


 Cite this: *RSC Adv.*, 2017, 7, 11616

Physicochemical properties of $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ionic liquids†

Da-Wei Fang, Fang Zhang, Rui Jia, Wei-jun Shan, Li-xin Xia* and Jia-zhen Yang

A series of ionic liquids based on trifluoroacetic acid, namely, $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) (1-alkyl-3-methylimidazolium trifluoroacetate), were designed and synthesized. The density, surface tension and refractive index were measured in the temperature range of 293.15 to 343.15 ± 0.05 K, and some physicochemical properties of the ILs were calculated. Using the concept of molar surface Gibbs free energy, the traditional Eötvös equation was improved into a modified Eötvös equation, in which the intercept and the slope represented the molar surface enthalpy and the molar surface entropy, respectively, for $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$). The thermal expansion coefficient (α) of $[C_n\text{mim}][\text{TFA}]$ was calculated according to the interstitial model, and the order of magnitude of the calculated values was in good agreement with the corresponding experimental values. A new hypothesis was proposed, stating that the interstitial molar surface Gibbs free energy (g_s) is not determined by the type of IL. From the refractive index and the molar surface Gibbs free energy, an equation to predict the surface tension of ILs was derived and the predicted values were highly correlated with the corresponding experimental values. Finally, a new polarity scale for ILs was developed, and the polarity order of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs was estimated.

 Received 6th January 2017
Accepted 1st February 2017

DOI: 10.1039/c7ra00197e

rsc.li/rsc-advances

1. Introduction

Ionic liquids (ILs) are room-temperature molten organic salts that have attracted considerable attention from the industrial and academic community because of their special physicochemical properties, such as low melting temperature, negligible vapor pressure, high electrical conductivity, large liquid range, selective solubility and electrochemical stability. As green environmentally friendly solvents, ILs are considered to be the best alternative to traditional solvents.^{1–5} The predicted results for the physicochemical properties of ILs were not fully consistent with the literature values, but the level of agreement is sufficient as reference data to select the ionic liquids for industry applications.^{6–9}

As a continuation of our previous study,^{10–13} and to expand our knowledge on IL chemistry, we synthesized a new series of ILs, namely, $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) (1-alkyl-3-methylimidazolium trifluoroacetate), and then measured their density, surface tension and refractive index in the temperature range of 293.15 to 343.15 K, at intervals of 5 K. Several important physical parameters, discussed in this article, were also estimated by semi-empirical methods.^{14–16}

2. Experimental

2.1 Chemicals

Ethyl acetate, acetone and acetonitrile (all from Shanghai Reagent Co. Ltd.) were distilled and then stored over molecular sieves in tightly-sealed glass bottles. The precursor 1-methylimidazole, of AR grade reagent, was obtained from ACROS and vacuum distilled prior to use. Moreover, 1-bromoethane, 1-bromopropane, 1-bromobutane, 1-bromopentane, and 1-bromohexane (99.8%), all from Shanghai Reagent Co. Ltd., were refined by redistillation before use. Trifluoroacetate (99.5%) was from Alading Reagent Co. Ltd.

2.2 Preparation of $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs

The intermediates 1-alkyl-3-methylimidazolium bromide ($[C_n\text{mim}]\text{Br}$, $n = 2, 3, 4, 5, 6$) were synthesized according to the procedure reported in ref. 17. The yields were approximately 80%.

In our laboratories, a series of imidazolium trifluoroacetate, namely $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$), have been synthesized (Fig. 1). A typical preparation of ILs is as follows: 1-alkyl-3-methylimidazolium bromide ($[C_n\text{H}_{2n+1}\text{mim}]\text{Br}$) and 1.2 equiv. of TFA are mixed in acetone under argon and stirred at room temperature for 48 h. The slurry is then filtrated with a Gooch funnel to remove the precipitates. Subsequently, acetone is removed, and the obtained target products are washed 3 times with *n*-hexane and dried under vacuum.

Institute of Rare and Scattered Elements, College of Chemistry, Liaoning University, Shenyang, 110036, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra00197e



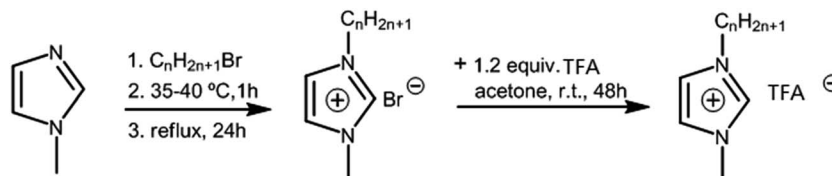


Fig. 1 Synthesis of the ILs $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$).

The obtained $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs were characterized by ^1H NMR and ^{19}F NMR spectroscopy. The water content was determined with a Karl Fischer moisture titrator (ZSD-2 type), and all ILs showed a water content of less than 500 ppm. The Br^- content was determined by dripping a silver nitrate solution, *i.e.*, dissolving 0.5 mL of the product in water and then dripping aqueous silver nitrate; no yellow precipitates were observed. The structure of the synthesized ILs was confirmed by NMR, and this data can be found in the ESI.†

2.3 Density, surface tension and refractive index measurements

The density of degassed water was measured with a Westphal balance at 293.15 ± 0.05 K and was in good agreement with the value reported in ref. 18, within an experimental error of $\pm 0.0003 \text{ g cm}^{-3}$. Then, the densities of the samples were measured in the temperature range from 293.15 to 343.15 K. A sample was placed in a jacketed cell and then thermostated at each temperature with an accuracy of ± 0.05 K.

The surface tension of degassed water was measured in the temperature range from 293.15 to 343.15 K by the forced bubble method with a tensiometer (DPAW type produced by Sang Li Electronic Co.), and the results were in good agreement with the value reported in ref. 18, within an experimental error of $\pm 0.1 \text{ mJ m}^{-2}$. Then, the surface tension of the samples was measured by the same method in the same temperature range from 293.15 to 343.15 K.

The refractive index of the ILs was measured with an Abbe refractometer. The refractive index of degassed water, as measured by the Abbe refractometer, is 1.3329 ± 0.0001 , which is consistent with the value of 1.33299 reported in ref. 18. The refractive indices of a series of samples were measured in the temperature range from 293.15 to 343.15 K at intervals of 5 K.

3. Results and discussion

The density, surface tension and refractive index values for the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) samples are listed in Table 1, and each value is the average of triplicate measurements.

Table 1 Density ρ (g cm^{-3}) and surface tension γ (mJ m^{-2}) values of pure $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs from 293.15 to 343.15 ± 0.05 K

T/K	$[C_2\text{mim}][\text{TFA}]$	$[C_3\text{mim}][\text{TFA}]$	$[C_4\text{mim}][\text{TFA}]$	$[C_5\text{mim}][\text{TFA}]$	$[C_6\text{mim}][\text{TFA}]$
Density ρ (g cm^{-3}) of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs					
293.15	1.2772	1.2503	1.2242	1.1980	1.1705
298.15	1.2733	1.2462	1.2201	1.1939	1.1661
303.15	1.2705	1.2435	1.2159	1.1883	1.1622
308.15	1.2672	1.2405	1.2119	1.1831	1.1583
313.15	1.2632	1.2364	1.2078	1.1792	1.1542
318.15	1.2601	1.2328	1.2042	1.1758	1.1502
323.15	1.2562	1.2293	1.2003	1.1711	1.1467
328.15	1.2524	1.2259	1.1960	1.1661	1.1431
333.15	1.2489	1.2225	1.1921	1.1617	1.1394
338.15	1.2453	1.2190	1.1880	1.1572	1.1354
343.15	1.2420	1.2159	1.1841	1.1522	1.1320
Surface tension γ (mJ m^{-2}) of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs					
293.15	49.3	46.4	44.1	41.3	40.0
298.15	49.0	46.1	43.8	41.0	39.7
303.15	48.6	45.8	43.5	40.8	39.5
308.15	48.3	45.4	43.2	40.6	39.2
313.15	48.0	45.1	42.9	40.3	39.0
318.15	47.8	44.8	42.6	40.1	38.8
323.15	47.5	44.6	42.2	39.9	38.6
328.15	47.2	44.2	41.9	39.6	38.3
333.15	46.9	43.9	41.6	39.4	38.1
338.15	46.5	43.7	41.2	39.2	37.9
343.15	46.2	43.5	41.0	39.1	37.8



3.1 Estimation of the volumetric properties of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs

When plotting the $\ln \rho$ values against T , a straight line was obtained (see Fig. 2) for each IL, and the empirical linear equation is as follows:

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

where b is an empirical constant, and the negative slope value, $\alpha = -(\partial \ln \rho / \partial T)_p$, is the thermal expansion coefficient of the ILs. The α_{exp} values are listed in Table 7. The correlation coefficient of all $\ln \rho$ vs. T linear fittings was larger than 0.99 and standard deviations were within the experimental error.

The molecular volume (V_m) of ILs is the sum of the cation and anion volumes. The V_m value for the $[C_n\text{mim}][\text{TFA}]$ ILs was calculated using the following equation:

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

where M is the molar mass of the ILs and N is the Avogadro's constant. The V_m values were calculated using eqn (2) and are listed in Table 2. When plotting V_m against the number (n) of

carbons in the IL alkyl chain, a good straight line was obtained (see Fig. 3), and the slope of 0.0267 nm^3 , represents the mean contribution of each methylene ($-\text{CH}_2-$) to the molecular volume, which is in good agreement with the value of 0.0275 nm^3 of $[C_n\text{mim}][\text{BF}_4]$ and $[C_n\text{mim}][\text{NTf}_2]$ ILs.¹⁴

According to the Glasser's theory,¹⁴ the standard entropy values, S^0 (298), expressed in $\text{J K}^{-1} \text{ mol}^{-1}$, for the $[C_n\text{mim}][\text{TFA}]$ ILs, can be estimated using eqn (3), and the results are listed in Table 2. As calculated by the least-squares method, the linear regression slope of S^0 (298) vs. the number of carbons (n) is $33.2 \text{ J K}^{-1} \text{ mol}^{-1}$ (see Fig. 3), which represents the contribution of each methylene group to the standard entropy of the ILs. This value is in agreement with the value of $33.9 \text{ J K}^{-1} \text{ mol}^{-1}$ for $[C_n\text{mim}][\text{BF}_4]$.¹⁴

$$S^0(298) (\text{J K}^{-1} \text{ mol}^{-1}) = 1246.5 V_m (\text{nm}^3) + 29.5 \quad (3)$$

The crystal energy (U_{POT}) of the ILs can be estimated by the Glasser's empirical equation:¹⁴

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

The U_{POT} values were calculated and listed in Table 2. From Table 2, it can be seen that the crystal energies of $[C_n\text{mim}][\text{TFA}]$ are much lower than those of inorganic fused salts, for example, the U_{POT} of fused CsI ¹⁸ is 613 kJ mol^{-1} , which is the lowest

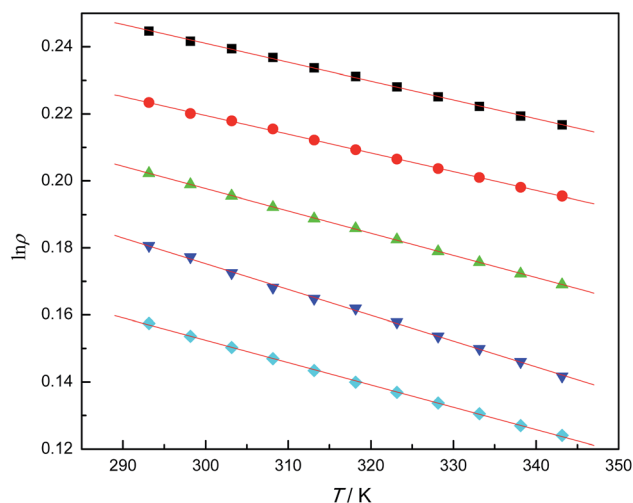


Fig. 2 Plot of $\ln \rho$ vs. T for the $[C_n\text{mim}][\text{TFA}]$ ILs. ■ $[C_2\text{mim}][\text{TFA}]$: $\ln \rho = 0.40949 - 5.62 \times 10^{-4}T$, $r = 0.999$, $s = 2.60 \times 10^{-4}$, ● $[C_3\text{mim}][\text{TFA}]$: $\ln \rho = 0.38740 - 5.60 \times 10^{-4}T$, $r = 0.999$, $s = 2.57 \times 10^{-4}$, ▲ $[C_4\text{mim}][\text{TFA}]$: $\ln \rho = 0.39668 - 6.63 \times 10^{-4}T$, $r = 0.999$, $s = 1.31 \times 10^{-4}$, ▼ $[C_5\text{mim}][\text{TFA}]$: $\ln \rho = 0.40619 - 7.70 \times 10^{-4}T$, $r = 0.999$, $s = 4.70 \times 10^{-4}$, ◆ $[C_6\text{mim}][\text{TFA}]$: $\ln \rho = 0.35238 - 6.66 \times 10^{-4}T$, $r = 0.999$, $s = 2.48 \times 10^{-4}$.

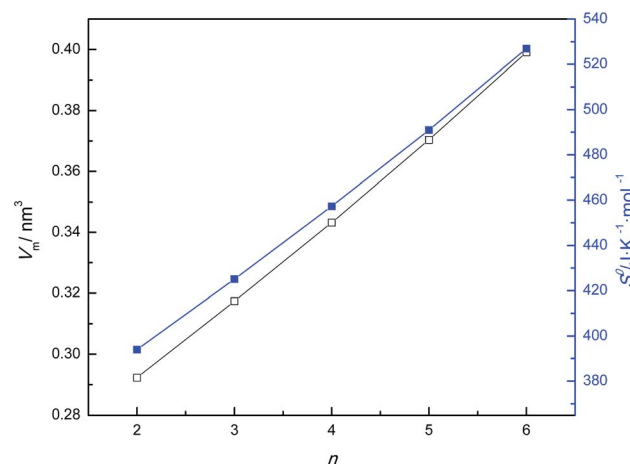


Fig. 3 Plots of V_m (298.15 K) vs. number of carbons (n) in the alkyl chains of the ILs and S^0 (298.15 K) vs. n . (□) $V_m = 0.23786 + 0.02665n$, with $s = 0.0014$ and $r = 0.999$, (●) $S^0 = 326.08 + 33.2n$, with $s = 1.6962$ and $r = 0.999$.

Table 2 Volume properties for the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs at 298.15 K

IL	$V_m (\text{nm}^3)$	$S^0 (\text{J K}^{-1} \text{ mol}^{-1})$	$10^3 S_a (\text{mJ K}^{-1} \text{ m}^{-2})$	$E_a (\text{mJ m}^{-2})$	$U_{\text{POT}} (\text{kJ mol}^{-1})$
$[C_2\text{mim}][\text{TFA}]$	0.2923	393.9	60.5	67.1	457
$[C_3\text{mim}][\text{TFA}]$	0.3174	425.1	59.5	63.8	448
$[C_4\text{mim}][\text{TFA}]$	0.3432	457.3	63.5	62.7	439
$[C_5\text{mim}][\text{TFA}]$	0.3703	491.0	45.1	54.4	431
$[C_6\text{mim}][\text{TFA}]$	0.3991	526.9	44.7	53.0	422



crystal energy among alkali halides. Their low crystal energy is the underlying reason why ILs can be formed at room temperature.

3.2 Estimation of surface properties for the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs

The γ experimental values for each $[C_n\text{mim}][\text{TFA}]$ were fitted against T by the least-squares method to a linear equation, and several good straight lines were obtained. All correlation coefficients of the fittings were larger than 0.99, and the standard deviations were within the experimental error (see Fig. 4).

From the fitting line slopes, the surface entropy (S_a) values were obtained and are listed in Table 2. In addition, the surface energy (E_a) values at 298.15 K may be obtained from the surface tension using the following equation: $E_a = \gamma - T(\partial\gamma/\partial T)_p$ and are also listed in Table 2. In comparison with fused salts (for example, E_a is 146 mJ m^{-2} for fused NaNO_3), E_a values for $[C_n\text{mim}][\text{TFA}]$ ILs are much lower and are closer to those of organic liquids (for example, E_a for benzene is 67 mJ m^{-2} , and for n -octane is 51.1 mJ m^{-2}).¹⁸ The surface excess energy depends on the interaction energy between ions, and hence these results show that the interaction energy between ions in the $[C_n\text{mim}][\text{TFA}]$ ILs is much lower than in inorganic fused salts, which in turn suggests that the crystal energy of the $[C_n\text{mim}][\text{TFA}]$ ILs is much lower than that of inorganic fused salts.

3.3 Eötvös equation and molar surface Gibbs free energy of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs

In general, the surface tension (γ) of several liquids decreases almost linearly as the temperature increases and the relationship is expressed by the Eötvös equation:¹⁹

$$\gamma V^{2/3} = k(T_c - T) \quad (5)$$

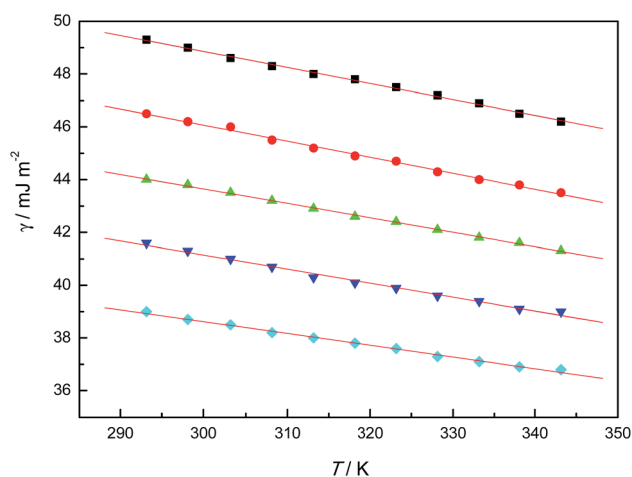


Fig. 4 Surface tension (γ) vs. T plots for the $[C_n\text{mim}][\text{TFA}]$ ILs in the temperature range from 293.15 to 343.15 K. ■ $[C_2\text{mim}][\text{TFA}]$: $\gamma = 67.0 - 0.06055T$, $r = 0.99$, $s = 0.0542$, ● $[C_3\text{mim}][\text{TFA}]$: $\gamma = 63.8 - 0.05945T$, $r = 0.99$, $s = 0.0704$, ▲ $[C_4\text{mim}][\text{TFA}]$: $\gamma = 62.7 - 0.06345T$, $r = 0.99$, $s = 0.0401$, ▼ $[C_5\text{mim}][\text{TFA}]$: $\gamma = 54.5 - 0.04509T$, $r = 0.99$, $s = 0.0528$, ◆ $[C_6\text{mim}][\text{TFA}]$: $\gamma = 53.0 - 0.04473T$, $r = 0.99$, $s = 0.0554$.

where V is the molar volume of the liquid, T_c is the critical temperature, and k is an empirical constant related to the polarity. The product of γ and $V^{2/3}$ values as obtained from this study was plotted against the absolute temperature T , and a series of good straight lines were obtained. The linear correlation coefficients were all above 0.99. From the regression line slope, the k values were determined to be from $0.909 \times 10^{-7} \text{ J mol}^{-2/3} \text{ K}^{-1}$ to $1.569 \times 10^{-7} \text{ J mol}^{-2/3} \text{ K}^{-1}$. For the majority of organic liquids, k is about $2.1 \times 10^{-7} \text{ J K}^{-1}$,²⁰ but for highly-polar fused salts, k is rather small, for example, $k = 0.4 \times 10^{-7} \text{ J K}^{-1}$ for fused NaCl .^{21,22} Therefore, the k value can indicate the polarity of an IL. The k values suggest that $[C_n\text{mim}][\text{TFA}]$ ILs have a medium polarity, which is between that of organic liquids and fused salts.

The molar enthalpy of vaporization, $\Delta_f^0 H_m^0$ (298 K), of ILs can be estimated according to the Kato's empirical equation:¹⁵

$$\Delta_f^0 H_m^0 (298 \text{ K}) = 0.01121(\gamma V^{2/3} N^{1/3}) + 2.4 \text{ kJ mol}^{-1} \quad (6)$$

where V is the molar volume, γ is the surface tension, and N is the Avogadro's constant.

Rebello²³ proposed another equation to estimate the molar enthalpy of vaporization of ILs from the product of the hypothetical normal boiling point (T_b) and the Trouton constant ($\approx 90 \text{ J mol}^{-1} \text{ K}^{-1}$):

$$\Delta_f^0 H_m^0 (T_b) = 90 T_b \quad (7)$$

The empirical relationship between the hypothetical boiling point (T_b) and the critical temperature (T_c) is as follows:

$$T_b = 0.6 T_c \quad (8)$$

The vaporization enthalpies of the ILs were calculated by the above two methods, and the results are listed in Table 3. The difference between the $\Delta_f^0 H_m^0 (T_b)$ as estimated by the Rebello's equation and the $\Delta_f^0 H_m^0 (298 \text{ K})$ as estimated by the Kato's equation is due to the heat capacity difference between the liquid and gas phases at different temperatures.

As regards the classical Eötvös equation, the relationship between surface tension and temperature is well reflected and the critical temperature can be calculated from it; however a drawback is that the units of $\text{J mol}^{-2/3}$ for $\gamma V^{2/3}$ make it complex and the significance of the slope is not clear. After adjustments, a modified Eötvös equation¹⁶ was derived and the concept of molar surface Gibbs free energy was proposed as follows:

$$g = \gamma V^{2/3} N^{1/3} = a_0 - a_1 T \quad (9)$$

where g is the molar surface Gibbs free energy, N is the Avogadro's constant, and the empirical parameters a_0 and a_1 have a clear physical meaning, with a_0 being the surface molar enthalpy and a_1 , the molar surface entropy. The g values are displayed in Table 4.

In order to further confirm the reliability of the modified Eötvös equation, we conducted an extensive literature review,^{20,24–28} and the molar surface Gibbs free energy ($g/\text{kJ mol}^{-1}$)



Table 3 Molar enthalpies of vaporization, $\Delta^{\text{v}}H_{\text{m}}^0$ (298 K) and $\Delta^{\text{v}}H_{\text{m}}^0(T_{\text{b}})$, for the $[\text{C}_n\text{mim}][\text{TFA}]$ ILs

IL	T_{c} (K)	T_{b} (K)	$\Delta^{\text{v}}H_{\text{m}}^0(T_{\text{b}})$ (kJ mol ⁻¹)	$\Delta^{\text{v}}H_{\text{m}}^0$ (298 K) (kJ mol ⁻¹)
$[\text{C}_2\text{mim}][\text{TFA}]$	1437	862	77.6	148
$[\text{C}_3\text{mim}][\text{TFA}]$	1369	821	73.9	147
$[\text{C}_4\text{mim}][\text{TFA}]$	1271	763	68.6	147
$[\text{C}_5\text{mim}][\text{TFA}]$	1956	1173	105.6	145
$[\text{C}_6\text{mim}][\text{TFA}]$	1731	1039	93.5	148

values of other ILs are shown in Table 5. The k and T_{c} values were calculated according to the Eötvös equation and the parameters a_0 and a_1 were determined according to the modified Eötvös equation, and results are included in Table 6. The empirical parameters a_0 and a_1 of each IL can be easily compared in Table 6.

3.4 The interstitial model for ILs

For pure ILs, a new theoretical model,²⁹ obtained by classical statistical mechanics, provides an expression for the calculation of the interstitial volume (ν):

$$\nu = 0.6791(k_{\text{b}}T/\gamma)^{3/2} \quad (10)$$

where k_{b} is the Boltzmann constant and γ is the surface tension of the IL.

There are some papers about studies on voids in ILs,^{30,31} in which the voids are defined by the volume occupied by an ion pair, *i.e.*, the sum $V^+ + V^-$ of the cationic and anionic volumes

(known from the crystal structure). The void can also be defined by the mean hole volume and the hole free volume. However, these are different from our interstitial model. For pure ionic liquids, our model is proposed on the basis of the following assumptions: (1) due to their large size and asymmetric shape, the ions may not be closely packed, generating lots of interstices between ions; (2) in order to calculate the volume easily, the interstice is regarded as a bubble; (3) there are $2N$ interstices for 1 mol of 1 : 1 ionic liquid, where N is the Avogadro's constant; (4) the interstice in ILs can move around in the same way as an ion or another particle, and in the movement the interstice does not vanish and instead it can be compressed and expanded, which is an additional feature of interstitial motion called the breathing motion. According to the hole model of molten salts, the interstitial volume (ν) can be calculated using eqn (10).

The average interstitial volume values for the $[\text{C}_n\text{mim}][\text{TFA}]$ ILs at different temperatures were determined using eqn (10) and are listed in Table 7.

Table 4 Molar surface Gibbs free energy ($g/\text{kJ mol}^{-1}$) for $[\text{C}_n\text{mim}][\text{TFA}]$ and the parameters of new Eötvös equation

T/K	$[\text{C}_2\text{mim}][\text{TFA}]$		$[\text{C}_3\text{mim}][\text{TFA}]$		$[\text{C}_4\text{mim}][\text{TFA}]$		$[\text{C}_5\text{mim}][\text{TFA}]$		$[\text{C}_6\text{mim}][\text{TFA}]$	
	$10^5\gamma V^{2/3}$ (J mol ^{-2/3})	g (kJ mol ⁻¹)	$10^5\gamma V^{2/3}$ (J mol ^{-2/3})	g (kJ mol ⁻¹)	$10^5\gamma V^{2/3}$ (J mol ^{-2/3})	g (kJ mol ⁻¹)	$10^5\gamma V^{2/3}$ (J mol ^{-2/3})	g (kJ mol ⁻¹)	$10^5\gamma V^{2/3}$ (J mol ^{-2/3})	g (kJ mol ⁻¹)
293.15	15.46	13.05	15.36	12.97	15.38	12.99	15.15	12.80	15.42	13.03
298.15	15.39	13.00	15.30	12.92	15.31	12.93	15.08	12.73	15.35	12.96
303.15	15.29	12.91	15.22	12.85	15.24	12.87	15.05	12.71	15.30	12.92
308.15	15.22	12.85	15.11	12.76	15.17	12.81	15.02	12.69	15.22	12.86
313.15	15.16	12.80	15.04	12.71	15.10	12.75	14.94	12.62	15.18	12.82
318.15	15.12	12.77	14.97	12.65	15.02	12.69	14.90	12.58	15.14	12.78
323.15	15.06	12.72	14.93	12.61	14.92	12.60	14.86	12.55	15.09	12.74
328.15	14.99	12.66	14.83	12.52	14.85	12.54	14.79	12.49	15.00	12.67
333.15	14.92	12.60	14.75	12.46	14.77	12.47	14.76	12.46	14.96	12.63
338.15	14.83	12.52	14.72	12.43	14.66	12.38	14.72	12.43	14.91	12.60
343.15	14.76	12.46	14.67	12.39	14.62	12.35	14.72	12.43	14.90	12.59
	$10^7k/\text{J mol}^{-2/3} \text{ K}^{-1}$	$a_0/\text{kJ mol}^{-1}$	$10^7k/\text{J mol}^{-2/3} \text{ K}^{-1}$	$a_0/\text{kJ mol}^{-1}$	$10^7k/\text{J mol}^{-2/3} \text{ K}^{-1}$	$a_0/\text{kJ mol}^{-1}$	$10^7k/\text{J mol}^{-2/3} \text{ K}^{-1}$	$a_0/\text{kJ mol}^{-1}$	$10^7k/\text{J mol}^{-2/3} \text{ K}^{-1}$	$a_0/\text{kJ mol}^{-1}$
	1.347	16.38	1.427	16.48	1.569	16.89	0.909	15.06	1.075	15.66
	T_{c}/K	$a_1/\text{kJ mol}^{-1} \text{ K}^{-1}$	T_{c}/K	$a_1/\text{kJ mol}^{-1} \text{ K}^{-1}$	T_{c}/K	$a_1/\text{kJ mol}^{-1} \text{ K}^{-1}$	T_{c}/K	$a_1/\text{kJ mol}^{-1} \text{ K}^{-1}$	T_{c}/K	$a_1/\text{kJ mol}^{-1} \text{ K}^{-1}$
	1437	0.0114	1369	0.0120	1271	0.0133	1956	0.0078	1731	0.0090
r	0.994	0.992	0.990	0.991	0.997	0.996	0.983	0.980	0.989	0.987
	$10^5s/\text{J mol}^{-2/3}$	$s/\text{kJ mol}^{-1}$	$10^5s/\text{J mol}^{-2/3}$	$s/\text{kJ mol}^{-1}$	$10^5s/\text{J mol}^{-2/3}$	$s/\text{kJ mol}^{-1}$	$10^5s/\text{J mol}^{-2/3}$	$s/\text{kJ mol}^{-1}$	$10^5s/\text{J mol}^{-2/3}$	$s/\text{kJ mol}^{-1}$
	0.0174	0.0167	0.0238	0.0183	0.0149	0.0132	0.0197	0.0184	0.0186	0.0170



Table 5 Molar surface Gibbs free energy ($g/\text{kJ mol}^{-1}$) of other ILs calculated by basic data in the literature

IL	T (K)				
	298.15	308.15	318.15	328.15	338.15
[C ₂ mim][OAc]	9.04	8.92	8.74	8.60	8.46
[C ₃ mim][OAc]	9.34	9.11	8.97	8.82	8.67
[C ₄ mim][OAc]	9.50	9.37	9.21	8.94	8.81
[C ₅ mim][OAc]	9.75	9.58	9.38	9.15	8.98
[C ₆ mim][OAc]	9.95	9.77	9.53	9.32	9.10
[C ₂ mim][Ala]	11.96	11.84	11.72	11.55	11.45
[C ₃ mim][Ala]	12.07	11.94	11.81	11.63	11.52
[C ₄ mim][Ala]	12.14	11.99	11.86	11.67	11.55
[C ₅ mim][Ala]	12.30	12.16	12.01	11.81	11.69
[C ₃ mim][Gly]	12.12	12.01	11.85	11.73	
[C ₄ mim][Gly]	12.23	12.10	11.98	11.85	
[C ₅ mim][Gly]	12.29	12.15	12.02	11.82	11.71
[C ₆ mim][Gly]	12.75	12.58	12.43	12.24	12.11
[C ₂ mim][Lact]	11.35	11.23	11.07	10.95	10.81
[C ₄ mim][Lact]	12.81	12.67	12.48	12.35	12.18
[C ₅ mim][Lact]	13.01	12.79	12.62	12.49	12.29
[C ₂ mim][Thr]	15.59	15.48	15.31	15.17	
[C ₄ mim][Thr]	16.18	16.09	15.89	15.73	
[C ₂ mim][Pro]	9.62	9.50	9.38	9.21	9.09
[C ₃ mim][Pro]	10.09	9.99	9.87	9.74	9.62
[C ₄ mim][Pro]	10.29	10.16	10.02	9.86	9.72
[C ₅ mim][Pro]	10.48	10.37	10.26	10.08	9.91
[C ₆ mim][Pro]	10.77	10.61	10.49	10.31	10.16

The molar volume of the interstice ($\sum \nu = 2N\nu$) and the volume fraction of the interstice ($\sum \nu/V$) range from 11.3% to 11.7%. These results are in good agreement with the values for the majority of materials that exhibit a 10–15% volume

expansion during the solid to liquid state transition³² and suggest that the interstitial model is reasonable.

The IL volume (V) consists of the inherent volume (V_i) and the total volume of all interstices:

$$V = V_i + 2N\nu \quad (11)$$

If the increase of the IL volume only results from the expansion of the interstices when temperature increases, then the expression for the calculation of the thermal expansion coefficient (α) can be derived from the interstitial model:

$$\alpha = (1/V)(\partial V/\partial T)_p = 3N\nu/VT \quad (12)$$

The α_{est} values, calculated using eqn (12), and the corresponding experimental values (α_{exp}) for the [C_nmim][TFA] ILs at 298.15 K are listed in Table 7. From Table 7, it can be observed that the order of magnitude of the α_{est} values is in good agreement with the α_{exp} values, indicating that the interstitial model is reasonable.

We assumed that the interstices in the ILs are particles with zero static mass, and therefore the molar interstitial volume can be expressed as the product of the interstitial volume (ν) and the Avogadro's constant (N). The definition of the interstitial molar surface Gibbs free energy of the ILs can be expressed as follows:

$$g_s = N^{1/3}\gamma(N\nu)^{2/3} \quad (13)$$

According to the interstitial model of ILs, the following formula can be introduced:

$$\gamma(N\nu)^{2/3} = (0.6791N)^{2/3}k_bT \quad (14)$$

Table 6 The parameters of the modified Eötvös equation for other ILs

IL	a_0 (kJ mol ⁻¹)	a_1 (kJ mol ⁻¹ K ⁻¹)	R	s (kJ mol ⁻¹)	$10^7 k$ (J mol ^{-2/3} K ⁻¹)	T_c (K)
[C ₂ mim][OAc]	13.50	0.0149	0.998	0.0129	1.7660	905
[C ₃ mim][OAc]	14.19	0.0164	0.996	0.0217	1.9410	865
[C ₄ mim][OAc]	14.95	0.0182	0.994	0.0288	2.1522	823
[C ₅ mim][OAc]	15.79	0.0202	0.998	0.0208	2.3892	783
[C ₆ mim][OAc]	16.49	0.0218	0.999	0.0139	2.5857	755
[C ₂ mim][Ala]	15.74	0.0127	0.997	0.0179	1.5019	1241
[C ₃ mim][Ala]	16.12	0.0136	0.997	0.0194	1.6099	1186
[C ₄ mim][Ala]	16.47	0.0145	0.997	0.0202	1.7208	1133
[C ₅ mim][Ala]	16.87	0.0154	0.997	0.0213	1.8204	1098
[C ₃ mim][Gly]	15.98	0.0129	0.998	0.0098	1.5331	1234
[C ₄ mim][Gly]	15.95	0.0125	0.999	0.0124	1.4793	1277
[C ₅ mim][Gly]	16.60	0.0145	0.997	0.0211	1.7131	1148
[C ₆ mim][Gly]	17.63	0.0164	0.999	0.0145	1.9390	1077
[C ₂ mim][Lact]	16.75	0.0140	0.999	0.0112	1.6541	1199
[C ₄ mim][Lact]	17.61	0.0161	0.999	0.0133	1.9033	1095
[C ₅ mim][Lact]	18.91	0.0174	0.998	0.0188	2.0662	1042
[C ₂ mim][Thr]	19.80	0.0141	0.996	0.0130	1.6750	1401
[C ₄ mim][Thr]	20.69	0.0151	0.990	0.0230	1.7890	1371
[C ₂ mim][Pro]	13.57	0.0132	0.999	0.0119	1.5658	1026
[C ₃ mim][Pro]	13.72	0.0122	0.999	0.0082	1.4374	1131
[C ₄ mim][Pro]	14.47	0.0140	0.999	0.0132	1.6612	1031
[C ₅ mim][Pro]	14.76	0.0143	0.995	0.0262	1.6875	1035
[C ₆ mim][Pro]	15.24	0.0150	0.999	0.0140	1.7776	1015



Table 7 Parameters of the interstitial model for the [C_nmim][TFA] ILs at 298.15 K

Ionic liquid	10 ⁻²⁴ <i>v</i> (cm ³)	∑ <i>v</i> (cm ³)	<i>V</i> (cm ³ mol ⁻¹)	10 ² ∑ <i>v</i> / <i>V</i>	10 ⁴ α _{est} (K ⁻¹)	10 ⁴ α _{exp} (K ⁻¹)
[C ₂ mim][TFA]	16.53	19.91	176.1	11.3	5.69	5.62
[C ₃ mim][TFA]	18.12	21.82	191.1	11.4	5.74	5.60
[C ₄ mim][TFA]	19.56	23.56	206.7	11.4	5.74	6.63
[C ₅ mim][TFA]	21.60	26.01	223.0	11.7	5.87	7.70
[C ₆ mim][TFA]	22.67	27.30	240.4	11.4	5.72	6.66

Combining eqn (13) and (14), the interstitial molar surface Gibbs free energy of the [C_nmim][TFA] ILs is ultimately expressed as follows:

$$g_s = 0.6791^{2/3}RT \quad (15)$$

where *R* is the gas constant and it is equal to the product of the Avogadro's constant and the Boltzmann constant, *i.e.*, *R* = *Nk_B*.

The interstitial molar surface entropy of the ILs is calculated as *s_s* = -0.6791^{2/3}*R* = -6.42 J K⁻¹ mol⁻¹, which is a constant. Thus, the interstitial molar surface enthalpy can be obtained according to the following equation:

$$h_s = g_s + Ts_s \quad (16)$$

It is clear that the interstitial molar surface enthalpy values of the ILs are approximately equal to zero. Thus, it can be concluded that the interstitial molar surface Gibbs free energy (*g_s*), the interstitial molar surface entropy (*s_s*) and the interstitial molar surface enthalpy (*h_s*) are independent of the type of the ILs formed in the interstice.

From the IL interstitial model, we can conclude that the nature of the interstice is only related to the volume and the shape of the interstice, but not to the type of IL. Thus, we hypothesized that the Schottky defects in crystals, holes in molten salts and interstices in thin films have similar properties.³²

3.5 Molar refraction and improved Lorentz–Lorenz equation

The refractive index values for the [C_nmim][TFA] (*n* = 2, 3, 4, 5, 6) ILs are listed in Table 8. Each value in the table is the average of triplicate measurements.

The Lorentz–Lorenz relationship²⁸ between the refractive index and the mean molecular polarisability (α_p) leads to the definition of the molar refraction (*R_m*):

$$R_m = [(n_D^2 - 1)/(n_D^2 + 2)](M/\rho) = (4\pi N/3)\alpha_p \quad (17)$$

The *R_m* and α_p values were calculated according to eqn (17), from the *n_D* values of [C_nmim][TFA] (see Table 9).

A short calculation revealed that the contribution value of each methylene (-CH₂-) group to the molar refraction is almost equal to that in the [C_nmim][TFA] (*n* = 2, 3, 4, 5, 6) homologue, which also suggests that all methylene (-CH₂-) groups in the alkyl chains of the imidazolium-based ILs have very similar chemical environments.

The new concept of molar surface Gibbs free energy (*g*/kJ mol⁻¹) was applied to improve the Lorentz–Lorenz equation:³³

$$\gamma^{3/2} = [g^{3/2}/(N^{1/3}R_m)][(n_D^2 - 1)/(n_D^2 + 2)] \quad (18)$$

The surface tension (γ_{est}) of the [C_nmim][TFA] ILs was predicted based on eqn (18), and results are listed in Table 9.

As can be seen in Table 9, *R_m* and α_p are temperature-independent physical properties. When plotting the estimated γ_{est} values of the [C_nmim][TFA] (*n* = 2, 3, 4, 5, 6) ILs against the corresponding experimental γ_{exp} values, a good straight line was obtained (see Fig. 5). The γ_{est} and γ_{exp} values are correlated, with a correlation coefficient of 0.999, and the standard deviation is within the experimental range (Fig. 6).

In order to further explore the applicability of eqn (18), we estimated the surface tension of other ILs^{20,24–28} using the improved Lorentz–Lorenz equation, fitting γ_{est} and the

Table 8 Refractive index (*n_D*) values of pure [C_nmim][TFA] (*n* = 2, 3, 4, 5, 6) ILs at 293.15 to 343.15 ± 0.05 K

<i>T</i> /K	[C ₂ mim][TFA]	[C ₃ mim][TFA]	[C ₄ mim][TFA]	[C ₅ mim][TFA]	[C ₆ mim][TFA]
293.15	1.5669	1.5309	1.4978	1.4677	1.4428
298.15	1.5651	1.5298	1.4962	1.4656	1.4409
303.15	1.5632	1.5282	1.4943	1.4640	1.4398
308.15	1.5611	1.5262	1.4915	1.4614	1.4388
313.15	1.5588	1.5244	1.4896	1.4595	1.4363
318.15	1.5566	1.5222	1.4879	1.4574	1.4352
323.15	1.5554	1.5203	1.4858	1.4555	1.4341
328.15	1.5530	1.5183	1.4836	1.4539	1.4328
333.15	1.5517	1.5163	1.4815	1.4514	1.4308
338.15	1.5501	1.5144	1.4792	1.4498	1.4295
343.15	1.5484	1.5126	1.4779	1.4493	1.4281



Table 9 Molar refraction R_m , molecular polarisability α_p and the estimation of surface tension γ (mJ m^{-2}) with improved Lorentz–Lorenz equation

		T (K)										
IL		293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
[C ₂ mim][TFA]	R_m	57.33	57.36	57.32	57.30	57.28	57.24	57.31	57.28	57.33	57.36	57.36
	$10^{24}\alpha_p$	22.72	22.73	22.72	22.71	22.70	22.69	22.72	22.70	22.72	22.73	22.74
	γ_{est}	49.2	49.0	48.7	48.3	48.0	47.7	47.5	47.1	46.9	46.6	46.4
[C ₃ mim][TFA]	R_m	58.94	59.03	59.00	58.96	58.99	58.95	58.94	58.91	58.88	58.87	58.84
	$10^{24}\alpha_p$	23.36	23.40	23.39	23.37	23.38	23.37	23.36	23.35	23.34	23.33	23.32
	γ_{est}	46.4	46.2	45.9	45.6	45.4	45.0	44.7	44.4	44.1	43.8	43.5
[C ₄ mim][TFA]	R_m	60.37	60.41	60.42	60.34	60.33	60.34	60.32	60.29	60.27	60.22	60.29
	$10^{24}\alpha_p$	23.93	23.95	23.95	23.92	23.91	23.92	23.91	23.90	23.89	23.87	23.90
	γ_{est}	44.1	43.8	43.5	43.1	42.8	42.5	42.2	41.8	41.5	41.2	40.9
[C ₅ mim][TFA]	R_m	61.75	61.73	61.83	61.80	61.78	61.72	61.75	61.82	61.76	61.81	62.01
	$10^{24}\alpha_p$	24.48	24.47	24.51	24.50	24.49	24.46	24.48	24.50	24.48	24.50	24.58
	γ_{est}	41.3	41.0	40.8	40.5	40.2	40.0	39.7	39.5	39.2	39.0	38.9
[C ₆ mim][TFA]	R_m	63.46	63.46	63.54	63.62	63.53	63.61	63.67	63.70	63.65	63.71	63.71
	$10^{24}\alpha_p$	25.15	25.15	25.18	25.22	25.18	25.21	25.24	25.25	25.23	25.25	25.25
	γ_{est}	39.8	39.6	39.4	39.2	38.9	38.8	38.6	38.4	38.1	37.9	37.7

corresponding experimental results γ_{exp} as obtained from the literature, which shows that the values are in good agreement, with a correlation coefficient of up to 0.99 (Table 10).

3.6 Polarity of the [C_nmim][TFA] ($n = 2, 3, 4, 5, 6$) ILs

There is no widely accepted standard for evaluating the polarity of liquids, and it is common to determine whether a substance has polarity or not according to its dielectric constant, but as indicated in the related literature, this approach is not feasible for ILs.¹⁶ For example, the dielectric constant of [C₄mim][NTf₂],³¹ as measured by Daguenet *et al.* is 11.7. Wakai *et al.* measured the dielectric constants of a different IL, [C₄mim][BF₄],³⁴ and yet obtained the same result. However, there is a great difference between the polarity of these two ILs. [C₄mim]

[NTf₂] is a hydrophobic IL, while [C₄mim][BF₄] is hydrophilic. Based on the Hildebrand's theory,³⁵ we proposed a new standard, δ_μ , to describe the polarity of an IL:³⁶

$$\delta_\mu^2 = \Delta H_\mu^v/V - (1 - x)RT/V \quad (19)$$

where V is the molar volume and x is $\Delta H_n^v/\Delta H_\mu^v$ (298.15). ΔH_n^v is the contribution of the induced dipole moment to the molar enthalpy of vaporization, $\Delta_f^v H_m^0$ (298 K). ΔH_μ^v is the contribution of the average permanent dipole moment of ion pairs in the IL and its value can be calculated by the following equation:

$$\Delta H_\mu^v = \Delta_f^v H_m^0 (298) - \Delta H_n^v \quad (20)$$

The $\Delta_f^v H_m^0$ values have been calculated according to the Kabo's empirical eqn (6)^{15,37} and listed in Table 3.

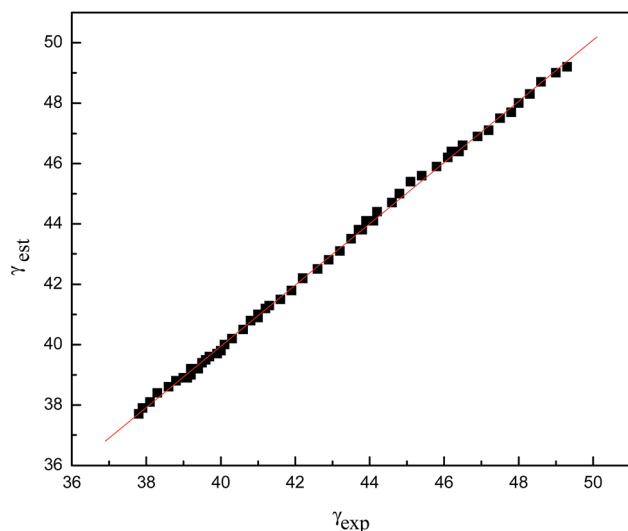


Fig. 5 Plot of γ_{est} vs. γ_{exp} for the [C_nmim][TFA] ILs. $\gamma_{\text{est}} = 1.01439\gamma_{\text{exp}} - 0.6287$; $r = 0.999$, $s = 0.1059$.

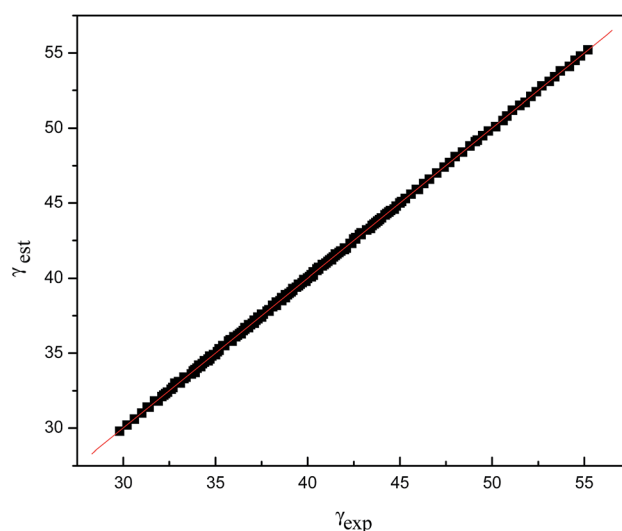


Fig. 6 Plot of γ_{est} vs. γ_{exp} for other ILs. $\gamma_{\text{est}} = 0.99957\gamma_{\text{exp}} - 2.02 \times 10^{-2}$; $r = 0.99$, $s = 5.82 \times 10^{-2}$.



Table 10 Estimation of the surface tension for other ILs

IL	T/K							
	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
[C ₂ mim][OAc]	38.2	37.8	37.4	37.0	36.7	36.3	35.9	35.5
[C ₃ mim][OAc]	36.7	36.3	35.9	35.5	35.1	34.8	34.4	34.0
[C ₄ mim][OAc]	35.3	34.9	34.5	34.1	33.7	33.4	33.0	32.6
[C ₅ mim][OAc]	34.2	33.8	33.4	33.0	32.6	32.2	31.8	31.4
[C ₆ mim][OAc]	33.1	32.7	32.3	31.8	31.4	31.0	30.6	30.2
[C ₂ mim][Ala]	44.8	44.5	44.2	43.9	43.6	43.2	42.9	42.6
[C ₃ mim][Ala]	42.6	42.3	42.0	41.7	41.4	41.0	40.7	40.4
[C ₄ mim][Ala]	40.6	40.3	40.0	39.7	39.4	39.0	38.7	38.4
[C ₅ mim][Ala]	39.1	38.8	38.5	38.2	37.9	37.5	37.2	36.9
[C ₃ mim][Gly]	45.6	45.3	45.0	44.6	44.3	44.0	43.7	43.4
[C ₄ mim][Gly]	43.5	43.2	42.9	42.6	42.3	42.0	41.7	41.4
[C ₅ mim][Gly]	41.5	41.2	40.9	40.6	40.2	39.9	39.6	39.3
[C ₆ mim][Gly]	40.9	40.6	40.2	39.9	39.6	39.2	38.9	38.6
[C ₂ mim][Lact]	48.8	48.4	48.1	47.7	47.4	47.0	46.6	46.3
[C ₄ mim][Lact]	44.0	43.7	43.3	43.0	42.6	42.3	41.9	41.6
[C ₅ mim][Lact]	42.3	41.9	41.6	41.2	40.9	40.5	40.1	39.8
[C ₂ mim][Thr]	54.8	54.5	54.1	53.8	53.4	53.1	52.8	52.4
[C ₄ mim][Thr]	51.2	50.8	50.5	50.1	49.8	49.5	49.1	48.8
[C ₂ mim][Pro]	39.5	39.2	38.9	38.5	38.2	37.9	37.6	37.2
[C ₃ mim][Pro]	38.7	38.5	38.2	37.9	37.6	37.3	37.0	36.7
[C ₄ mim][Pro]	37.1	36.8	36.5	36.2	35.8	35.5	35.2	34.9
[C ₅ mim][Pro]	35.8	35.5	35.2	34.9	34.6	34.3	34.0	33.7
[C ₆ mim][Pro]	34.8	34.5	34.2	33.9	33.6	33.3	33.0	32.7

The ΔH_n^v value is obtained according to the Lawson–Ingham equation:³⁸

$$\Delta H_n^v = C[(n_D^2 - 1)/(n_D^2 + 2)]V \quad (21)$$

where C is an empirical parameter, whose value is 1.297 kJ cm^{-3} , n_D is the refractive index, and V is the molar volume. Thus the ΔH_n^v , ΔH_μ^v and δ_μ values can be calculated, and are listed in Table 11.

From Table 11, it can be observed that the polarity (δ_μ) of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs decreases with the increase of the number of methylene ($-\text{CH}_2-$) groups in the alkyl chains of the ILs and this behavior is consistent with the literature.²⁸

According to Seddon³⁹ *et al.*, the δ_μ value for $[C_4\text{mim}][\text{BF}_4]$ was calculated to be $20.42 \text{ J}^{1/2} \text{ cm}^{-3/2}$, which is greater than the polarity of $[C_4\text{mim}][\text{NTf}_2]$ ($\delta_\mu = 10.23 \text{ J}^{1/2} \text{ cm}^{-3/2}$) and this result is consistent with our experience, *i.e.*, $[C_4\text{mim}][\text{BF}_4]$ is hydrophilic and $[C_4\text{mim}][\text{NTf}_2]$ is hydrophobic. These observations prove that the new polarity scale for ILs has certain reliability. In our experiment, the polarity value obtained for $[C_4\text{mim}][\text{TFA}]$

was between that of $[C_4\text{mim}][\text{BF}_4]$ and $[C_4\text{mim}][\text{NTf}_2]$, which is reasonable.

4. Conclusion

In summary, a series of 1-alkyl-3-methylimidazolium tri-fluoroacetate ionic liquids were synthesized and characterized. Their density, surface tension and refractive index were measured in the temperature range from 293.15 to $343.15 \pm 0.05 \text{ K}$. The standard molar entropy and lattice energy of the ILs were calculated according to the Glasser's theory. The molar enthalpy of vaporization ($\Delta_f^v H_m^0$) of the ILs at 298 K was estimated by the Kabo's method. The Eötvös equation was modified by introducing the molar surface Gibbs free energy. In the modified Eötvös equation, the slope represents the molar surface entropy and the intercept represents the molar surface enthalpy. The interstitial model was applied to calculate the thermal expansion coefficient (α) of the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs, and the order of magnitude for the calculated and experimental coefficients was the same. According to the interstitial model, a new concept was proposed, that is the interstitial molar surface Gibbs free energy (g_s), which is independent of the type of IL. Similarly, the molar surface Gibbs free energy was applied to improve the Lorentz–Lorenz equation, which can predict the surface tension, and the predicted values for $[C_n\text{mim}][\text{TFA}]$ ILs and other ILs were in good agreement with the corresponding experimental values. The polarity of the $[C_n\text{mim}][\text{TFA}]$ ILs was estimated by the new polarity scale for ILs, and the results obtained show the reliability of this scale.

Table 11 ΔH_n^v , ΔH_μ^v and δ_μ values for the $[C_n\text{mim}][\text{TFA}]$ ($n = 2, 3, 4, 5, 6$) ILs

IL	ΔH_n^v , kJ mol^{-1}	ΔH_μ^v , kJ mol^{-1}	δ_μ , $\text{J}^{1/2} \text{ cm}^{-3/2}$
[C ₂ mim][TFA]	74.39	64.45	19.13
[C ₃ mim][TFA]	76.56	61.44	17.93
[C ₄ mim][TFA]	78.36	69.02	18.27
[C ₅ mim][TFA]	80.06	56.00	15.85
[C ₆ mim][TFA]	82.31	56.14	15.28



Acknowledgements

This project was supported by the NSFC (21373005, 21471073, 21671089), the Education Bureau of the Liaoning Province (LZ2014001), and the Liaoning BAIQIANWAN Talent research funding 2014.

References

- 1 J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263–1264.
- 2 J. Robinson and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1979, **101**, 323–327.
- 3 J. Robinson, R. C. Bugle, H. L. Chum and D. Koran, *J. Am. Chem. Soc.*, 1979, **101**, 3776–3779.
- 4 N. W. N. Muhammad, Z. Omar, M. A. Man, S. Bustam, Y. Rafiq and Y. Uemura, *Ind. Eng. Chem. Res.*, 2012, **51**, 2280–2289.
- 5 F. Endres, *ChemPhysChem*, 2002, **3**, 144–154.
- 6 J. S. Wilkes and M. J. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965.
- 7 J. Dupout, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667–3692.
- 8 M. D. Zhou, J. Zhao, S. L. Zang and K. E. Fritz, *Chem.–Eur. J.*, 2007, **13**, 158–166.
- 9 M. D. Zhou, Y. Yu, S. L. Zang and K. E. Fritz, *Chem.–Asian J.*, 2009, **4**, 411–418.
- 10 J. Z. Yang, Y. Jin, W. G. Xu, Q. G. Zhang and S. L. Zang, *Fluid Phase Equilib.*, 2005, **227**, 41–46.
- 11 D. W. Fang, J. Tong, W. Guan, H. Wang and J. Z. Yang, *J. Phys. Chem. B*, 2010, **114**, 13808–13814.
- 12 J. Tong, Q. S. Liu, W. G. Xu, D. W. Fang and J. Z. Yang, *J. Phys. Chem. B*, 2008, **112**, 4381–4386.
- 13 D. W. Fang, X. J. Gu, Y. Xiong, S. Yue, J. Li and S. L. Zang, *J. Chem. Eng. Data*, 2010, **55**, 4440–4443.
- 14 L. Glasser, *Thermochim. Acta*, 2004, **421**, 87–93.
- 15 D. H. Zaitsau, G. J. Kabo, A. A. Strechan, Y. U. Paulechka, A. Tschersich, S. P. Verevkin and A. Heintz, *J. Phys. Chem. A*, 2006, **110**, 7303–7306.
- 16 J. Tong, H.-X. Yang, R.-J. Liu, C. Li, L. X. Xia and J.-Z. Yang, *J. Phys. Chem. B*, 2014, **118**, 12972–12978.
- 17 J. G. Huddleston, A. E. Visser, W. M. Reichert and H. D. Willauer, *Green Chem.*, 2001, **3**, 156–164.
- 18 D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 90th edn, 2010, pp. 1528–1529.
- 19 Z. F. Zhang, J. B. Li, J. Tong and J. Z. Yang, *Chin. J. Appl. Chem.*, 2009, **26**, 426–430.
- 20 D. W. Fang, W. Guan, J. Tong, Z. W. Wang and J. Z. Yang, *J. Phys. Chem. B*, 2008, **112**, 7499–7505.
- 21 J. M. Slattery, C. Daguenet, J. Paul, D. Thomas, J. S. Schubert and I. Krossing, *Angew. Chem., Int. Ed.*, 2007, **46**, 5384–5388.
- 22 J. Z. Yang, J. Tong, J. B. Li, J. G. Li and J. Tong, *J. Colloid Interface Sci.*, 2007, **313**, 374–377.
- 23 L. P. N. Rebelo, J. N. Canongia, J. M. S. S. Esperança and E. Filipe, *J. Phys. Chem. B*, 2005, **109**, 6040–6043.
- 24 K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.*, 2005, **127**, 2398–2399.
- 25 H. Ohno and K. Fukumoto, *Acc. Chem. Res.*, 2007, **40**, 1122–1129.
- 26 X.-X. Ma, J. Wei, Q.-B. Zhang, F. Tian, Y.-Y. Feng and W. Guan, *Ind. Eng. Chem. Res.*, 2013, **52**, 9490–9496.
- 27 M. Hong, S. Ao, L. Chun, W. Guan, J. Tong and J. Z. Yang, *Ind. Eng. Chem. Res.*, 2013, **52**, 15679–15683.
- 28 J. Tong, L. F. Wang and D. L. Liu, *J. Chem. Thermodyn.*, 2016, **97**, 221–227.
- 29 J. Z. Yang, X. M. Lu and J. S. Gui, *Green Chem.*, 2004, **6**, 541–543.
- 30 C. Larriba, Y. Yoshida and J. F. Mora, *J. Phys. Chem. B*, 2008, **112**, 12401–12407.
- 31 W. Beichel, Y. Yu, G. Dlubek, R. K. Rehberg, J. Pionteck, D. P. S. Bulut, D. Bejan, C. Friedrich and I. Krossing, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8821–8830.
- 32 R. J. Gale and R. A. Osteryoung, *Inorg. Chem.*, 1980, **19**, 2240–2242.
- 33 C. Daguenet, P. J. Dyson, I. Krossing, A. Oleinikova, J. Slattery, C. Wakai and H. Weingärtner, *J. Phys. Chem. B*, 2006, **110**, 12682–12688.
- 34 C. Wakai, A. Oleinikova, M. Ott and H. Weingärtner, *J. Phys. Chem. B*, 2005, **109**, 17028–17030.
- 35 J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, Reinhold, New York, 3rd edn, 1950.
- 36 T. I. Morrow and E. J. Maginn, *J. Phys. Chem. B*, 2002, **106**, 12807–12813.
- 37 A. A. Strechan, G. J. Kabo and Y. U. Paulechka, *Fluid Phase Equilib.*, 2006, **250**, 125–130.
- 38 D. D. Lawson, *Nature*, 1969, **223**, 614–615.
- 39 M. Deetlefs, K. R. Seddon and M. Shara, *Phys. Chem. Chem. Phys.*, 2006, **8**, 642–649.

