Study on Thermodynamic Properties of Ionic Liquid *N*-Butyl-3-methylpyridinium Bis(trifluoromethylsulfonyl)imide

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Ⓢ *Supporting Information*

ABSTRACT: An air- and water-stable hydrophobic ionic liquid *N*-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([c₄3mpy][NTf₂]) was synthesized and characterized. Density, surface tension, dynamic viscosity, and electrical conductivity of the IL were measured and calculated from (278.15 to 353.15) K. The glass transition temperature and decomposition temperature were determined by the differential scanning calorimetry and thermogravimatric analysis. The physicochemical properties like molecular volume, standard molar entropy, lattice energy, parachor, molar enthalpy of vaporization, interstice volume, thermal expansion coefficient, interstice fraction, etc. of the IL were estimated by the reported empirical and semiempirical equations. The dynamic viscosity and electrical conductivity data of the IL were described by Vogel−Fulcher−Tamman and Arrhenius equations, respectively. Then, the relationship between the molar conductivity and dynamic viscosity of this IL was expressed through the Walden rule.
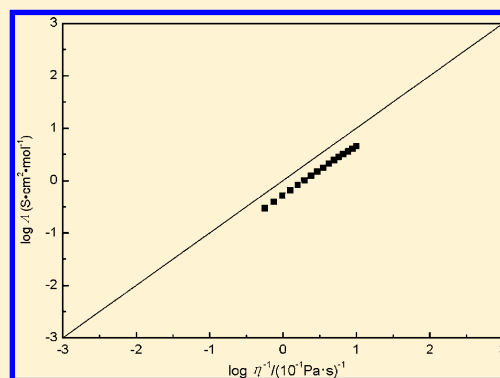
INTRODUCTION

Ionic liquids (ILs) are liquid organic salts at ambient temperature that exhibit outstanding physicochemical properties like low melting temperature, good capability of solvation, negligible vapor pressure, high electrical conductivity, as well as high thermal stability. The ILs have attracted more and more attention as "green" solvents from both the industrial and scientific communities.[1−6] Most ILs have hydrophilic backgrounds, whereas the hydrophobic ILs with functional anions like $[PF_6]^-$, $[NTf_2]^-$, $[PF_3(CF_2CF_3)_3]^-$, etc. have greater practical potential in industrial application,[7−14] particularly in electrochemistry as a advanced electrolyte materials.[15−19] The properties of series hydrophobic imidazolium-based ILs with a functional anion $[NTf_2]^-$, such as melting temperature, glass transition temperature, dynamic viscosity, electrical conductivity, etc. have been studied by Tokuda et al.[20,21]

Because of a current trend of seeking for easily obtained and low-cost ILs other than alkyl imdazolium-based ILs,[14,22] the previous works of our group[14,23,24] focused on a family of pyridinium-based ILs. Some important properties of the ILs like density, surface tension, dynamic viscosity, electrical conductivity, melting temperature, and decomposition temperature were determined. Herein, as a continuous work, a hydrophobic and easily obtained pyridinium-based ionic liquid *N*-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide $[C_43mpy][NTf_2]$ was prepared and characterized. For a deeper understanding of the characteristics of this IL and to broaden its applicability, the physicochemical properties of the IL $[C_43mpy][NTf_2]$, such as density, surface tension, dynamic

viscosity, and electrical conductivity, were measured at different temperatures. Some important thermodynamic parameters like standard molar entropy and lattice energy were estimated in terms of Glasser's theory,[25] and the parachor was estimated by an empiric equation from the literature.[26] In terms of Kabo's empirical equation[27] and interstice model theory,[28] the molar enthalpy of vaporization, the interstice volume, interstice fraction, and thermal expansion coefficient of the IL were also estimated. The dynamic viscosity or the electrical conductivity of the IL as a function of temperature were described by the Vogel−Fulcher−Tammann (VFT) method and Arrhenius equations, respectively.[23,24,29−31] Compared to the reported ILs,[24] the effect of the structural and positional isomerism on the physicochemical properties was also discussed in this work. Through the Walden rule, the relationship between the molar conductivity and dynamic viscosity of this IL was expressed.

EXPERIMENTAL SECTION

Preparation of [C₄3mpy][Br] and [C₄3mpy][NTf₂]. [C₄3mpy][Br] was synthesized according to our previously reported method.[32] The final product [C₄3mpy][Br] was characterized by ¹H NMR spectra (See the Figure A of the Supporting Information).

The IL $[C_43mpy][NTf_2]$ was synthesized following the previous method.[14] The IL product was characterized by ^{1}H NMR and ^{13}C NMR (see the Figures B and C of the Supporting Information). The residual Br^- tested by $AgNO_3/HNO_3$ solution was below the detection limit of approximately 50 ppm. The IL product was further dried for 24 h at 353.15 K under high vacuum before used. The final purity of the IL was estimated better than 99% in mass. The reactions are as follows:
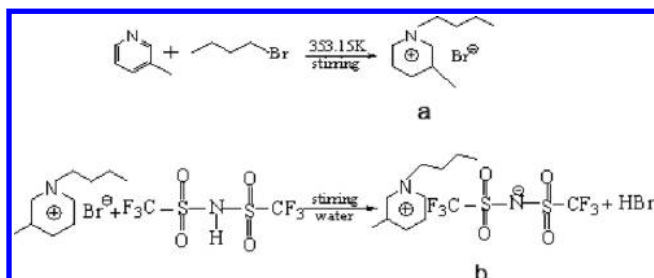
where a is $[C_43mpy][Br]$ and b is $[C_43mpy][NTf_2]$,

DSC and TG. Differential scanning calorimetry (DSC) was carried out on NETZSCH DSC 204 under nitrogen atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from 165 to 370 K. The temperature was directly cooled to 165 K by liquid nitrogen. The decomposition temperature of the $[C_43mpy][NTf_2]$ was determined on a NETZSCH TG 209 at a heating rate of 10 $K \cdot min^{-1}$ from 313 to 873 K. (See the Figures D and E of the Supporting Information).

Water Content. The water content of the IL measured by Karl Fischer moisture titrator (ZSD-2 type) was less than 500 ppm before the determination of properties and 800 ppm after the determination.

Measurement of Density and Surface Tension. The densities of $[C_43mpy][NTf_2]$ were measured from 278.15 to 338.15 ± 0.05 K by a Westphal balance. Each value of the density is the average of three measurements. The experimental error is ± 0.0002 $g \cdot cm^{-3}$. The surface tension of $[C_43mpy][NTf_2]$ was measured using the tensiometer (DP-AW type produced by Sang Li Electronic Co.) by the forced bubble method from 283.15 to 338.15 ± 0.05 K. Each value of the surface tension is the average of five measurements. The experimental error is ± 0.1 $mJ \cdot m^{-2}$. The values of the density and surface tension of the IL are listed in Table 1. The Westphal balance and the tensiometer were calibrated by degassed water.

Measurement of Dynamic Viscosity and Electrical Conductivity. The dynamic viscosity of $[C_43mpy][NTf_2]$ were measured by an Ostwald viscometer from 298.15 to 353.15 ± 0.1 K. The electrical conductivity of $[C_43mpy][NTf_2]$ were measured by a MP522 conductivity meter (Sang Xin Electronic Co.) with the 1 cm^{-1} cell constant (the cell was calibrated with the standard aqueous KCl solution) under the high pure argon from 278.15 to 353.15 ± 0.05 K. Each value of the dynamic viscosity and electrical conductivity are the average of three measurements. The uncertainties are about ± 1 %. The results are listed in Table 1.

■ RESULTS AND DISCUSSION

The density and dynamic viscosity in the present work have a small discrepancies with the reported values[22] at 298.15 K. The density and dynamic viscosity of this work at 298.15 K are 1.4226 $g \cdot cm^{-3}$ and 63.2 mPa·s, respectively, whereas the

Table 1. Experimental Values of Density, ρ, Surface Tension, γ, Dynamic Viscosity, η and Electrical Conductivity, σ, of IL $[C_43mpy][NTf_2]$ from (278.15 to 353.15) K

T	ρ	γ	η	σ
K	$g \cdot cm^{-3}$	$mJ \cdot m^{-2}$	mPa·s	$mS \cdot cm^{-1}$
278.15	1.4399	29.5[b]	177.0[c]	1.00
283.15	1.4357	29.2	133.3[c]	1.32
288.15	1.4315	28.8	102.3[c]	1.72
293.15	1.4271	28.4	79.9[c]	2.17
298.15	1.4226	28.2	63.2	2.72
303.15	1.4183	27.8	51.1	3.35
308.15	1.4142	27.4	41.4	4.09
313.15	1.4098	27.2	34.0	4.90
318.15	1.4051	26.7	28.4	5.76
323.15	1.4007	26.4	23.9	6.90
328.15	1.3964	26.1	20.3	7.96
333.15	1.3921	25.8	17.5	9.10
338.15	1.3876	25.4	15.2	10.31
343.15	1.3832[a]	25.1[b]	13.0	11.60
348.15	1.3787[a]	24.7[b]	11.3	12.96
353.15	1.3742[a]	24.4[b]	10.0	14.37

[a]The calculated values from the fitting equation $Y = 1.6576 - 7.07 \times 10^{-4}T - 2.70 \times 10^{-7}T^2$. [b]The calculated values from the fitting equation $Y = 51.1 - 8.55 \times 10^{-2}T + 2.80 \times 10^{-5}T^2$. [c]The calculated values from the fitting equation $D = 0.0474 \exp(1151.7/(T - 138.134))$.

literature values are 1.4128 $g \cdot cm^{-3}$ and 64.359 mPa·s for density and dynamic viscosity at 298.15 K.[22]

Thermal Analysis. From the DSC thermograms, the glass transition temperature of the IL $[C_43mpy][NTf_2]$, $T_g = 190.8$ ± 0.1 K, was obtained; because the melting temperature (T_m) of the IL could not be found, it indicated that the IL could exist as a liquid until 190.8 K, like other reported ILs.[33] From the TG, the decomposition temperature of $[C_43mpy][NTf_2]$ is higher than 620.0 ± 0.1 K. The samples exhibited excellent thermal stability up to 620.0 ± 0.1 K at a scanning rate of 10 $K \cdot min^{-1}$; the mass loss is more than 90% from the onset temperature to the terminal temperature. The percent of the mass loss at different temperatures is listed in Table 2.

Table 2. Mass Loss of the ILs $[C_43mpy][NTf_2]$ following the Temperature Recorded by TG

100 δ_m/m	T	100 δ_m/m	T
	K		K
2	628	52	690
5	643	78	705
10	658	88	713
19	670	97	723

Estimation of Properties of $[C_43mpy][NTf_2]$. The temperature dependence of density and surface tension for IL $[C_43mpy][NTf_2]$ were illustrated in Figure 1. Compared to the structural isomer IL $[C_5py][NTf_2]$,[14] there are little differences of the density and the surface tension like $\rho[C_43mpy][NTf_2] > \rho[C_5py][NTf_2]$, $\gamma[C_43mpy][NTf_2] < \gamma[C_5py][NTf_2]$ at 298.15 K, respectively. According to the literature,[19,22] the side groups (like alkyl chains) attached to the imidazolium[19] or pyridinium ring[22] of the ILs result in difference of physical properties such as density, viscosity, conductivity, glass transition temperature, and so on. That suggests the methyl in the meta position of
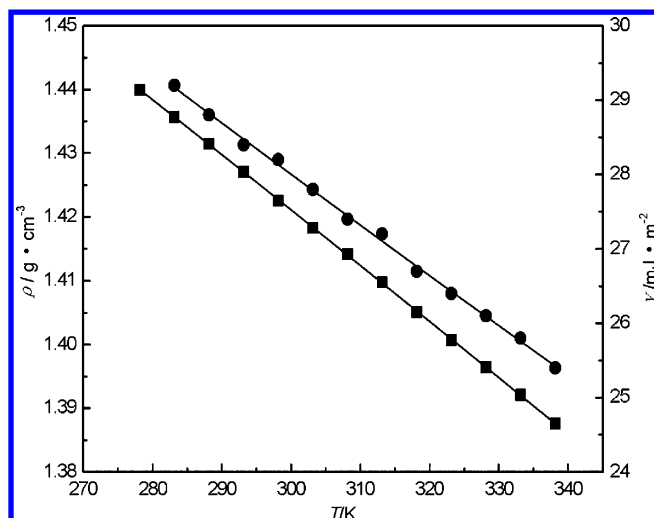
Figure 1. Plot of experimental density, ρ, and surface tension, γ, vs T/K: ■, density; ●, surface tension.

pyridinium ring increase the density and decrease the surface tension of the IL $[C_43mpy][NTf_2]$.

The relationship between the temperature and the density or the surface tension of ILs can be fitted by the following empiric equation:

$$Y = A + BT + CT^2 \tag{1}$$

where Y is the density or surface tension and A, B, and C are adjustable parameters. The fitting equations are obtained: $Y = 1.6576 - 7.07 \times 10^{-4}T - 2.70 \times 10^{-7}T^2$, $R = 0.9999$ for density; $Y = 51.1 - 8.55 \times 10^{-2}T + 2.80 \times 10^{-5}T^2$, $R = 0.9977$ for surface tension, respectively.

Moreover, a straight line can be obtained by using the following empirical equation:

$$\ln \rho/\text{g·cm}^{-3} = b - \alpha(T/K - 298.15) \tag{2}$$

where b is an empirical constant and the negative value of the slope, $\alpha = -(\partial \ln \rho/\partial(T - 298.15))_p = 6.20 \times 10^{-4}$ K^{-1}, is the thermal expansion coefficient of the IL at 298.15 K. The correlation coefficient is $R = 0.9999$, the standard deviation $s = 1.2 \times 10^{-4}$ g·cm^{-3}, and $b = 0.3525$, respectively. The thermal expansion coefficient of $[C_43mpy][NTf_2]$ is so closed to the ILs with similar structure.[14]

The experimental data of the surface tension, γ, as a function of T is also linear fitted (see Figure 1). The correlation coefficient R, is =0.9979. From the Figure 1, the surface entropy of the IL at 298.15 K, $S_a = -(\partial \gamma/\partial T)_p = 68.0 \times 10^{-3}$ mJ·K^{-1}·m^{-2}, can be obtained from the slope. The surface energy of the IL can be calculated from the surface tension at 298.15 K: $E_a = \gamma - T(\partial \gamma/\partial T)_p = 48.5$ mJ·m^{-2}. Compared with the fused salts and organic liquids, for example, 146 mJ·m^{-2} for NaNO$_3$, 67 mJ·m^{-2} for benzene and 51.1 mJ·m^{-2} for octane,[34] the value of the IL $[C_43mpy][NTf_2]$ is close to the organic liquids, even less than some organic liquids. This fact shows that the alkyl group of the ionic liquid at the liquid/vapor interface can decrease the superficial area of the IL.

Since the density and surface tension are a type of easily obtained properties, based on them, some important physicochemical parameters of ILs can be estimated.

The molecular volume, V_m, can be calculated from the experimental density by the following equation:

$$V_m = M/(N\rho) \tag{3}$$

where M is the molar mass, ρ is the density, N is Avogadro's constant, and $V_m = 0.5025$ nm^3 is obtained. The molecular volume of the structural isomer IL $[C_5py][NTf_2]$[14] at 298.15 K is 0.5030 nm,[3] and there is no obvious change between them.

According to Glasser's theory,[25] the standard molar entropy, S^0, and the lattice energy, U_{POT}, can be estimated from the following equation:

$$S^0(298.15 \text{ K})/\text{J·K}^{-1}\text{·mol}^{-1} = 1246.5(V_m/\text{nm}^3) + 29.5 \tag{4}$$

$$U_{POT}(298.15 \text{ K})/\text{kJ·mol}^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \tag{5}$$

where V_m is the molecular volume, M is the molar mass, and ρ is the density at 298.15 K. The results are listed in Table 3. In

Table 3. Estimated Physicochemical Properties of IL $[C_4mpy][NTf_2]$ at 298.15 K

properties	values	properties	values
M/g·mol^{-1}	430.38	$\Delta_l^g H_m^0$/kJ·mol^{-1}	121.2
V_m/nm^3	0.5025	$10^{24}v$/cm^3	37.91
S^0/J·K^{-1}·mol^{-1}	655.9	$\sum v$/cm^3	45.64
U_{pot}/kJ·mol^{-1}	399	$10^4\alpha$/K^{-1} (exp)	6.20
V/cm^{-3}·mol^{-1}	302.5	$10^4\alpha$/K^{-1} (cal)	7.59
p	696.7		

comparison with fused salts, the lattice energy of $[C_43mpy]$-$[NTf_2]$ is much lower. The low lattice energy may be an underlying reason for the liquid state of the IL at room temperature.

The parachor, P, is estimated from the following equation[26] and listed in Table 3:

$$P = (M\gamma^{1/4})/\rho \tag{6}$$

where M is the molar mass, ρ is the density, and γ is the surface tension.

The value of molar enthalpy of vaporization is estimated by Kabo's empirical equation:[27]

$$\Delta_l^g H_m^0 = 0.01121(\gamma V^{2/3} N^{1/3}) + 2.4 \tag{7}$$

where V is the molar volume, γ is the surface tension, and N is Avogadro's constant and the results are listed in Table 3.

According to the interstice model[28] for pure ILs, the interstice parameters of IL $[C_43mpy][NTf_2]$, like interstice volume, v, can be estimated by classical statistical mechanics at 298.15 K:

$$v = 0.6791(k_bT/\gamma)^{3/2} \tag{8}$$

where k_b is the Boltzmann constant, T is the thermodynamic temperature, and γ is the surface tension.

The molar volume of ionic liquids, V, consists of the inherent volume, V_i, and total volume of the all interstices, $\sum v = 2Nv$, that is:

$$V = V_i + 2Nv \tag{9}$$

If the expansion volume of IL only results from the expansion of the interstices with the increased temperature, the thermal expansion coefficient at 298.15 K, α, can be predicted from the interstice model:

$$\alpha = (1/V)(\partial V/\partial T)_p = 3N\nu/VT \qquad (10)$$

The above estimated interstice model parameters are listed in Table 3, too.

The comparison of $\alpha(\exp) = 6.20 \times 10^{-4} \cdot K^{-1}$ and $\alpha(\text{cal}) = 7.59 \times 10^{-4} \cdot K^{-1}$ shows that both values are of the same order of magnitude and about 22% deviation, which implies that the interstice model is reasonable for the IL $[C_4 3mpy][NTf_2]$.

Dynamic Viscosity and Electrical Conductivity. The dynamic viscosity and electrical conductivity of IL $[C_4 3mpy]$-$[NTf_2]$ as a function of temperature were listed in Table 1 and illustrated in Figure 2.
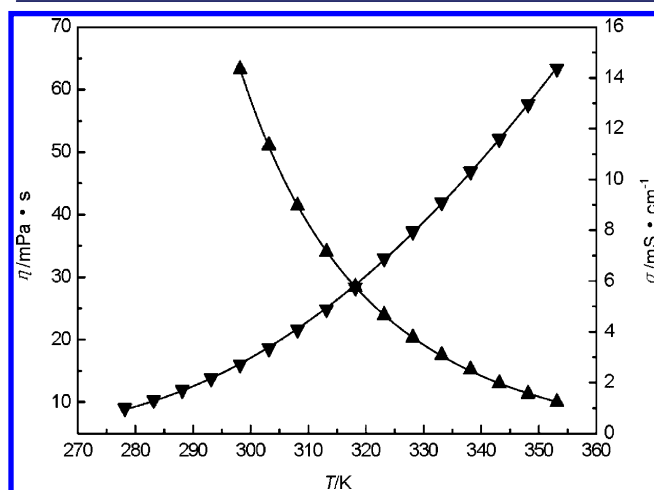
Figure 2. Plot of experimental dynamic viscosity, η and electrical conductivity, σ vs T/K: ▲, dynamic viscosity; ▼, electrical conductivity.

The molar electrical conductivity was calculated according to the following equation:

$$\Lambda = \sigma M \rho^{-1} \qquad (11)$$

where Λ is the molar conductivity, σ is the electrical conductivity, M is the molar mass, and ρ is the density. The values of the molar conductivity are listed in Table 4.

Table 4. Molar Conductivity, Λ, of ILs $[C_4 3mpy][NTf_2]$ at the Temperature from 273.15 to 353.15 K

T	Λ	T	Λ	T	Λ
K	S·cm²·mol⁻¹	K	S·cm²·mol⁻¹	K	S·cm²·mol⁻¹
278.15	0.30	308.15	1.24	338.15	3.20
283.15	0.40	313.15	1.50	343.15	3.61
288.15	0.52	318.15	1.76	348.15	4.05
293.15	0.65	323.15	2.12	353.15	4.50
298.15	0.82	328.15	2.45		
303.15	1.02	333.15	2.81		

The values of dynamic viscosity, electrical conductivity and molar electrical conductivity of IL $[C_4 3mpy][NTf_2]$ can be fitted using the Vogel–Fulcher–Tamman (VFT) equation which is commonly used for ILs:[20,21,30,31]

$$D = D_0 \exp(E_D/(T - T_0)) \qquad (12)$$

where D is the dynamic viscosity, electrical conductivity, or molar electrical conductivity and D_0 and E_D are adjustable

parameters. The best fitted parameters of D_0, E_D, and T_0 and correlation coefficient, R^2, are listed in Table 5.

Table 5. Fitted Values of Dynamic Viscosity, η, Electrical Conductivity, σ, and Molar Conductivity, Λ, According to VFT Equation

		E_D	T_0	
properties	D_0	K	K	R^2
η/mPa·s	0.0474	1151.7	138.1	0.9999
σ/mS·cm⁻¹	493.6	608.4	181.0	0.9999
Λ_0/S·cm²·mol⁻¹	186.1	653.5	177.4	0.9999

Activation Energy of Viscous Flow and Electrical Conductivity. A empiric equation derived from the $\ln \eta/\sigma$ against T^{-1} will be obtained according to the Arrhenius equation:[23,24,29,31]

$$\ln D' = \ln D'_\infty - E_{D'}/(RT) \qquad (13)$$

where D' is the dynamic viscosity or electrical conductivity, D'_∞ is the empirical constant, and $E_{D'}$ is the activation energy for viscous flow or for electrical conductivity (which indicates the energy for an ion jump to a free hole). The fitting equations are obtained: $\ln \eta = \ln(4.58 \times 10^{-4}) - 29.25/(RT)$, $R = 0.9987$ for dynamic viscosity; $\ln \sigma = \ln(30.40 \times 10^4) - 28.91/(RT)$, $R = 0.9936$ for electrical conductivity, respectively. From the empiric equations, there is a relative small discrepancies between the activation energies of dynamic viscosity, $E_\eta = 29.25$ kJ·mol⁻¹, and electrical conductivity, $E_\sigma = 28.91$ kJ·mol⁻¹. That is agreement with the result suggested by Hagiwara et al.[35] that the high electrical conductivity can be explained by the low viscosity without introducing some special conduction mechanism such as ion hopping. The sequence order of the dynamic viscosity and the electrical conductivity are $[C_4 3mpy]$-$[NTf_2]$ < $[C_5py][NTf_2]$[24] and $[C_4 3mpy][NTf_2]$ > $[C_5py]$-$[NTf_2]$[24] at 298.15 K of two isomers, respectively. The results show that the methyl in meta-position decrease the viscosity and increase the electrical conductivity of the IL $[C_4 3mpy]$-$[NTf_2]$.

The relationship between the molar conductivity and dynamic viscosity has been described by Walden rule:[36−39]

$$\Lambda \eta = k \qquad (14)$$

where Λ is the molar conductivity, η is the dynamic viscosity, and k is a temperature dependent constant. The walden's product (in $[S·cm²·mol^{-1}][mP·s]$) is 52 for $[C_4 3mpy][NTf_2]$ at 298.15 K.

The dependence of $\log \Lambda$ on $\log \eta^{-1}$ were illustrated in Figure 3 for $[C_4 3mpy][NTf_2]$ from 278.15 to 353.15 K. From the Figure 3, the curves approximate to straight lines, which indicates that the IL obey the Walden rule to a certain extent. The position of the ideal line was established using aqueous KCl solutions at high dilution.[37−39] The lines for IL $[C_4 3mpy][NTf_2]$ below is closed to the ideal KCl line. Most of the reported ILs[36−42] and our previous studied ILs[23,24] have the same tendency. And it is illustrated in Figure 3. The slope of the lines for IL $[C_4 3mpy][NTf_2]$ is 0.949. The result indicates that the relationship between the conductivity and fluidity is a constant.
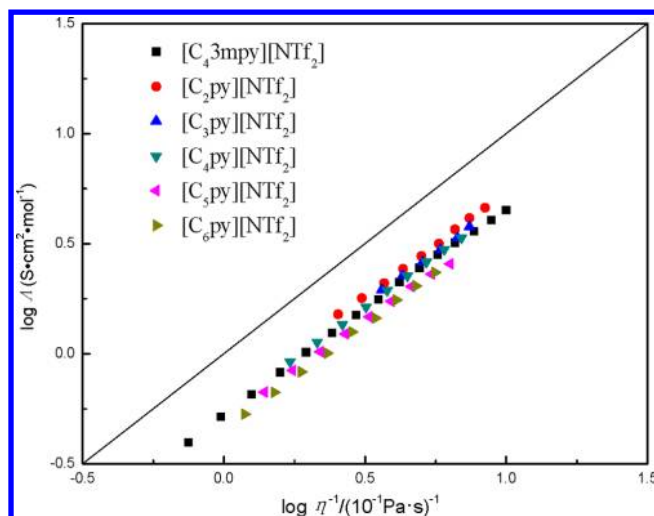
Figure 3. Data of the Walden rule for ILs $[C_43mpy][NTf_2]$ and $[C_npy][NTf_2]$ n = 2, 4, and 5[24] and n = 3 and 6.[23] The solid straight line is the ideal line for a 0.01 M aqueous KCl solution.

CONCLUSION

The glass transition temperature of the IL $[C_43mpy][NTf_2]$, T_g = 190.8 ± 0.1 K, was obtained from the DSC thermograms. That indicates the IL could exist as liquid until 190.8 K. From the TG, the decomposition temperature of $[C_43mpy][NTf_2]$ is higher than 620.0 K. The density, surface tension, dynamic viscosity, and electrical conductivity of $[C_43mpy][NTf_2]$ were experimentally determined and the temperature dependences were illustrated. The physicochemical properties of the IL $[C_43mpy][NTf_2]$ were estimated by the empirical and semiempirical equations. It is found that most properties of $[C_43mpy][NTf_2]$ show little differences with the isomer $[C_5py][NTf_2]$. The estimation provides us a convenient method to obtain some important parameters of ILs properties. The Vogel−Fulcher−Tamman equation and Arrhenius equation were used to describe the relationship between the dynamic viscosity or the electrical conductivity and temperature. The activation energies of viscous flow and electrical conduction were obtained according to the Arrhenius equation. The relationship between the molar conductivity and dynamic viscosity can be expressed by the Walden rule to a certain extent. These empiric equations are valuable for predicting the relative properties of ILs in further research.

ASSOCIATED CONTENT

ⓈSupporting Information
^{1}H-NMR of $[C_4M_3py][Br]$ (Figure A). ^{1}H-NMR of $[C_4M_3py]$-$[NTf_2]$ (Figure B). ^{13}C-NMR of $[C_4M_3py][NTf_2]$ (Figure C). DSC curve of $[C_4M_3py][NTf_2]$ (Figure D). TG curve of $[C_4M_3py][NTf_2]$ (Figure E). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

GLOSSARY

^{1}H NMR = nuclear magnetic resonance
$\Delta_l^g H_m°$ = molar enthalpy of vaporization
k_b = Boltzmann constant
M = molar mass
N = Avogadro constant
S_a = surface entropy
E_a = surface energy
P = parachor
S^0 = standard molar entropy
T_g = glass transition temperature
U_{POT} = lattice energy
V = interstice volume
v_i = inherent volume
V_m = molecular volume

Greek Letters

γ = surface tension
ρ = density
σ = electrical conductivity
η = dynamic viscosity
α = thermal expansion coefficients
α_p = polarization coefficient
Λ = molar conductivity
k = Walden constant

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