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1. Introduction

Ionic liquids are attracting increasing attention in many fields with their special physical and chemical properties, such as non-flammability, dual natural polarity, thermal stability, liquidity over a wide temperature range, easy recycling, and being a good solvent for a wide variety of organic and inorganic chemical compounds. Actually, most ILs are water miscible; therefore, the anions for bis(trifluoromethyl sulfonyl)imide (NTf₂⁻) ILs attracted much concern as water immiscible compounds when they appeared.¹⁻⁴ Bis(trifluoromethyl sulfonyl)imide ionic liquids have attracted considerable attention from industry and the academic community, because they have several unique properties including negligible vapor pressure at ambient temperatures,⁵ good thermal stability

Study on thermodynamic properties and estimation of polarity of ionic liquids {[C_n mmim]-[NTf_2] (n = 2, 4)}⁺

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Two bis(trifluoromethyl sulfonyl)imide ionic liquids $[C_n mmim][NTf_2]$ (n = 2, 4) {1-alkyl-2,3dimethyimidazolium-N,N-bis(trifluoromethyl sulfonyl)imide} were prepared and characterized by ¹H NMR spectroscopy and differential scanning calorimetry (DSC). The values of their density, surface tension and refractive index were measured in the temperature range of (298.15 to 338.15 \pm 0.01) K and the average contributions to the density, surface tension, and refractive index per methyl group in the alkyl chain and the addition of a methylene group in the imidazolium ring for the ILs were discussed. The dependence of volumetric properties, surface properties and molar refraction on temperature was discussed. Based on Kabo's method and Verevkin's experimental values, the molar enthalpies of vaporization, ΔH^{v} , for $[C_n mmim][NTf_2]$ (n = 2, 4) were estimated. As a new idea, it was put forward that ΔH^{v} can be assumed to consist of two parts: a part corresponds with the induced energy, $\Delta H_{\rm p}^{\rm v}$, and another part corresponds with orientation energy from the permanent dipole moment of the ion pair in ILs, ΔH_{μ}^{v} . The values of ΔH_n^{v} were calculated in terms of the Lawson–Ingham equation so that the values of ΔH_n^{v} could be estimated. Using the values of ΔH^{v} , ΔH^{v}_{n} and ΔH^{v}_{μ} , cohesive energy density, δ^{2} (δ is Hildebrand solubility parameter), the contribution of induced energy, δ_n^2 , and the contribution of orientation energy, δ_{μ}^2 , were obtained. If a liquid only has δ_n then it is a non-polar liquid and if a liquid not only has δ_n , but also has δ_u then it is a polar liquid. Since the ion pairs in ILs have a permanent dipole moment, the ionic liquid has a certain polarity. Therefore, using δ_{μ} as the polarity scaling of ILs is very convenient because the values of δ_{μ} are very easy to calculate from the enthalpy of vaporization and refractive index data.

> properties.^{6,7} As we all know, the fundamental thermodynamic properties,8-12 as the indispensable parameters which reflect the structures of compounds, play crucial role in the application and study. In recent years, there has been a developing trend in the literature toward estimation of the physicochemical properties for compounds by semiempirical methods, in particular, for ILs.13-15 Although the estimated result cannot be regarded as accurate physicochemical data, it is commended because it provides valuable insight into the origins behavior of materials. As a continuation of our previous investigation,¹⁶⁻¹⁸ this paper reports: (1) two bis(trifluoromethyl sulfonyl)imide ionic liquids $[C_n mmim][NTf_2]$ (n = 2, 4) {1-alkyl-2,3-dimethy imidazolium-N,N-bis(trifluoromethyl sulfonyl)imide} were prepared and characterized. (2) The values of density, surface tension and refractive index for $[C_n mmim][NTf_2]$ (n = 2, 4) were measured in the temperature range of (298.15 to 338.15 \pm 0.01) K. (3) The dependence of volumetric properties, surface properties and molar refraction on temperature were discussed. (4) Based on the Kabo's method and Verevkin's experimental values, the molar enthalpies of vaporization, ΔH^{v} , for the [C_nmmim][NTf₂] (n = 2, 4) were estimated. (5) A new scale of polarity, δ_{μ} , for the ILs was put forward and values of δ_{μ} can be estimated easily based on the vaporization enthalpy and refractive index data.

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2. Experimental section

2.1 Chemicals

Deionized water was distilled in a quartz still, and its conductance was $(0.8-1.2) \times 10^{-4}$ S m⁻¹. 1,2-Dimethyimidazolium (ARgrade reagent) was vacuum-distilled prior to use. 1-Bromoethane and 1-bromobutane, (AR-grade reagent) were distilled before use. The purity of HN(SO₂CF₃)₂ is 99.9%. After absorbing the water by molecular sieves, ethyl acetate and acetonitrile were distilled and used in the synthesis process. The source and purity of the materials are listed in Table 1.

2.2 Preparation of $[C_n mmim][NTf_2]$ (n = 2, 4)

Fig. 1 is a schematic of this synthetic route. $[C_nmmim][NTf_2]$ (n = 2, 4) were synthesized according to the ion exchange reaction. First, 1,2-dimethylimidazole (1 mol) was placed in a roundbottomed flask and stirred, and 1-bromoethane or 1-bromobutane (1.1 mol) was added dropwise into the flask at 70 °C. A slight excess of the 1-bromoethyl or 1-bromobutane was used to guarantee the consumption of 1,2-dimethylimidazole. Ethyl acetate was added to reduce the viscosity of the mixture, which was left to stir under reflux at 70 °C for 48 h. The halide salt separated as a second phase from the ethyl acetate. Excess of ethyl acetate was removed by decantation.

The products were recrystallized from acetonitrile. The volume of acetonitrile used for the recrystallization was approximately half that of the halide salt. Acetonitrile was then decanted after crystallization; this step was repeated twice. After the third cycle, the remaining acetonitrile and 1-bromoethane or 1-bromobutane were removed under reduced pressure using a rotary evaporator at 70 $^{\circ}$ C, and the bromide salt was finally dried in high vacuum at 70 $^{\circ}$ C.

A certain quality of $[C_n \text{mmim}][\text{Br}]$ (n = 2, 4) was placed in a round-bottomed flask and dissolved in deionized water. Then, the equivalent amount of bis(trifluoromethyl sulfonyl)imide $HN(SO_2CF_3)_2$ purchased from Rhodia Co. was added dropwise into the flask at room temperature and stirred for 3 h. The $HN(SO_2CF_3)_2$ was dissolved in the deionized water, and the mass fraction of the aqueous solution is 70%. The lower liquid was washed several times with 30 mL of distilled water until no Br^- was indicated by the solution of $AgNO_3/HNO_3$. The final product was dried under the vacuum at 353.15 K for 24 h. Structures of the $[C_n \text{mmim}][NTf_2]$ (n = 2, 4) were confirmed by ¹H NMR spectroscopy (see Fig. S1 and S2 in the ESI†). Differential scanning calorimetry (DSC) measurements showed that $[C_n mmim][NTf_2]$ (n = 2, 4) had no obvious melting point, but the glass transition temperature, $T_{g(n=2)} = -16.47$ °C in Fig. S3 of ESI.† The traces of DSC for $[C_4 mmim][NTf_2]$ are listed Fig. S4 of ESI.†

2.3 Determination of the density, surface tension and refractive index of $[C_n mmim][NTf_2]$ (n = 2, 4)

The density (ρ /g cm⁻³), surface tension (γ /mJ m⁻²) and refractive index (n_D) were measured at atmospheric pressure in the temperature range of (298.15 to 338.15 ± 0.01) K. Since the trace water still exists in the ILs after drying by common methods, the presence of water becomes the most problematic impurity and needs to be confirmed before and after measurement. The mass fraction of water is the average of three measurements carried out Karl Fischer moisture titrator (ZSD-2 type) for [C_nmmim]-[NTf₂] (n = 2, 4) were listed in Table 2.

An Anton Paar DMA 4500 oscillating U-tube densitometer was used to measure the density of $[C_n mmim][NTf_2]$ (n = 2, 4). The temperature in the cell was regulated to ± 0.01 K with solid state thermostat. Before the measurement, the apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Then the values of density of pure water were measured by the calibrated apparatus from (298.15 to 338.15 \pm 0.01) K with 5 K interval and were in good agreement with literature¹⁹ within experimental error ± 0.00001 g cm⁻³. Finally, the densities of the samples were measured at the same temperature.

By use of the tensiometer of the forced bubble method (DPAW type produced by Sang Li Electronic Co.), the surface tension of water was measured at 298.15 \pm 0.01 K and was in good agreement with the literature¹⁹ within experimental error ± 0.1 mJ m $^{-2}$. Then, the values of surface tension of the samples were measured by the same method at (298.15 to 338.15 \pm 0.01) K.

The refractive index, $n_{\rm D}$, of the samples was measured by an Abbe refractometer. First, the refractive index of degassed water was measured by the instrument at 298.15 \pm 0.01 K and was in good agreement with the literature¹⁹ within experimental error \pm 0.0001. Then, the values of the samples were measured by the instrument at (298.15 to 338.15 \pm 0.01) K.

The values of density, surface tension, and refractive index for the samples of the ILs $[C_n mmim][NTf_2]$ (n = 2, 4) at different temperatures are listed in Table 3. Each value in the table is the average of triple measurements.

Table 1 The source and purity of the materia	als
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Chemical name	Source	Purification method	Mass fraction purit				
1,2-Dimethyimidazolium	ACROS	Further purification	≥0.998				
1-Bromoethane	Shanghai Reagent Co. Ltd.	Further purification	>0.985				
1-Bromobutane	Shanghai Reagent Co. Ltd.	Further purification	>0.985				
$HN(SO_2CF_3)_2$	Rhodia Co. Ltd.	Molecular sieves	>0.999				
Ethyl acetate	Shanghai Reagent Co. Ltd.	Further purification	>0.985				
Acetonitrile	Shanghai Reagent Co. Ltd.	Further purification	>0.995				
1,2-Dimethyimidazolium 1-Bromoethane 1-Bromobutane HN(SO ₂ CF ₃) ₂ Ethyl acetate Acetonitrile	ACROS Shanghai Reagent Co. Ltd. Shanghai Reagent Co. Ltd. Rhodia Co. Ltd. Shanghai Reagent Co. Ltd. Shanghai Reagent Co. Ltd.	Further purification Further purification Further purification Molecular sieves Further purification Further purification	≥0.998 >0.985 >0.985 >0.999 >0.985 >0.995				



Fig. 1 Preparation of $[C_n mmim][NTf_2]$ (n = 2, 4) by the ion exchange method.

 Table 2
 Mass fraction of water before and after the measurement of density, surface tension, and refractive index

	Density		Surface tension		Refractive index	
$10^4 w$	Before	After	Before	After	Before	After
[C ₂ mmim][NTf ₂] [C ₄ mmim][NTf ₂]	2.12 1.78	2.88 2.67	2.67 2.19	4.12 3.58	2.67 2.19	3.01 2.53

In order to compare with this work, the experimental data of these properties in literature were collected and are also listed in Table 3. It can be seen that the experimental values of density, surface tension and refractive index for $[C_2mmim]$ - $[NTf_2]$ and $[C_4mmim][NTf_2]$ at 298.15 K are different by different authors from the literature.^{20–23} The crucial reason is mainly caused by the different water content of the samples. From the Table 2, the water content of the samples is very low, the ILs samples may be regarded as pure ionic liquids.

The values of density, surface tension, refractive index and the average contributions to the density, surface tension, and refractive index of per methyl group (-CH₂-) in alkyl chain of [C_nmmim][NTf₂] (n = 2, 4) at 298.15 K are listed in Table 4, and the values of [C_nmim][NTf₂] (n = 2, 4) at 298.15 K were taken from the literature²⁴⁻²⁶ are also listed in Table 4. It shows that the average contributions to the density, surface tension, and refractive index of per methyl group (-CH₂-) in alkyl chain for [C_nmmim][NTf₂] (n = 2, 4) are in good agreement with [C_nmim]-[NTf₂] (n = 2, 4). The average contributions to the addition of a methylene group (-CH₃) in the imidazolium ring for [C_nmmim]-[NTf₂] (n = 2, 4) vs. [C_nmim][NTf₂] (n = 2, 4) are 0.02521 g cm⁻³, 2.82 mJ m⁻², and 0.0063, respectively, and they are much larger

Table 3 Values of density, ρ , surface tension, γ , and refractive index, n_D , the molar refraction, R_m , the mean molecular polarizability, α_{pr} , of $[C_n mmim][NTf_2]$ (n = 2, 4) in the temperature range of 298.15–338.15 K^e

T/K	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
[C ₂ mmim][NTf ₂]									
$\rho/\mathrm{g}~\mathrm{cm}^{-3}$	$1.49107 \\ 1.4931^a$	1.48624	1.48142	1.47662	1.47183	1.46706	1.46231	1.45757	1.45284
$\gamma/mJ m^{-2}$	33.5 39.98 ^a	33.3	33.0	32.8	32.6	32.4	32.2	32.0	31.8
n _D	$1.4280 \\ 1.4296^{a}$	1.4265	1.4250	1.4235	1.4220	1.4205	1.4190	1.4175	1.4161
$R_{\rm m}/{\rm cm}^3~{\rm mol}^{-1}$	69.95	69.96	69.97	69.98	69.99	70.00	70.01	70.02	70.04
$10^{24} \alpha_{\rm p}$	27.75	27.76	27.76	27.77	27.77	27.77	27.78	27.78	27.79
[C₄mmim][NTf ₂]									
$\rho/\mathrm{g}~\mathrm{cm}^{-3}$	1.41852 1.4224^{a} 1.4159^{b} 1.40^{c}	1.41391	1.40929	1.40468	1.40007	1.39548	1.3909	1.38633	1.38178
$\gamma/{ m mJ}~{ m m}^{-2}$	32.5 38.21^{a}	$32.2 \\ 35.54^d$	32.0	31.8 33.83 ^d	31.6	$31.4\\32.20^d$	31.2	$31.0 \\ 30.49^d$	30.7
n _D	$1.4325 \\ 1.4334^a$	1.4311	1.4298	1.4286	1.4273	1.4260	1.4247	1.4232	1.4218
$R_{\rm m}/{\rm cm}^3~{\rm mol}^{-1}$	79.32	79.36	79.41	79.48	79.53	79.57	79.62	79.64	79.67
$10^{24} \alpha_{\rm p}$	31.47	31.49	31.51	31.53	31.55	31.57	31.59	31.6	31.61

^{*a*} Ref. 21. ^{*b*} Ref. 22. ^{*c*} Ref. 20. ^{*d*} Ref. 23. ^{*e*} The standards uncertainty $\mu(\rho) = 0.00005$ g cm⁻³; the standards uncertainty $\mu(\gamma) = 0.5$ mJ m⁻²; the standards uncertainty $\mu(n_D) = 0.0005$.

Table 4 Values of density, ρ , surface tension, γ , refractive index, n_D and $\Delta(-CH_2-)$ of $[C_n mmim][NTf_2]$ (n = 2, 4) and $[C_n mim][NTf_2]$ (n = 2, 4) at 298.15 K, respectively^{*a*,*e*}

	[C ₂ mmim][NTf ₂]	[C ₄ mmim][NTf ₂]	$\Delta(-CH_2-)$	[C ₂ mim][NTf ₂]	[C ₄ mim][NTf ₂]	Δ(-CH ₂ -)
$ ho/{ m g}~{ m cm}^{-3}$	1.49107	1.41852	0.036	1.52^{a}	1.44^b	0.040
$ ho/{ m mJ}~{ m m}^{-2}$	33.5	32.5	0.50	36.17 ^b	35.46^c	0.36
$ ho_{ m D}$	1.4280	1.4325	0.0023	1.421 ^c	1.427^d	0.0030

^{*a*} Δ (-CH₂-) the average contributions to ρ , γ , and $n_{\rm D}$ per methyl group (-CH₂-) in alkyl chain for [C_nmmim][NTf₂] and [C_nmim][NTf₂] (n = 2, 4). ^{*b*} Ref. 24. ^{*c*} Ref. 25. ^{*d*} Ref. 26. ^{*e*} The standards uncertainty $\mu(\rho) = 0.00005$ g cm⁻³; the standards uncertainty $\mu(\gamma) = 0.5$ mJ m⁻²; the standards uncertainty $\mu(n_{\rm D}) = 0.0005$.

than that of per methyl group ($-CH_2-$) in alkyl chain, it means that the addition of a methylene group ($-CH_3$) in the imidazolium ring of [C_n mmim][NTf₂] (n = 2, 4) can have a stronger impact in some properties, for example the density, surface tension, and refractive index in the work.

3. Results and discussion

3.1 Dependence of volumetric and surface properties of $[C_n mmim][NTf_2]$ (n = 2, 4) on temperature

Using the experimental values of density, the molecular volume (the sum of positive and negative ion volumes), $V_{\rm m}$, of $[C_n \text{mmim}][\text{NTf}_2]$ (n = 2, 4), were calculated from the following equation:

$$V_{\rm m} = M/(N\rho) = V/N \tag{1}$$

where *V* is molar volume, *M* is molar mass and *N* is Avogadro constant. According to eqn (1), $V_{\rm m}$ (n = 2, 4) = 0.4516 nm³, 0.5075 nm³ for [C_nmmim][NTf₂] (n = 2, 4) at 298.15 K. The difference between the molecular volumes of [C₂mmim][NTf₂] and [C₄mmim][NTf₂] (0.0559 nm³) can be seen as the contribution of two methylene (-CH₂-) groups to the molecular volume; this means that the contribution per methylene (-CH₂-) group to the molecular volume is 0.0280 nm³, which is in good agreement with the value of 0.0278 nm³ for the ILs [C_nmim][Ala] (n = 2-6), found in our previous investigation,²⁷ and with the mean contribution of 0.0275 nm³ per methylene (-CH₂-) group, obtained by Glasser²⁸ for the ILs [C_nmim][BF₄] and

 $[C_n mim][NTf_2]$. The calculated values of molar volume, *V*, and molecular volume, *V*_m, for $[C_n mmim][NTf_2]$ (n = 2, 4) are listed in Table 5.

Plotting the experimental values of ln *V* for $[C_n mmim][NTf_2]$ (n = 2, 4) against ΔT , ($\Delta T/K = T/K - 298.15$ K), a set of good straight lines were obtained (see Fig. 2). The correlation coefficients of these regression lines are larger than 0.999, and their empirical equation is:

$$\ln V = A + \alpha (T - 298.15)$$
(2)



Fig. 2 The plot of ln *V* against Δ*T*. ■ [C₂mmim][NTf₂]: ln *V* = 5.6054– 6.4867 × 10⁻⁴ Δ*T*, *s* = 3.24 × 10⁻⁵, *r* = 0.9999; ● [C₄mmim][NTf₂]: ln *V* = 5.7220–6.5700 × 10⁻⁴ Δ*T*, *s* = 3.05 × 10⁻⁵, *r* = 0.9999.

Table 5 The values of molar volume, V, molecular volume, V_m , and Gibbs energy of surface formation, E_a , for ILs [C_nmmim][NTf2] (n = 2, 4) at 298.15–338.15 K

<i>T</i> /K	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
[C2mmim][NTf2]									
$V/cm^3 \text{ mol}^{-1}$	271.8786	272.7621	273.6496	274.5392	275.4326	276.3282	277.2258	278.1273	279.0328
$\ln(V/cm^3 mol^{-1})$	5.6054	5.6086	5.6118	5.6151	5.6183	5.6216	5.6248	5.6281	5.6313
$V_{\rm m}/{\rm nm}^3$	0.4516	0.4531	0.4546	0.4560	0.4575	0.4590	0.4605	0.4620	0.4635
$E_{\rm a}/{\rm mJ}~{\rm m}^{-2}$	46.1	46.1	46.0	46.1	46.1	46.1	46.1	46.1	46.1
[C4mmim][NTf2]									
$V/\mathrm{cm}^3 \mathrm{mol}^{-1}$	305.5227	306.5188	307.5236	308.5329	309.5488	310.5670	311.5896	312.6168	313.6462
$\ln(V/cm^3 mol^{-1})$	5.7220	5.7253	5.7286	5.7318	5.7351	5.7384	5.7417	5.7450	5.7483
$V_{\rm m}/{\rm nm^3}$	0.5075	0.5092	0.5108	0.5125	0.5142	0.5159	0.5176	0.5193	0.5210
$E_{\rm a}/{\rm mJ}~{\rm m}^{-2}$	45.2	45.1	45.1	45.2	45.2	45.2	45.2	45.2	45.1

Paper

where *A* is the intercept and α is the slope. According to the definition, the slope, α , is the coefficient of thermal expansion:

$$\alpha \equiv (1/V)(\partial V/\partial T)_{\rm p} = (\partial \ln V/\partial T)_{\rm p}$$
(3)

From Table 6, it can be seen that, with the increase in the number of methylene on alkyl side chains, the values of thermal expansion coefficients are increased only slightly.

The Gibbs energy of surface formation E_a likewise may be obtained from the surface tensions measured in this work:

$$E_{\rm a} = \gamma - T(\partial \gamma / \partial T)_{\rm p} \tag{4}$$

The calculated values of E_a for the ILs $[C_nmmim][NTf_2]$ (n = 2, 4) are also listed in Table 5. According to Table 5, we can see that the values of E_a for $[C_nmmim][NTf_2]$ (n = 2, 4) are nearly equivalent in the temperature range of (298.15–338.15) K, that is, the Gibbs energy of surface formation is temperature-independent.

In comparison with fused salts, for example, $E_a = 146$ mJ m⁻² (for fused NaNO₃),²⁹ the values of E_a for the ILs are much lower and are close to organic liquids, for example, $E_a = 67$ mJ m⁻² for benzene and 51.1 mJ m⁻² for *n*-octane.³⁰ This fact shows that interaction energy between ions in the ILs is much less than that in inorganic fused salts because the Gibbs energy of surface formation is dependent on interaction energy between ions. The low Gibbs energy of surface formation is the underlying reason for forming ILs [C_nmmim][NTf₂] (n = 2, 4) at room temperature.

3.2 Eötvös equation and estimation of the enthalpy of vaporization

In general, the dependence of surface tension, γ , on temperature may be expressed in Eötvös equation:²⁹

$$\gamma V^{2/3} = k (T_{\rm c} - T) \tag{5}$$

where *V* is molar volume, T_c is critical temperature, and *k* is an empirical constant. The linear regressions of product of γ and $V^{2/3}$ for the ILs against absolute temperature *T* were made and good straight lines were obtained (see Fig. 3).

From the slopes and the intercepts of the straight lines, the values of k and T_c were obtained respectively, and they are listed in Table 6.

Rebelo *et al.*³¹ put forward a method of estimating the hypothetical temperature of normal boiling point (NBP) of ionic liquids, $T_{\rm b}$, in terms of critical temperature, $T_{\rm c}$. They thought

Table 6 The values of	of α , k , $T_{\rm c}$, and $T_{\rm b}$ o	of ILs [C _n mmim]	$[NTf_2] (n =$	2, 4)
Ionic liquids	$\alpha \times 10^{-4} / K^{-1}$	$10^7 k/J K^{-1}$	$T_{\rm c}/{ m K}$	T _b /K
[C ₂ mmim][NTf ₂] [C ₄ mmim][NTf ₂]	6.49 6.57	1.194 1.320	1475 1414	885 848



Fig. 3 Plot of $\gamma V^{2/3}$ vs. *T* for [C_nmmim][NTf₂] (*n* = 2, 4). ■ [C₂mmim]-[NTf₂]: $\gamma V^{2/3} = 1760.745 + 1.194$ *T*, *s* = 1.29, *r* = 0.997; ● [C₄mmim]-[NTf₂]: $\gamma V^{2/3} = 1865.791 + 1.320$ *T*, *s* = 1.68, *r* = 0.996.

that the relationship between $T_{\rm b}$ and $T_{\rm c}$ is $T_{\rm b} \approx 0.6 T_{\rm c}$ for ionic liquids. The values of $T_{\rm c}$ and $T_{\rm b}$ are listed in Table 6.

Kabo and colleagues³² put forward an empirical equation for the estimation of the standard molar enthalpy of vaporization, ΔH^{v} at 298.15 K, for the ILs:

$$\Delta H^{\rm v} = A(\gamma V^{2/3} N^{1/3}) + B \tag{6}$$

where *V* is the molar volume, γ is surface tension, *N* is Avogadro's constant, *A* and *B* are the empirical parameters,³² their values are *A* = 0.01121 and *B* = 2.4 kJ mol⁻¹, respectively. The values of molar enthalpy of vaporization for [C_nmmim][NTf₂] (*n* = 2, 4) calculated from eqn (6) are listed in Table 7. The mean contribution to vaporization enthalpy per methylene (-CH₂-) group, ΔH^{v} (-CH₂-) = 3.3 kJ mol⁻¹.

Based on the Verevkin's experimental data,³³ and the contribution to vaporization enthalpy of per methylene (–CH₂–) group (3.89 kJ mol⁻¹), the molar enthalpies of vaporization, ΔH^{v} , for the ILs [C_nmmim][NTf₂] (n = 2, 4) were estimated and are also listed in Table 7.

From Table 7, the values of δ_{μ} for the $[C_n mmim][NTf_2]$ (n = 2, 4) based on the Verevkin's experimental data are a little bit larger than that of using Kabo's method.

Table 7 The values of vaporization enthalpy and δ_{μ} of ILs [C_nmmim] [NTf_2] (n = 2, 4)

Ionic liquids	$\Delta H^{\rm v}/{ m kJ}~{ m mol}^{-1}$	$\Delta H_n^v/kJ$ mol ⁻¹	$\frac{\Delta H_{\mu}^{v}/kJ}{mol^{-1}}$	$\delta_{\mu}/J^{1/2}~{ m cm}^{-3/2}$
Kabo's				
[C ₂ mmim][NTf ₂]	135.5	90.7	44.8	12.72
[C ₄ mmim][NTf ₂]	142.0	102.9	39.1	11.21
Verevkin's				
[C ₂ mmim][NTf ₂]	130.79	130.79	40.07	12.02
[C ₄ mmim][NTf ₂]	136.29	136.29	33.41	10.36

Table 8 The values of *n*, *D*, *M*, ρ , R_n , $\Delta_{vap}H_n$, $\Delta_{vap}H(exp)$, $\Delta_{vap}H_\mu$ and δ_μ for some ILs

Ionic liquids	n _D	D	$M/g ext{ mol}^{-1}$	$ ho/{ m g~cm^{-3}}$	$R_{\rm m}/{\rm cm}^3~{ m mol}^{-1}$	$\Delta_{ m vap}H_{ m n}/ m kJ~mol^{-1}$	$\Delta_{\rm vap} H(\exp)/kJ$ mol ⁻¹	$\Delta_{ m vap}H_{\mu}/{ m kJ}$ ${ m mol}^{-1}$	$\delta_{\mu}/J^{1/2}~{ m cm}^{-3/2}$
[Comim][NTfo]	1 421 ^a		391 31 ^{<i>a</i>}	1.50^{e}		85.8	132.7 ^g	46.9	13 28
[C ₄ mim][NTf ₂]	1.427^{a}	11.7 ^c	419.37^{a}	1.42^{e}		98.4	132.7 137.8 ^g	39.5	11.45
[C ₆ mim][NTf ₂]	1.431 ^{<i>a</i>}		447.42^{a}	1.33 ^e		112.9	142.3^{g}	29.4	9.26
[C ₈ mim][NTf ₂]	1.434^{a}		475.47 ^a	1.31^{e}		122.6	147.0^{g}	24.4	8.13
$[C_{10}mim][NTf_2]$	1.436^{a}		503.53 ^a	1.21^{e}		141.1	147.5^{g}	6.4	3.88
$[C_2 mim][BF_4]$	1.409^{a}	12.8^{d}	197.97	1.2798^{f}		49.6	135.5^{h}	85.9	23.35
[C ₄ mim][BF ₄]	1.420^{a}	11.7^{d}	226.02	1.2015^{f}		61.7	152.5^{i}	90.3	21.72
[C ₂ C ₁ im][SCN]	1.5506^{b}				48.32^{b}	62.7	153.7^{h}	91.0	24.3
$[C_2C_1im][N(CN)_2]$	1.5112^{b}				48.1^{b}	62.4	156.4^{h}	94.0	24.0
$[C_2C_1im][C(CN)_3]$	1.5124^{b}				55.84^{b}	72.4	138.5^{h}	66.1	18.7
$[C_2C_1im][B(CN)_4]$	1.4469^{b}				58.28^{b}	75.6	135.6^{h}	60.0	16.4
^a Ref. 26. ^b Ref. 44.	^c Ref. 38. ^d	^l Ref. 37.	^e Ref. 39. ^f Ref	. 40. ^g Ref. 42	1. ^{<i>h</i>} Ref. 43. ^{<i>i</i>} Ref. 4	12.			

3.3 Molar refraction R_m and estimation of polarity for $[C_n mmim][NTf_2]$ (n = 2, 4)

The Lorentz–Lorenz relationship between the refractive index and the mean molecular polarizability, $\alpha_{\rm p}$, leads to the definition of the molar refraction $R_{\rm m}$:³⁴

$$R_{\rm m} = [(n_{\rm D}^2 - 1)/(n_{\rm D}^2 + 2)](M/\rho) = (4\pi N/3)\alpha_{\rm p}$$
(7)

where *M* and ρ are molar mass and density of the ILs. α_p is the static polarizability caused by the induced dipole. According to eqn (7), values of R_m were calculated from n_D values of the ILs in the temperature range of (298.15–338.15) K and are listed in Table 3. As can be seen from Table 3, the values of R_m and α_p only slightly change with the increasing temperature. This fact shows that the static polarization is caused by the dispersion force of the ILs.

In this work, we assume that a new method for the estimation of the polarity of ILs using the enthalpy of vaporization ΔH^{v} , and there are four hypotheses as follows:

1. The enthalpy of vaporization ΔH^{v} ionic liquid is composed of two parts, a part corresponds with polarization from the induced dipole moment, ΔH_{n}^{v} , which is contribution of induced energy, and another part corresponds with polarization from permanent dipole moment, ΔH_{μ}^{v} , which is orientation energy:

$$\Delta H^{\rm v} = \Delta H^{\rm v}_{\rm n} + \Delta H^{\rm v}_{\rm \mu} \tag{8}$$

2. Typically, the polarity of the liquid mainly depends on the cohesive energy which may be calculated from the enthalpy of vaporization of the liquid. Lawson and Ingham³⁵ pointed out that the relationship between the enthalpy of vaporization and the refractive index can be expressed. Using the following equation, the contribution of induced energy ΔH_n^v can be obtained.

$$\Delta H_{\rm n}^{\rm v} = CR_{\rm m} = C[(n_{\rm D}^2 - 1)/(n_{\rm D}^2 + 2)]V \tag{9}$$

where $R_{\rm m}$ is the molar refraction, *V* is molar volume of the liquid, *C* is empirical constant which is equal to C = 1.297 kJ cm⁻³ for a van der Waals liquid. However, the calculated values of the

enthalpy of vaporization for ionic liquids by using eqn (9) are too small because this equation may be applied only to nonpolar van der Waals liquid. The polarization of non-polar van der Waals liquid in the electric field is caused only by induced dipole moment. But, for the ionic liquids the polarization in electric field is caused by both self-induced dipole moment and mean permanent dipole moment of ion pair in ILs.

3. In terms of the Hildebrand theory,³⁶ ΔH^v , ΔH^v_n , and ΔH^v_μ correspond with δ^2 , δ_n^2 , and δ_μ^2 (δ Hildebrand solubility parameter), respectively:

$$\delta^2 = -E/V = (\Delta H^{\rm v} - RT)/V \tag{10}$$

where *E* is the potential energy of a mole of material.

$$\delta_{\rm n}^{\ 2} = \Delta H_{\rm n}^{\rm v}/V - xRT/V \tag{11}$$

$$\delta_{\mu}^{2} = \Delta H_{\mu}^{\rm v} / V - (1 - x) RT / V \tag{12}$$

where $x = (\Delta H_n^v / \Delta H^v)$ represents the fraction of contribution of induced energy to polarity of ionic liquid, and $(1 - x) = (\Delta H_{\mu}^v / \Delta H^v)$ is the contribution fraction of orientation energy from permanent dipole moment.

4. Non-polar organic solvent only has the induced dipole moment δ_n , but orientation energy of the permanent dipole moment δ_{μ} , while δ_{μ} as the new scale to the polarity, there is a positive correlation between the δ_{μ} and the polarity.

As we all know, the polarity of ILs is often assessed with the dielectric constant, for example, the values of dielectric constant of $[C_2mim][BF_4]$ and $[C_4mim][BF_4]$ measured by Wakai *et al.*³⁷ are 12.8 and 11.7, respectively, however, in some case, it is not, for example, the dielectric constant value of $[C_4mim]$. [NTf₂] measured by Daguenet *et al.*³⁸ is 11.7 which is the same with $[C_4mim][BF_4]$ by Wakai *et al.*³⁷ If δ_{μ} is used as criterion, it is easy to determine the order of polarity for the two ILs. According to the eqn (8), (9) and (12), using the values of literature^{26,39-42} δ_{μ} = 11.45 J^{1/2} cm^{-3/2} for $[C_4mim][NTf_2]$ and $\delta_{\mu} = 21.72$ J^{1/2} cm^{-3/2} for $[C_4mim][BF_4]$ were obtained according to the method in this work so that it has seen that the polarity of $[C_4mim][BF_4]$ is much larger than one of $[C_4mim][NTf_2]$. This result is in good agreement with our experience, that is, $[C_4mim][NTf_2]$ is hydrophobic, $[C_4mim][BF_4]$ hydrophilic.

Using the method in this work, the values of $\delta_{\mu} = 12.02$ (12.72) $J^{1/2}$ cm^{-3/2} and 10.36 (11.21) $J^{1/2}$ cm^{-3/2} for the ILs [C2mmim][NTf2] and [C4mmim][NTf2] were obtained respectively which are listed in Table 7 and the values of δ_{μ} for other ILs were calculated from other literature^{26,39,41,43,44} and are listed in Table 8. From Table 8, the average contributions to δ_{μ} of per methyl group in alkyl chain, $\Delta \delta_{\mu}$ (-CH₂-) = 0.83 J^{1/2} cm^{-3/2} between [C₂mmim][NTf₂] and [C₄mmim][NTf₂], which is in good agreement with the value $\Delta \delta_{\mu}(-CH_2-) = 0.82 \text{ J}^{1/2} \text{ cm}^{-3/2}$ between [C₂mim][BF₄] and [C₄mim][BF₄]. Compared with the average contributions to δ_{μ} of per methyl group (-CH₂-) in alkyl chain, the average contributions to the addition of a methylene group in the imidazolium ring, $\Delta \delta_u$ (-CH₃) = 1.18 J^{1/2} cm^{-3/2} for $[C_n mmim][NTf_2]$ (*n* = 2, 4) *vs.* $[C_n mim][NTf_2]$ (*n* = 2, 4) are much larger, it also means that the addition of a methylene group in the imidazolium ring of $[C_n mmim][NTf_2]$ (n = 2, 4) can have a stronger impact in δ_{μ} . And from the table, it shows that the polarity of the ionic liquids reduces with the increase in the number of methylene on side chain, for example, the ILs $[C_n \min][NTf_2]$ (n = 2, 4, 6, 8, 10), the polarity of hydrophilic ILs is larger than the hydrophobic, which these results are consistent with our experience.

4. Conclusions

Two ILs $[C_n mmim][NTf_2]$ (n = 2, 4) were prepared and characterized. The density, ρ , the surface tension, γ , and the refractive index, $n_{\rm D}$, for the two ILs were measured at (298.15 to 338.15 \pm 0.01) K. The average contributions to the density, surface tension, and refractive index of per methyl group in alkyl chain and the addition of a methylene group in the imidazolium ring for the ILs were obtained, according to compare with the both average contributions $\Delta(-CH_2-)$ and $\Delta(-CH_3)$, it turns out the addition of a methylene group in the imidazolium ring, Δ (-CH₃), for [C_nmmim][NTf₂] (n = 2, 4) are larger than that of $[C_n \min][NTf_2]$ (n = 2, 4), which means that the addition of a methylene group has stronger effect on the density, surface tension, and refractive index. The values of molar volume V, molecular volume, $V_{\rm m}$, the thermal expansion coefficient, α , were calculated. With the increase in the number of methylene on alkyl side chains, the values of α are increased only slightly. The contribution to $V_{\rm m}$ and $\Delta H^{\rm v}$ per methylene (-CH₂-) group are 0.0280 nm³ and 3.3 kJ mol⁻¹, respectively. The values of Gibbs energy of surface formation, E_a , molar refraction, R_m , and the polarization coefficient, $\alpha_{\rm p}$, are temperature-independent. Based on the Kabo's method and Verevkin's experimental values, the values of δ_{μ} were estimated by enthalpy of vaporization and refractive index data for $[C_n mmim][NTf_2]$ (n = 2, 4), the average contributions to δ_{μ} , $\Delta \delta_{\mu}$ (-CH₂-) = 0.83 J^{1/2} cm^{-3/2} between [C2mmim][NTf2] and [C4mmim][NTf2], which is in good agreement with the value $\Delta \delta_{\mu}(\text{-CH}_{2}\text{-})$ = 0.82 $J^{1/2}~\text{cm}^{-3/2}$ between [C₂mim][BF₄] and [C₄mim][BF₄]. Compared with the average contributions to δ_{μ} of per methyl group in alkyl chain, the average contributions to the addition of a methylene group in the imidazolium ring, $\Delta \delta_{\mu}(-CH_3) = 1.18 \text{ J}^{1/2} \text{ cm}^{-3/2}$ for $[C_n mmim][NTf_2] (n = 2, 4) \nu s. [C_n mim][NTf_2] (n = 2, 4)$ are much larger, it means that the addition of a methylene group of $[C_n mmim][NTf_2] (n = 2, 4)$ can have a stronger impact in δ_{μ} , the result shows that using δ_{μ} as the polarity scaling of ILs is very convenient and reasonable.

Glossary

DSC

	0
$E_{\rm a}$	Gibbs energy of surface formation
^{1}H	Nuclear magnetic resonance
NMR	
M	Molar mass
Ν	Avogadro's constant
$n_{\rm D}$	Refractive index
R _m	Molar polarization
V	Molar volume
Vm	Molecular volume
$T_{\rm c}$	Critical temperature
$T_{\rm b}$	Temperature of normal boiling point
$\Delta H^{\rm v}$	Enthalpy of vaporization
$\Delta H_{\rm n}^{\rm v}$	The contribution to ΔH^{v} from the induced dipole
	moment enthalpy of vaporization
$\Delta H^{ m v}_{\mu}$	The contribution to ΔH^{v} from the average permanent
	dipole moment of ion pair in ILs
x	The fraction of contribution of induced energy to
	polarity of ionic liquid
1 - x	The fraction of contribution fraction of orientation

Differential scanning calorimetry

energy from permanent dipole moment.

Greek letters

- α Coefficient of thermal expansion
- δ^2 Cohesive energy density
- ${\delta_n}^2~$ The contribution of induced energy to cohesive energy density
- ${\delta_{\mu}}^2~$ The contribution of orientation energy to cohesive energy density
- δ Hildebrand solubility parameter
- δ_n The contribution of the permanent dipole moment to solubility parameter
- δ_{μ} ~ The contribution of the induced dipole moment to solubility parameter
- γ Surface tension
- ρ Density

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