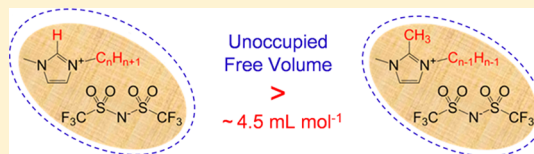


Free Volume Model for the Unexpected Effect of C2-Methylation on the Properties of Imidazolium Ionic Liquids

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ABSTRACT: For 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides and their cationic C2-methylated isomers, that is, $[C_n\text{MIm}]\text{NTf}_2$ and $[C_{n-1}\text{DMIm}]\text{NTf}_2$ ($n = 3-8$), the latter always has much higher viscosities (~ 1.66 times at 25°C) than the former. This finding is unexpected and contrary to the loss of the predominant hydrogen bonding between the cation and anion, caused by the C2-methylation in the imidazolium ionic liquids. In the present study, we propose a free volume model to explain this mysterious phenomenon. For the isomeric pairs, $[C_{n-1}\text{DMIm}]\text{NTf}_2$ was found to possess less unoccupied (free) volume than $[C_n\text{MIm}]\text{NTf}_2$ by $\sim 4.5\text{ mL mol}^{-1}$ determined by both Fürth's surface tension and molar volume methods, and the free volume difference can be quantitatively correlated with the C2-methylation effect on viscosity. Generally, the less free volume in $[C_{n-1}\text{DMIm}]\text{NTf}_2$ relative to $[C_n\text{MIm}]\text{NTf}_2$ reduces the number of the hole carriers for molecular transport with a resulting increase in viscosity. Besides, the free volume model can also be applied to account for the C2-methylation effect on other properties, such as conductivity, surface tension, density, and refractive index.



INTRODUCTION

Ionic liquids (ILs) are composed entirely of ions, leading to a unique set of characters such as negligible vapor pressure, low flammability, wide liquid temperature range, intrinsic ionic conductivity, and so on.¹⁻³ The featured characters have been shown to be beneficial for a wide range of applications, mainly solvents,^{3,4} catalysts,^{5,6} supporting electrolytes,^{4,7} and functional materials.^{8,9} Besides, the physicochemical properties of ILs can be tailored for any purpose by an appropriate combination of cations and anions. However, up to now, there has been no reliable model to accurately predict the ILs' properties, especially when the unexpected happens.

A case in point is the unexpected increases in viscosities and melting points caused by the replacement of H with CH₃ at the C2 position of imidazolium ILs (ImILs),¹⁰⁻¹⁷ which are the most widely studied type of cations of ILs. For the C2-protonated ImILs, the C2-H is of inherent acidity and reactive toward strong bases to form carbene.^{18,19} Also, the acidic C2-H can donate hydrogen bonds to anions to increase the cation-anion interaction.²⁰⁻²⁵ For the C2-methylated ImILs, the C2-H hydrogen bonds with the anion cease to exist. As a consequence, the reduction of the cation-anion interaction caused by the C2-methylation in ImILs could be expected to result in decreases in viscosity and melting point. However, the experimental results run counter to the expectation; both the viscosity and melting point increase instead.¹⁰⁻¹⁷

Since the initial discovery of the mysterious phenomenon by Bonhôte et al. in 1996,¹⁰ many experimental and theoretical studies have been conducted to account for its origin. Counterintuitively, Ludwig et al.^{26,27} related the low viscosity and melting point of the C2-protonated ImILs to the C2-H hydrogen bonding with anions. It was hypothesized that these directional hydrogen bonds deviate from the charge symmetry of ions and thus introduce "defects" into the Coulomb network,

leading to the decreased viscosity and melting point. In this case, the C2-methylation effect should be dependent on the hydrogen-bonding strength between the C2-H and anions. However, similar results could be observed for both coordinating and noncoordinating anions,¹⁰⁻¹⁷ although the hydrogen bonds of the C2-H with the latter are very weak.²⁰⁻²⁵

Alternatively, another explanation was emphasized on the role of entropy or the amount of disorder. On the basis of the quantum chemical calculations, the C2-methylated ImILs were found to have fewer stable ion pair conformers than their C2-protonated counterparts, and the larger steric bulk of the C2-CH₃ relative to the C2-H serves to increase the potential energy barrier of the rotational motion of *N*-alkyl chains.²⁸ The decrease in conformers appears to play a major role in reducing the entropy, and the role of the inhibition of alkyl group rotation is only minor, based on the spin-lattice relaxation time of ¹³C NMR.²⁹ Besides, Izgorodina et al.³⁰ observed an increase in the transition barriers between ion pair conformations in the C2-methylated ImILs. Hunt²⁸ proposed that the reduction in entropy caused by the C2-methylation can relieve ionic packing frustration, with resulting increases in both the viscosity and melting point. This hypothesis was supported by the evidence that the fusion entropy of several pairs of ImILs decreases upon the substitution of H with CH₃ at the C2 position.^{31,32} Yet, the role of enthalpy should also be considered, although the origin of the C2-methylation effect is primarily entropic.^{31,32} Kiefer et al.,³³ however, suggested that the "defect" and "entropy" mechanisms complement each other, and they both are necessary to provide a complete explanation.

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Table 1. Physicochemical Properties of the Studied ImILs at 25 °C

entry	IL sample	γ^a (mN m ⁻¹)	V_f^b mL mol ⁻¹	V_f/V_m^c %	ρ^d g mL ⁻¹	V_m^e mL mol ⁻¹	η^f cP	κ^g mS cm ⁻¹	n^h
1	[C ₂ MIm]NTf ₂	38.31	28.78	11.17	1.5182	257.75	32.0	8.96	1.4231
2	[C ₃ MIm]NTf ₂	36.18	31.36	11.41	1.4756	274.70	43.7	5.31	1.4252
3	[C ₄ MIm]NTf ₂	34.91	33.08	11.33	1.4366	291.91	51.7	3.98	1.4270
4	[C ₅ MIm]NTf ₂	34.13	34.22	11.10	1.4050	308.46	61.5	2.85	1.4289
5	[C ₆ MIm]NTf ₂	33.51	35.18	10.81	1.3747	325.47	72.2	2.14	1.4301
6	[C ₇ MIm]NTf ₂	32.86	36.23	10.58	1.3471	342.54	84.3	1.63	1.4317
7	[C ₈ MIm]NTf ₂	32.75	36.41	10.13	1.3231	359.36	95.8	1.26	1.4331
8	[C ₂ DMIm]NTf ₂	39.98	26.99	9.94	1.4931	271.48	72.2	3.89	1.4296
9	[C ₃ DMIm]NTf ₂	39.14	27.87	9.69	1.4579	287.65	88.9	2.58	1.4320
10	[C ₄ DMIm]NTf ₂	38.21	28.89	9.48	1.4224	304.70	101.6	2.12	1.4334
11	[C ₅ DMIm]NTf ₂	37.03	30.28	9.42	1.3924	321.33	124.6	1.56	1.4350
12	[C ₆ DMIm]NTf ₂	36.14	31.41	9.30	1.3668	337.61	135.4	1.22	1.4360
13	[C ₇ DMIm]NTf ₂	35.47	32.30	9.12	1.3428	354.09	152.3	0.96	1.4370
14	[C ₈ DMIm]NTf ₂	34.41	33.81	9.09	1.3160	371.96	180.0	0.71	1.4380

^aSurface tension. ^bThe total free volume per mole calculated from the surface tension and eq 1. ^cThe fraction of free volume to molar volume. ^dDensity. ^eMolar volume. ^fViscosity. ^gConductivity. ^hRefractive index.

Recently, hole theory^{34–45} has been applied to understand the macroscopic properties, such as viscosity,^{34–37} conductivity,^{38–40} gas solubility and selectivity,⁴¹ and so forth, of ILs on a microscopic level. In hole theory, (1) the liquid ions in constant movement cannot pack closely, and therefore, lots of interstitial holes can come into existence; (2) the bulk volume consists of the inherent volume and the total volume of holes, of which the former is a constant while the latter is expandable and compressible; (3) the holes are of random shape, size, and position, and their volume fraction is expected to be 10–15% for major materials; (4) the transport properties involve an exchange of position between a hole and its adjacent molecule, as expressed in the Cohen–Turnbull equation,^{46–48} $\eta \propto \exp(V_f^*/V_f)$, where η is viscosity, V_f^* is the required minimum volume of the hole, and V_f is the total volume of holes, also known as the free volume.

The free volume in liquids is usually assessed by two methods, using pressure–volume–temperature data with the Simha–Somcynsky equation of state^{49–51} and using surface tension data with F urth’s cavity theory.^{34,42,52–60} Recently, positron annihilation lifetime spectroscopy^{61–63} and X-ray diffraction⁶³ were also applied to determine the free volume in ILs, owing to their nonvolatility that enables their applications in vacuum conditions. The resulting values agree well with those obtained by the above two traditional methods.^{61–63} Generally, in the surface tension method, the average volume of the holes is equal to $0.6791(kT/\gamma)^{3/2}$, where k is the Boltzmann constant (1.38×10^{-23} J K⁻¹), T is the absolute temperature (K), γ is the surface tension (N m⁻¹), and the number of holes was deemed to be equal to the molecule (ion) number. As a result, the free volume per mole (V_f) in ILs can be evaluated by eq 1,^{42,55–59} where N is the Avogadro constant (6.02×10^{23}).

$$V_f = 2N \times 0.6791(kT/\gamma)^{3/2} \quad (1)$$

In the present study, a free volume model was proposed to understand the unexpected effect of C2-methylation on the properties of ImILs. Generally, the C2-methylation was found to significantly decrease the local free volume in ImILs, and this free volume decrease can serve as the reason for the C2-methylation effect on not only the viscosity but also the conductivity, surface tension, density, and refractive index.

EXPERIMENTAL SECTION

First of all, a series of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imides and their C2-methylated counterparts, that is, [C_{*n*}MIm]NTf₂ and [C_{*n*}DMIm]NTf₂, where $n = 2–8$, were synthesized and characterized. The synthesis is a two-step process via the N-alkylation of 1-(2-di)-methylimidazole with alkyl bromides and then the anion exchange of bromide by NTf₂.⁶⁴ Generally, the bromide salts would be recrystallized twice from an acetone–ethyl acetate mixture before use in the anion exchange. The final NTf₂ products were washed with sufficient water until their AgNO₃ test was negative. The freshly prepared samples were confirmed by ¹H NMR (BRUKER NMR spectrometer, 300 MHz) and FT-IR (Nicolet 6700 FT-IR instrument).

The physicochemical properties, surface tension (γ), density (ρ), viscosity (η), conductivity (κ), refractive index (n), molar volume (V_m), molar free volume (V_f), and the free volume fraction (V_f/V_m), of these ImILs were characterized and are summarized in Table 1. Before property testing, all of the ILs were vacuum-dried for 20 h at 80 °C and 10^{-2} – 10^{-3} mbar. The surface tension (mN m⁻¹) at 25 °C was determined using the du No uy method on a Kibron EZ-Pi^{plus} tensiometer, with uncertainties less than 0.05 mN m⁻¹. The density (g mL⁻¹) was measured by a DMA 35 portable density meter at 25 °C or by a pycnometer as a function of temperature between 20 and 80 °C. The densitometers were calibrated with ultrapure water, and the deviations were less than 0.0002 g mL⁻¹. The viscosity (cP) was recorded with a BROOKFIELD DV-II+ Pro viscometer with an accuracy of 1% in a glovebox with a moisture concentration less than 1 ppm. The conductivity (mS cm⁻¹) was estimated using a Mettler Toledo FiveGo conductivity meter, which was accurate within $\pm 1\%$. The refractive index was investigated by an Atago NAR-1T liquid Abbe refractometer with precision of ± 0.0002 . During the measurement, the temperature was controlled within ± 0.1 °C by means of an external controller.

RESULT AND DISCUSSION

The surface tension (γ) of the studied ImILs was investigated and is shown in Table 1, ranging over 32.75–39.98 mN m⁻¹ at 25 °C. Generally, the surface tension increases with the cation alkyl chain length, coinciding with previous reports.^{58,65} Significantly, [C_{*n*}MIm]NTf₂ always has a smaller γ value than

$[C_{n-1}\text{DMIm}]\text{NTf}_2$, for example, $[C_4\text{MIm}]\text{NTf}_2$ (34.91 mN m^{-1}) and $[C_3\text{DMIm}]\text{NTf}_2$ (39.14 mN m^{-1}), although they are isomers with only minor structural differences. According to eq 1, described by Yang et al.,^{42,55–59} the free volume per mole (V_f) of these ILs was calculated and is presented in Table 1 and Figure 1, varying in the range of 26.99–36.41 mL mol^{-1} at 25

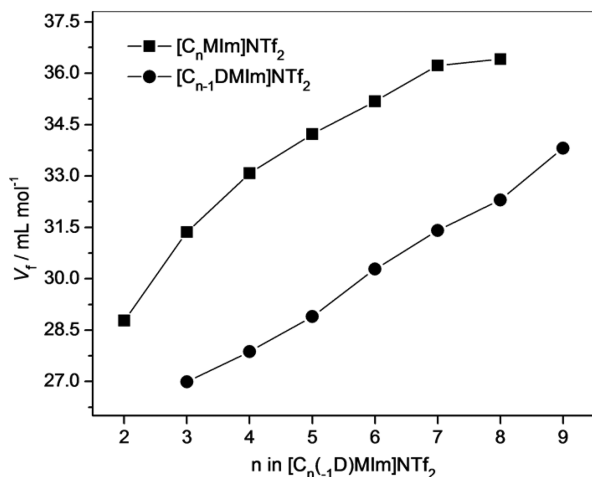


Figure 1. The molar free volume (V_f) of the ImILs calculated from eq 1 and the surface tension at 25 °C.

°C. The free volume fraction (V_f/V_m ; V_m is the molar volume) was also calculated and is shown in Table 1. These V_f/V_m values (9.09–11.41%) fall within or slightly below the expected range (10–15%) for the major materials.⁴³ Although the V_f values invariably increase with the alkyl chain length, as shown in Figure 1, a generally reverse trend was observed for the V_f/V_m values, for example, $[C_4\text{MIm}]\text{NTf}_2$ (33.08 mL mol^{-1} , 11.33%) and $[C_5\text{MIm}]\text{NTf}_2$ (34.22 mL mol^{-1} , 11.10%). Such a trend for the V_f/V_m values should be related to the increasing van der Waals force with the side alkyl chain length.⁶⁶ For the isomeric ILs, $[C_n\text{MIm}]\text{NTf}_2$ uniformly contains some more free volume than $[C_{n-1}\text{DMIm}]\text{NTf}_2$, with ΔV_f ranging over 4.36–5.33 mL mol^{-1} , as shown in Figure 1 and Table 2. As will be seen below, these ΔV_f values could be attributed to the C2 methylation effect on the properties of ImILs.

In order to defend the rationality of the ΔV_f values evaluated from surface tension, the molar volume (V_m) of the ILs was also calculated from their densities ($\rho = 1.3160$ – 1.5182 g mL^{-1} , 25 °C) and is presented in Table 1 and Figure 2. As can be seen, the molar volume grows almost linearly with the side alkyl chain length. Also, the mean contribution per methylene to the molar volume (the slope of the lines in Figure 2) was

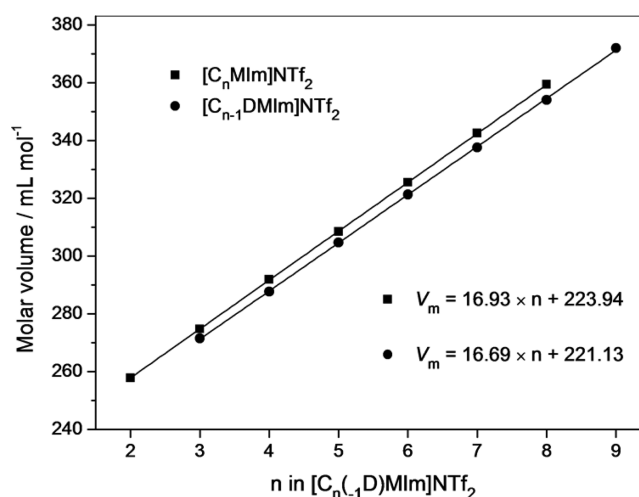


Figure 2. The molar volume (V_m) of the ImILs at 25 °C.

determined to be 16.93 mL mol^{-1} for $[C_n\text{MIm}]\text{NTf}_2$ and 16.69 mL mol^{-1} for $[C_{n-1}\text{DMIm}]\text{NTf}_2$, respectively, close to the literature value of 16.74 mL mol^{-1} for the $[C_n\text{MIm}]\text{alanine}$ series ($n = 2$ – 6).⁵⁹ This result conforms to the group additivity principle for the calculation of molar volume.^{67,68} However, the volume increment of the imidazolium C2–CH₂, by comparison of $[C_n\text{DMIm}]\text{NTf}_2$ with $[C_n\text{MIm}]\text{NTf}_2$, was estimated to be only 11.55–13.73 mL mol^{-1} , as shown in Table 3, much less

Table 3. Contribution of the C2–CH₂ in ImILs to the Molar Volume at 25 °C^a

n^b	V_{CH_2} (mL mol^{-1})	n^b	V_{CH_2} (mL mol^{-1})
2	13.73	6	12.14
3	12.95	7	11.55
4	12.81	8	12.6
5	12.87		

^aCalculated as the molar volume difference between $[C_n\text{DMIm}]\text{NTf}_2$ and $[C_n\text{MIm}]\text{NTf}_2$. ^bThe subscript in $[C_n(\text{D})\text{MIm}]\text{NTf}_2$.

than the expected value of ~ 16.8 mL mol^{-1} . This deviation is most likely due to the decreases in abundance of conformers and the flexibility of alkyl chains caused by imidazolium C2-methylation,^{28–32} resulting in closer packing and therefore less free volume available as the variable part of the molar volume.⁶⁹ Besides, the intrinsic volume occupied by the structurally similar isomers should be close to a constant.^{36,67,68} As a result, $[C_n\text{MIm}]\text{NTf}_2$ uniformly has a larger molar volume than its isomeric $[C_{n-1}\text{DMIm}]\text{NTf}_2$, and the molar volume difference (ΔV_m) between these isomeric ILs was determined to be in the

Table 2. C2-Methylation Effect on Properties of ImILs, Based on the Difference in Free Volume (ΔV_f), Molar Volume (ΔV_m), Viscosity (η_2/η_1), Conductivity (κ_1/κ_2), Density (ρ_2/ρ_1), and Refractive Index $[(n_2^2 - 1)/(n_2^2 + 2)]/[(n_1^2 - 1)/(n_1^2 + 2)]$ between $[C_n\text{MIm}]\text{NTf}_2$ and $[C_{n-1}\text{DMIm}]\text{NTf}_2$ ^a

n^b	ΔV_f mL mol^{-1}	ΔV_m mL mol^{-1}	η_2/η_1	κ_1/κ_2	ρ_2/ρ_1	$[(n_2^2 - 1)/(n_2^2 + 2)]/[(n_1^2 - 1)/(n_1^2 + 2)]$
3	3.22	4.36	1.65	1.37	1.012	1.009
4	4.26	5.22	1.72	1.54	1.015	1.010
5	3.76	5.33	1.65	1.34	1.012	1.009
6	4.14	4.89	1.73	1.37	1.013	1.010
7	4.93	4.82	1.61	1.34	1.015	1.009
8	5.27	4.11	1.59	1.31	1.015	1.008

^aThe subscripts 1 and 2 denote $[C_n\text{MIm}]\text{NTf}_2$ and $[C_{n-1}\text{DMIm}]\text{NTf}_2$, respectively. ^bThe subscript in $[C_n\text{MIm}]\text{NTf}_2$ and $[C_{n-1}\text{DMIm}]\text{NTf}_2$.

range of 3.22–5.27 mL mol⁻¹, close to the ΔV_f values of 4.36–5.33 mL mol⁻¹, as shown in Figure 2 and Table 2. The approximate relationship between the ΔV_f and ΔV_m values, of which the latter arises from the free volume difference, corroborates each other and that $[C_n\text{MIm}]\text{NTf}_2$ possesses more unoccupied (free) volumes than its isomeric $[C_{n-1}\text{DMIm}]\text{NTf}_2$.

The molar volume of $[C_4\text{MIm}]\text{NTf}_2$ and $[C_3\text{DMIm}]\text{NTf}_2$ as a function of temperature from 20 to 80 °C was also investigated and is presented in Table 4 and Figure 3. It can

Table 4. Molar Volume (V_m) and Viscosity (η) of $[C_3\text{DMIm}]\text{NTf}_2$ and $[C_4\text{MIm}]\text{NTf}_2$ and the Molar Volume Difference (ΔV_m) between Them at Temperatures from 20 to 80 °C

°C	$[C_3\text{DMIm}]\text{NTf}_2$		$[C_4\text{MIm}]\text{NTf}_2$		ΔV_m mL mol ⁻¹
	V_m mL mol ⁻¹	η cP	V_m mL mol ⁻¹	η cP	
20	286.72	116.0	290.94	65.9	4.22
25	287.65	88.9	291.91 ^a	51.7 ^b	4.26
30	288.58	70.8	292.88	41.3	4.30
40	290.46	46.9	294.81	29.0	4.35
50	292.33	32.2	296.76 ^c	20.6 ^d	4.43
60	294.21	23.0	298.70	15.5	4.49
70	296.10	16.9	300.64	11.9	4.54
75	297.03	14.7	301.61 ^e	10.5 ^f	4.58
80	297.96	13.0	302.58	9.35	4.62

^aCalculated value: 291.90.⁴⁵ ^bExperimental value: 51.0.⁴⁵ ^cCalculated value: 296.82.⁴⁵ ^dExperimental value: 20.5.⁴⁵ ^eCalculated value: 301.80.⁴⁵ ^fExperimental value: 10.7.⁴⁵

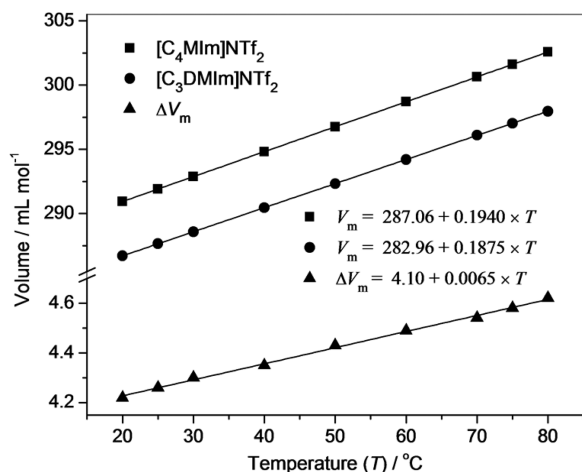


Figure 3. Temperature dependence of the molar volume (V_m) of two isomeric ImILs and their molar volume difference (ΔV_m).

be seen that the two ILs expand almost linearly with temperature, providing the thermal expansion coefficient of 0.1940 mL mol⁻¹ K⁻¹ for $[C_4\text{MIm}]\text{NTf}_2$ and 0.1875 mL mol⁻¹ K⁻¹ for $[C_3\text{DMIm}]\text{NTf}_2$. As a result of the larger thermal expansion coefficient of $[C_4\text{MIm}]\text{NTf}_2$ relative to $[C_3\text{DMIm}]\text{NTf}_2$, the ΔV_m value between them slightly increases with temperature by 0.0065 mL mol⁻¹ K⁻¹.

The measured viscosity (η) of the ILs is shown in Table 1 and Figure 4, ranging over 32.0–180 cP at 25 °C. As expected, the η value generally increases with the alkyl chain length due to the associated increase in the ion size and interionic van der Waals force^{66,70} and, additionally, the decreasing free volume

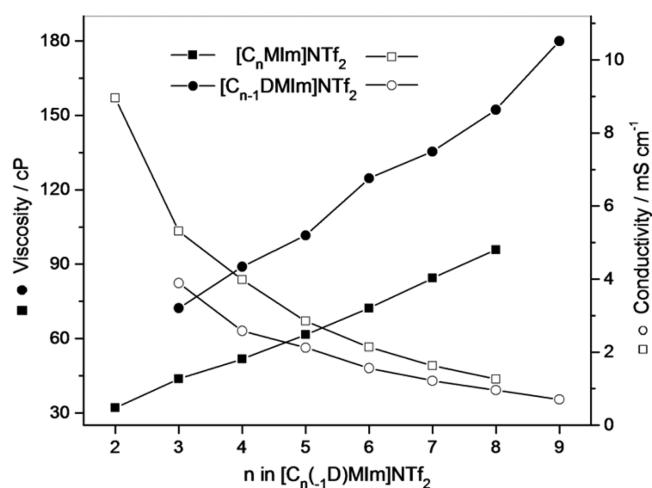


Figure 4. The viscosity (left ordinate) and conductivity (right ordinate) of the ImILs at 25 °C.

fraction (V_f/V_m , Table 1). For the isomeric samples, $[C_{n-1}\text{DMIm}]\text{NTf}_2$ is uniformly much more viscous than $[C_n\text{MIm}]\text{NTf}_2$, yielding the viscosity ratio ranging from 1.59 to 1.73, as shown in Table 2. According to hole theory,^{34–37} the viscosity difference between the isomers should be attributable to the above-stated ΔV_f and ΔV_m values (~ 4.5 mL mol⁻¹). In detail, relative to $[C_{n-1}\text{DMIm}]\text{NTf}_2$, $[C_n\text{MIm}]\text{NTf}_2$ always has more available free volume and thus can provide more accessible hole locations for more convenient mass transport and lower viscosity.

For further quantitative study of the viscosity dependence on the free volume of these isomeric ILs, we look at an alternative approach, which is to apply external pressure to the compressible ILs. In detail, when the excess free (molar) volume of $[C_n\text{MIm}]\text{NTf}_2$ compared with $[C_{n-1}\text{DMIm}]\text{NTf}_2$ was compressed by an external pressure, the viscosity of the former at that pressure should have been equal to or at least close to the latter at atmospheric pressure. Figure 5 describes the relationship curves between the molar volume and viscosity of $[C_4\text{MIm}]\text{NTf}_2$ at atmospheric (the leftmost point in each curve) and elevated pressures and different constant temper-

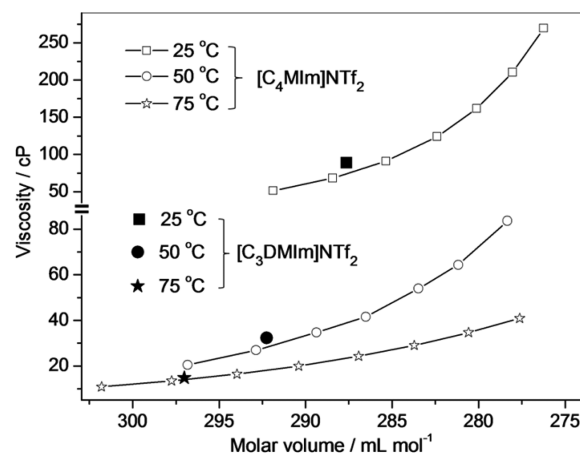


Figure 5. The curves of the dependence of the viscosity on the molar volume (decreased free volume) of $[C_4\text{MIm}]\text{NTf}_2$ from atmospheric pressure (the leftmost point) to the elevated pressures (cited from ref 45). The symbols \blacksquare , \bullet , and \star stand for the values (viscosity and molar volume) of $[C_3\text{DMIm}]\text{NTf}_2$ at 25, 50, and 75 °C, respectively.

atures (25, 50, and 75 °C), based on the available literature data.⁴⁵ It can be seen that the molar volume would be compressed and the viscosity would be raised with increasing pressure. For instance, at 25 °C, when the external pressure is enhanced from 0.1 to 49.3 MPa, $[C_4MIm]NTf_2$ would be compressed by 6.53 mL mol⁻¹ from 291.90 to 285.37 mL mol⁻¹, and its viscosity would be raised by 1.78 times from 51.0 to 90.9 cP.⁴⁵ According to the hole theory,^{34–37} the free volume change of 6.53 mL mol⁻¹ is responsible for the viscosity variation of 1.78 times. This result is close to the free volume (~4.50 mL mol⁻¹) influence on viscosity (~1.66 times) between the isomeric ILs. Additionally, the molar volume and viscosity of $[C_3DMIm]NTf_2$ at 25, 50, and 75 °C were measured and are plotted in Figure 5. Clearly, the three points of $[C_3DMIm]NTf_2$ are close to or cross the curves of $[C_4MIm]NTf_2$. That is to say, when $[C_4MIm]NTf_2$ is compressed by high pressure to be of the same molar (free) volume as its isomeric $[C_3DMIm]NTf_2$, its viscosity would also be raised to be close to that of the latter at atmospheric pressure. Therefore, the quantitative dependence of the viscosity on the free volume between the isomeric ILs was confirmed to be appropriate.

The conductivity (κ) of the ILs was measured and is shown in Table 1 and Figure 4. As expected, the conductivity drops rapidly with the alkyl chain length, and $[C_nMIm]NTf_2$ uniformly owns a larger κ value than $[C_{n-1}DMIm]NTf_2$, with a κ ratio of about 1.38, as listed in Table 2. On the basis of the formula $\kappa \propto \eta[(\xi_a r_a)^{-1} + (\xi_c r_c)^{-1}]$, where η is the degree of dissociation, η is the viscosity, ξ_a and ξ_c are the anion and cation microviscosity, and r_a and r_c are the radii of the anion and cation, proposed by Bonhôte et al.,¹⁰ the conductivity of ILs is mainly dominated by their viscosity and ion sizes. Compared with viscosity, which increases gradually with the alkyl chain length, the κ value decreases more steeply due to the increases in both the viscosity and cationic size with lengthening of the alkyl chain. For example, for $[C_2MIm]NTf_2$ (32.0 cP, 8.96 mS cm⁻¹) and $[C_8MIm]NTf_2$ (95.8 cP, 1.26 mS cm⁻¹), the reciprocal of their viscosity ratio is only 3.0 (95.8/32.0), and their conductivity ratio is up to 7.1 (8.96/1.26). For the isomeric ILs, the viscosity should be the one and only major factor and should exert a reciprocal effect on conductivity. However, the conductivity ratio (~1.38) between the isomeric ILs is much less than the reciprocal of their viscosity ratio (~1.66). This result might be related to the lower dissociation constant of $[C_nMIm]NTf_2$ than $[C_{n-1}DMIm]NTf_2$ because the acidic C2–H in ImILs can promote the formation of large sized and uncharged ion clusters via hydrogen bonds with anions.^{20–25}

Figure 6 shows the measured density (ρ) and refractive index (n) in Table 1, ranging over 1.3160–1.5182 g mL⁻¹ and 1.4231–1.4380, respectively. As seen, the density declines with the lengthening of the “lightweight” alkyl chain. For the isomeric ILs, $[C_nMIm]NTf_2$ is apparently less dense than $[C_{n-1}DMIm]NTf_2$, indicating that the interionic packing in the former is looser than the latter, in good agreement with the above-stated ΔV_f and ΔV_m values between them. As also seen in Figure 6, the refractive index (n) increases slightly with the alkyl chain length, and $[C_nMIm]NTf_2$ owns a smaller n value than its isomeric $[C_{n-1}DMIm]NTf_2$. On the basis of the Lorenz–Lorentz equation⁷¹

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{4\pi\rho Na}{3M}$$

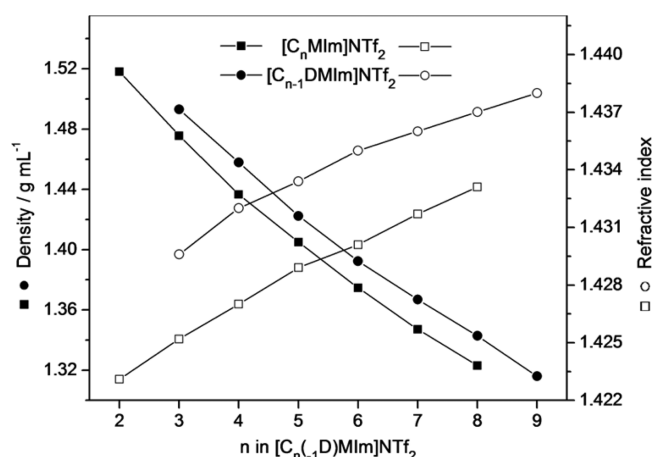


Figure 6. The density (left ordinate) and refractive index (right ordinate) of the ImILs at 25 °C.

where ρ is the density, N is a constant, a is the polarizability and M is the molar mass, the refractive index difference between the isomeric ILs should be mainly attributable to their difference in density as well as in free volume. As presented in Table 2, the value of $[(n_2^2 - 1)/(n_2^2 + 2)]/[(n_1^2 - 1)/(n_1^2 + 2)]$ (~1.009) is close to ρ_2/ρ_1 (~1.013), where the subscripts 1 and 2 denote $[C_nMIm]NTf_2$ and $[C_{n-1}DMIm]NTf_2$, respectively.

CONCLUSION

In conclusion, a new, simple free volume model was proposed to account for the unexpected effect of C2-methylation on the properties of ImILs, which is contrary to the loss of the C2–H···anion hydrogen-bonding interaction. By comparative studies of the isomeric $[C_nMIm]NTf_2$ and $[C_{n-1}DMIm]NTf_2$ ($n = 3–8$), the C2–CH₃ group was found to significantly reduce the free volume in ImILs by ~4.5 mL mol⁻¹ at 25 °C. In addition, the reduced free volume can be well correlated with the C2-methylation effect on ImILs' properties, such as surface tension, density, refractive index, conductivity, and especially viscosity. Generally, for viscosity, the reduced free volume dominates over the lost C2–H···anion hydrogen bonds in $[C_{n-1}DMIm]NTf_2$ relative to $[C_nMIm]NTf_2$ and reduces the amount of hole carriers for molecular motion and then causes a significant increase in viscosity. Actually, the free volume model can also be related to the increase in the melting point of ImILs caused by the C2-methylation. Because the C2-methylation decreases the (fusion) entropy,^{28–32} its decrease releases the molecular packing frustration and should lead to a decrease in free volume.

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Notes

The authors declare no competing financial interest.

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