boltzmann constant, $\eta_0 = \sigma_\infty$ and $B = E_\eta/k_B$.

The best fitted equation is $\eta = 0.16 \exp(882.1/(T + 176.2))$ by the equation (9). And the correlation coefficient, R , is 0.99989, which indicates that the VFT equation can also be used for the dynamic viscosity fitting. The dynamic viscosity activation energy can also be calculated and the value is $76.1 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [PCNMIM][NTf₂] according to equation (11). According to literature¹², the dynamic viscosity activation energies are $62.9 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [MCNMIM][NTf₂] and $59.7 \text{ kJ} \cdot \text{mol}^{-1}$ for FIL [EOHMIM][NTf₂], respectively. Like the electrical conductivity activation energies, the FIL [PCNMIM][NTf₂] have also exhibited

Fig.4 Plots of $\ln \eta$ and $\ln \sigma$ vs $1000/T$ for FIL [PCNMIM][NTf₂]

the highest energy than other two FILs [MCNMIM][NTf₂] and [EOHMIM][NTf₂].

According to equation (10), the $\ln \eta$ vs $1000T^{-1}$ was also described in Fig.4 like electrical conductivity for the FIL [PCNMIM][NTf₂].

In Fig.4, the black lines are straight lines for fitting of $\ln \sigma$ vs $1000T^{-1}$ and $\ln \eta$ vs $1000T^{-1}$. From the Fig.4, the experimental points are distributed on both sides of the black straight lines. It indicated that the Arrhenius equation is not well fit for the fitting of the electrical conductivity and dynamic viscosity on temperature.

3.5 Walden product

The relationship of molar conductivity and dynamic viscosity can be built by the following Walden equation:

$$\Lambda \eta^\alpha = k \quad (12)$$

$$\lg \Lambda = \lg k + \alpha \lg \eta^{-1} \quad (13)$$

where α is the fitting parameter, k is a temperature dependent constant. The description of $\lg \Lambda$ vs $\lg \eta^{-1}$ is shown in Fig.5 for the FIL [PCNMIM][NTf₂] from 283.15 to 353.15 K. The slope, α , can be obtained and the value is 0.927 for FIL [PCNMIM][NTf₂]. In order to compare the relationship, the five others imidazolium type ILs^{12,23} are also plotted at 298.15 K in Fig.5. The solid straight line is the ideal line for aqueous KCl solutions³⁶.

From Fig.5, like the others five ILs, the Walden point of the FIL [PCNMIM][NTf₂] is below and close to the ideal line, so, the FIL [PCNMIM][NTf₂] is also called “subionic”³⁷. It means that the FIL [PCNMIM][NTf₂] did not yield the expected conductivity from the high fluidities because on average the proton transfer is incomplete³⁷. From the Fig.5, the Walden points have exhibited the different change tendency for the three series ILs at 298.15 K. For the traditional ILs, the Walden points of [BMIM][NTf₂] and [BMMIM][NTf₂] are lower than [EMIM][NTf₂] and [EMMIM][NTf₂] following the ideal line, respectively. However, the FIL is reversible, the Walden point of [MCNMIM][NTf₂] is lower than [PCNMIM][NTf₂]. We think that the FIL [PCNMIM][NTf₂] has a better fluidity than [MCNMIM][NTf₂]. The result can also be explained according to the dynamic viscosity and electrical conductivity. Compared with the literature¹², the dynamic viscosity values of FIL [PCNMIM][NTf₂] are lower than FIL [MCNMIM][NTf₂] and the electrical conductivity values of FIL [PCNMIM]

Fig.5 Plot of $\lg A$ vs $\lg \eta^{-1}$ for the FIL [PCNMIM][NTf₂] in the whole measurement temperature with other imidazolium type ILs at 298.15 K

The solid straight line is the ideal line for aqueous KCl solutions.

[NTf₂] are higher than FIL [MCNMIM][NTf₂] in the temperature range.

3.6 Refractive index

The relationship of refractive index and temperature can also be described for the FIL [PCNMIM][NTf₂] by a linear equation:

$$n_D = A + BT \quad (14)$$

where n_D is the refractive index; A , B are fitting parameters; T is experimental temperature. The fitted linear equation is $n_D = 1.5064 - 2.27 \times 10^{-4}T$. The correlation coefficient is 0.997 from the experimental values. It indicates that the linear equation is fit for the fitting of the refractive index on temperature.

4 Conclusions

The density, electrical conductivity, dynamic viscosity, and refractive index of the FIL [PCNMIM][NTf₂] were determined at atmospheric pressure at 283.15–353.15 K. The FIL [PCNMIM][NTf₂] exhibited the lower lattice energies than the traditional melt salts, it is the reason that the ionic liquid is liquid at room temperature. The dynamic viscosity of [PCNMIM][NTf₂] is lower than [MCNMIM][NTf₂] and the electrical conductivity of [PCNMIM][NTf₂] is higher than [MCNMIM][NTf₂]. The FIL [PCNMIM][NTf₂] exhibits a better fluidity than [MCNMIM][NTf₂], it is reversible with the traditional imidazolium type ionic liquids. The VFT equation can be well used for fitting of the electrical conductivity and dynamic viscosity on temperature, however, the Arrhenius equation not fit. The temperature dependence on refractive index can be well fitted by the linear equation. The property study of the FIL [PCNMIM][NTf₂] will be significant for industrial and engineering applications.

Supporting Information: The ¹H NMR and ¹³C NMR spectra have been included. This information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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1-丁腈-3-甲基咪唑双三氟甲基磺酸亚胺的性质

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Properties of 1-(Cyanopropyl)-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide

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Table S1 The purity (by mass), molecular weight (MW), and company name (Source) of the [PCNMIM][Cl], [Li][NTf₂], and [PCNMIM][NTf₂]

Name	Purity (by mass)	MW	Source
[PCNMIM][Cl]	≥ 0.99%	185.64	Lanzhou Institute of Chemical Physics
[Li][NTf ₂]	≥ 0.99%	287.09	Solvay (ZhenJiang) Chemicals Co., LTD
[PCNMIM][NTf ₂]	≥ 0.99%	430.35

Fig.S1 ¹H NMR of [PCNMIM][NTf₂]

Fig.S2 ^{13}C NMR of [PCNMIM][NTf₂]