



Structure–property relationships in ionic liquids: Influence of branched and cyclic groups on vaporization enthalpies of imidazolium-based ILs



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ABSTRACT

Ionic liquids (ILs) with branched and cyclic substituents are seldom studied in the literature, and as such there are little to no data characterizing their thermophysical properties. ILs with branched and cyclic substituents are just as convenient to synthesize and study as their counterparts with linear substituents, but the effects of these substituents on IL properties are not yet well-defined due to the preference for linear substituents. Standard molar vaporization enthalpies of six imidazolium based ionic liquids [Rmim][NTf₂] with iso-alkyl and cyclic substituents (R = iso-propyl, iso-butyl, sec-butyl, methylcyclopropyl, cyclopentyl and methylcyclohexyl) were derived from quartz-crystal microbalance (QCM) method. Enthalpies of vaporization measured at elevated temperatures have been adjusted to the reference temperature 298 K and tested for consistency by comparison with the homomorphy alkane, alkyl-benzenes and alkyl-imidazoles. It was found that vaporization enthalpies of ILs with the iso-alkyl and cyclic groups are generally on the same level within (± 2 to 3) kJ · mol⁻¹ significantly compared to the analogous ILs with the imidazolium cation substituted with the linear alkyl substituents of the same chain length. These findings are useful for the quick estimation of vaporization enthalpies of various substituted IL cations (e.g. pyrrolidinium, ammonium, pyridinium, etc.).

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1. Introduction

The 1-(*n*-alkyl)-3-methylimidazolium ([C_{*n*}mim]) cation motif is highly prevalent within the ionic liquid (IL) literature, most likely due to the convenience and low cost of 1-methylimidazole and *n*-alkyl halides as starting materials [1]. However, ILs with ‘R’ groups composed of C and H atoms featuring branching, cycles and/or π -bonds are entirely feasible, but seldom considered [2–11]. As known from works with neutral molecules, branched or cyclic isomers can present significantly different thermophysical properties [12,13], and such differences between isomers are also expected within ILs. Many of the requisite precursors needed to synthesize such ILs (e.g. benzyl chloride, 2-bromopropane)

are readily available. Yet, interest in the effects of non-linear hydrocarbon substituents on imidazolium cations has been limited over the past 20 years.

While the lack of studies pertaining to characterization of ILs with branched or cyclic substituents has been obvious to those who have worked within the field for some time, in preparation of this manuscript, we became interested as to exactly what extent ILs with substituents that featured branching, cycles or π -bonds have been explored relative to their *n*-alkyl analogues. To attempt to quantify these trends, structural searches for various imidazolium cations with the bistriflimide ([NTf₂]) anion were performed using SciFinder™. Results for each IL of interest were further narrowed by removing patent references, since patents often tend to claim broad structural groups, but this does not necessarily mean that the compound(s) of interest was actually examined within the work leading to the patent. Based on these SciFinder™ structural searches carried out immediately prior to the submission of this article, we noted that that the vast majority of studies relating to imidazolium-based ILs with bistriflimide

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anions have focused on those with linear alkyl chains, rather than branched or cyclic groups. Table 1 presents a summary of our findings, which not only illustrate a large preference for *n*-alkyl chains, but also a significant bias for side groups that have an even number (i.e. 2, 4, 6, ...) of carbons.

It is quite clear from table 1 that there has been much more effort put into fundamental and applied studies using the [C_nmim][NTf₂] ILs than all of their other analogous derivatives combined. Thus, we see a need and opportunity to further explore the thermophysical properties and potential applications/advantages of ILs with non-linear hydrocarbon chains. Given that there are potentially over 10⁶ “simple” ILs that can be synthesized from readily available starting materials [14] and many times more when mixtures of ILs [15], the use of branched/cyclic groups as a means of tuning IL properties may be another useful tool to achieve desired performances.

In this work we measured vaporization enthalpies of six [Rmim][NTf₂] ILs with the iso-alkyl and cyclic substituents (R = iso-propyl, iso-butyl, sec-butyl, methylcyclopropyl, cyclopentyl and methylcyclohexyl, see figure 1) in order to assess influence of branching of the side alkyl chain on the imidazolium cation as well as introduction of cyclic alkyl moieties, containing three, five and six carbon atoms.

2. Materials and methods

2.1. Materials

[Rmim][NTf₂] (1 to 6) ILs were synthesized on ~10 g scales according to published procedures employed in our prior works (figure 1) [16,17]. LiNTf₂ was purchased from IoLiTec (Tuscaloosa, AL USA). All other reagents were purchased from Sigma-Aldrich (Milwaukee, WI USA) at the highest available purities. All solvents were obtained from the University of Alabama Chemistry Dept. stockroom at ACS grade.

The synthesis of the ILs proceeds via the methylation of a corresponding *N*-functionalized imidazole with the ‘R’ group of interest [16] in the presence of 2 eq. of iodomethane in CH₃CN at 40 °C in a sealed vessel. The reactions were allowed to proceed for at least 16 h, and were then cooled to ambient temperature and poured into cold Et₂O which resulted in the precipitation of the [Rmim][I] crude product. This solid was taken up in ~100 mL deionized H₂O and the aqueous phase was washed with 3 × 75 mL Et₂O. Subsequent ion-exchange was performed by adding 1.1 eq. of LiNTf₂ to the aqueous phase. The IL was observed to separate as an oily liquid that was more dense than the water phase. The mixture was allowed to stir for at least 3 h followed by extraction into CH₂Cl₂ and washing the organic phase with H₂O until absence of any residual iodide anion was confirmed via the lack of a precipitate formed when AgNO₃ was introduced into the aqueous wash. Two additional water washes were performed thereafter and the CH₂Cl₂ phase was dried over MgSO₄ and activated carbon and filtered through a plug of activated basic Al₂O₃. CH₂Cl₂ was removed via rotary evaporation and the IL products dried at 40 °C under dynamic vacuum (<15 Pa) for more than 24 h. ¹H NMR data for 1 to 6 and spectral images are provided as Supporting Information.

It is important to note that as reflected in table 1 by the asterisk (*) appended to the structure of IL 3, which features a *sec*-butyl group, that this IL does indeed contain a chiral center. However, for the purposes of analysis, this IL was treated a racemic mixture of the (R) and (S) stereoisomers as there is no evidence to suggest enrichment of one enantiomer or the other.

Prior to the vaporization experiments, the ILs were dried by vacuum evaporation at *T* = 333 K and 10⁻³ mbar for at least 24 h. IL samples were subjected to additional purification inside of the

experimental equipment in order to remove possible traces of volatile impurities. A summary of the IL samples is provided in table 2.

2.2. Measurements of vaporization enthalpies by the quartz crystalline microbalance (QCM)

The standard molar vaporization enthalpies of ILs were derived from the temperature dependent change of the vibrational frequency of the quartz crystal. The QCM was developed for measuring of compounds with the extremely low vapor pressures at temperatures possibly close to the ambient temperatures. Experimental procedure was tested with measurements on the homologous series of [C_nmim][NTf₂] ILs [18]. In the QCM method, a sample of an IL is placed in an open cavity (Langmuir evaporation) inside of the thermostatted block and it is exposed to vacuum (10⁻⁵ Pa). The quartz crystal is placed directly over the measuring cavity containing the sample. During the vaporization into vacuum, a certain amount of sample is deposited on the quartz crystal. The change of the vibrational frequency Δ*f* was directly related to the mass deposition Δ*m* on the crystal according to equation:

$$\Delta f = -C \cdot f^2 \cdot \Delta m \cdot S_C^{-1} \quad (1)$$

where *f* is the fundamental frequency of the crystal (6 MHz in this case) with Δ*f* ≪ *f*, *S_C* is the surface of the crystal, and *C* is a constant [19]. Using the frequency change rate *df/dt* measured by the QCM the molar enthalpy of vaporization, Δ₁^g*H*_m^o(*T*₀), is obtained by:

$$\ln \left(\frac{df}{dt} T^{1/2} \right) = A' - \frac{\Delta_1^g H_m^o(T_0) - \Delta_1^g C_{p,m}^o T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta_1^g C_{p,m}^o}{R} \times \ln \left(\frac{T}{T_0} \right) \quad (2)$$

where the constant *A'* is essentially unknown and includes all empirical parameters specific to the apparatus and the substance under study. *T*₀ appearing in equation (2) is an arbitrarily chosen reference temperature, which we have set to *T* = 298.15 K. The value Δ₁^g*C*_{p,m}^o = *C*_{p,m}^o(g) - *C*_{p,m}^o(l) is the difference between the molar heat capacities of the gaseous *C*_{p,m}^o(g) and the liquid phase *C*_{p,m}^o(l) respectively. The temperature dependent vaporization enthalpy Δ₁^g*H*_m^o(*T*) obtained from the QCM study is given by:

$$\Delta_1^g H_m^o(T) = \Delta_1^g H_m^o(T_0) + \Delta_1^g C_{p,m}^o(T - T_0) \quad (3)$$

In order to detect and avoid any possible effect of impurities on the measured frequency loss rate (*df/dt*), a typical experiment was performed in a few consequent series with increasing and decreasing temperature steps. Every step consisted of 7 to 11 points of mass loss rate determination at each temperature. Several runs have been performed to test the reproducibility of the results. The study was finished when the enthalpy of vaporization, Δ₁^g*H*_m^o(*T* = 298 K), obtained in the sequential runs by adjusting equation (2) to the temperature dependent rates (*df/dt*) agreed within the assessed experimental uncertainty of ±1 kJ · mol⁻¹. In order to confirm the absence of decomposition of IL under the experimental conditions, the residual IL in the crucible and the IL-deposit on QCM were analyzed by ATR-IR spectroscopy. No changes in the spectra have been detected. Primary experimental results of the QCM studies are provided in table S1 in the Supporting Information.

3. Results and discussion

The standard molar enthalpies of vaporization at *T*_{av} for the six ILs are presented in table 2. According to the common praxis, the enthalpies of vaporization Δ₁^g*H*_m^o(*T*_{av}) have to be adjusted to

TABLE 1
Structures of iso- and cyclic-functionalized imidazolium-based ILs. Those with bold names were studied in this work.

# C atoms in 'R' Group	[C _n mim] Cation	Other Selected Cations with the Same # of Carbons		
2				
	ethyl 1978 References	vinyl 6 References		
3				
	<i>n</i> -propyl 170 References	allyl 20 References	propargyl 6 References	iso-propyl 3 References
4				
	<i>n</i> -butyl 2311 References	iso-butyl 9 References	sec-butyl 0 References	methylcyclopropyl 0 References
5				
	<i>n</i> -pentyl 114 References	<i>neo</i> -pentyl 3 References	cyclopentyl 1 Reference	
6				
	<i>n</i> -hexyl 763 References	cyclohexyl 2 References		
7				
	<i>n</i> -heptyl 58 References	cycloheptyl 1 Reference	methylcyclohexyl 4 References	benzyl 44 References

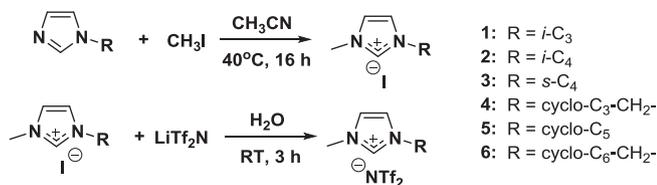


FIGURE 1. Synthesis of [Rmim][NTf₂] ILs (**1** to **6**).

the reference temperature 298.15 K. In our recent work [20], we suggested a simple $C_{p,m}^o(l)$ -based equation for estimation the $\Delta_l^g C_{p,m}^o$ -values:

$$\Delta_l^g C_{p,m}^o = -0.26 \times C_{p,m}^o(l) + 68.7 \quad (4)$$

This equation (4) was derived for the homologous series [C_nmim][NTf₂] with the linear alkyl chains and it should be also valid for the ILs (**1** to **6**) studied in this work, provided their $C_{p,m}^o(l)$ -values are available. However, only the liquid phase heat capacities for the linear ILs of this family can be found in the literature [21]. We used the latter values and re-calculated them to those for iso- and cyclic ILs (**1** to **6**) using the group-contribution method developed by Chickos [22], by exchanging of CH₂-fragments with

the appropriate groups (CH, cyclic CH₂ and CH) and derived the $C_{p,m}^o(l)$ -values for ILs (**1** to **6**) under study (see table 3). The $\Delta_l^g C_{p,m}^o$ -values calculated for ILs (**1** to **6**) with equation (4) (see table 3) have been used to adjust the $\Delta_l^g H_m^o(T_{av})$ to the reference temperature 298.15 K. Resulting values of $\Delta_l^g H_m^o(T=298.15 \text{ K})$ calculated according to equation (2) are given in the last column of table 3.

Temperature adjustments of experimental vaporization enthalpies to $T=298.15 \text{ K}$ is still subject of controversy disputation [20]. Thus, the very precise values of $\Delta_l^g H_m^o(T_{av})$ measured with uncertainty of $\pm 1.0 \text{ kJ} \cdot \text{mol}^{-1}$ should be less accurate at the reference temperature. Uncertainties of $\Delta_l^g C_{p,m}^o$ -values listed in table 3, column 7, have been assessed to be on the level of 15%. With this rigorous error quotation, the real uncertainties at $T=298.15 \text{ K}$ have been calculated (table 3, column 8).

In our recent work [20] we established that vaporization enthalpies in the family [C_nmim][NTf₂] with straight chains are linearly dependent on the alkyl chain length (see figure 2). For comparison, we also put the branched ILs studied in this work in the same plot. Surprisingly, it has turned out, that new data for branched ILs lie on the same line within their boundaries of experimental uncertainties of $(\pm 1.5 \text{ to } 2.0) \text{ kJ} \cdot \text{mol}^{-1}$.

This finding facilitates prediction of vaporization enthalpies in general, because the equation developed for the chain length

TABLE 2
Provenance and purity of the materials.

Chemical name	Source	Initial mole fraction purity	Purification method	Final mole fraction purity ^g	Analysis method
[i-C ₃ mim][NTf ₂] ^a	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR
[i-C ₄ mim][NTf ₂] ^b	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR
[s-C ₄ mim][NTf ₂] ^c	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR
[cyclo-C ₃ -CH ₂ -mim][NTf ₂] ^d	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR
[cyclo-C ₅ mim][NTf ₂] ^e	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR
[cyclo-C ₆ -CH ₂ -mim][NTf ₂] ^f	Synthesis	0.95	Vacuum drying	>0.95	¹ H NMR

^a 1-methyl-3-(1-methylethyl)-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^b 1-methyl-3-(2-methylpropyl)-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^c 1-methyl-3-(1-methylpropyl)-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^d 1-methyl-3-cyclopropylmethyl-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^e 1-methyl-3-cyclopentyl-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^f 1-methyl-3-cyclohexylmethyl-1*H*-imidazolium bis(trifluoromethane)sulfonimide.^g Given the large MW of the ILs (>400 g · mol⁻¹) a mole fraction purity of >95% (based on uncertainty in ¹H NMR signal) corresponds to a mass fraction purity > 99%.**TABLE 3**
Standard molar enthalpies of vaporization for branched [C_nmim][NTf₂] family derived from QCM.

1	IL	T-range K	T _{av} ^a	Δ _l ^g H _m ^o (T _{av}) ^b kJ · mol ⁻¹	C _{p,m} ^o (l) ^c J · K ⁻¹ · mol ⁻¹	Δ _l ^g C _{p,m} ^o ^d	Δ _l ^g H _m ^o (T = 298.15 K) ^f kJ · mol ⁻¹
2	3	4	5	6	7	8	
1	[i-C ₃ mim][NTf ₂]	343.3 to 390.4	366.3	123.3 ± 1.0	529.9	-69.1	128.0 ± 1.4
2	[i-C ₄ mim][NTf ₂]	345.4 to 393.0	368.7	126.0 ± 1.0	557.1	-76.1	131.4 ± 1.6
3	[s-C ₄ mim][NTf ₂]	345.7 to 392.9	368.6	123.0 ± 1.0	557.1	-76.1	128.4 ± 1.6
4	[cyclo-C ₃ -CH ₂ -mim][NTf ₂]	350.2 to 398.0	373.5	126.5 ± 1.0	539.1	-71.5	131.9 ± 1.6
5	[cyclo-C ₅ -mim][NTf ₂]	350.7 to 398.1	373.7	127.4 ± 1.0	560.6	-77.1	133.3 ± 1.8
6	[cyclo-C ₆ -CH ₂ -mim][NTf ₂]	360.2 to 408.1	383.6	134.1 ± 1.0	617.1	-91.7	142.0 ± 2.4

^a The standard uncertainty of the temperature determination is u(T) = 0.05 K.^b Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence).^c Calculated from the experimental data for linear species (see text).^d Calculated with equation (4) using C_{p,m}^o(l) – values from column 6, the expanded uncertainty (0.95 level of confidence) for this value is estimated at level of U = 0.2 Δ_l^gC_{p,m}^o.^f Calculated with equation (3) using Δ_l^gC_{p,m}^o – values from column 7, the expanded uncertainty (0.95 confidence level) was applied.dependence in our previous work for linear species of the [C_nmim][NTf₂] family

$$\Delta_{l}^{\text{g}}H_{\text{m}}^{\text{o}}(T = 298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = (3.9 \pm 0.2) \times N_{\text{C}} + 115.7 \text{ with } R^2 = 0.995 \quad (5)$$

can be now also used for estimation (within ±1.5 to 2.0 kJ · mol⁻¹) of vaporization enthalpies regardless on the branching of alkyl chain. However, the application of equation (5) for assessment of Δ_l^gH_m^o(T = 298.15 K) is restricted only with the *secondary* branching and also with alkyl chains without heteroatoms. Data on the ILs with a *tertiary* alkyl (e.g. *t*-butyl) substituted imidazolium cation are absent yet in order to propagate equation (5) on this kind of branching.

It is well established for the *molecular solvents*, that the degree of branching decreases the vaporization enthalpy. For example, the typical increments for estimation of vaporization enthalpy in their order of branching are as follows: CH₃(C) = 5.65 kJ · mol⁻¹, CH₂(C)₂ = 4.98 kJ · mol⁻¹, and CH(C)₃ = 3.00 kJ · mol⁻¹ [23]. Is there any explanation for similarity of vaporization enthalpies of the linear and branched *ionic liquids* demonstrated in figure 2 in contrast to the distinct differences in *molecular solvents*? In order to answer this question we collected similarly shaped alkanes and alkylbenzenes (see table 4) as well as alkyl-imidazoles (see table 5) with alkyl chains identical for the branched ILs (1 to 6) studied in this work. Such series of compounds are called homomorphs [24]. Enthalpies of vaporization of the molecular compounds listed in tables 3 and 4 are more accurate in comparison to ILs (table 3) and less affected with the temperature adjustments to 298.15 K. Thus, comparison with these data sets can reveal structure–property relations in the branched ILs (1 to 6) more definite, than comparison with the [C_nmim][NTf₂] family in figure 2. Graphical comparison for all three pairs of homomorphs is given in figure

3. For all three series a good linear correlation of vaporization enthalpies show, that the ILs studied in this work follow the same pattern of branching as in the molecular solvents and the ILs do sensitive to the degree of branching, however combined uncertainties of data presented in figure 2 conceal the differences, which are

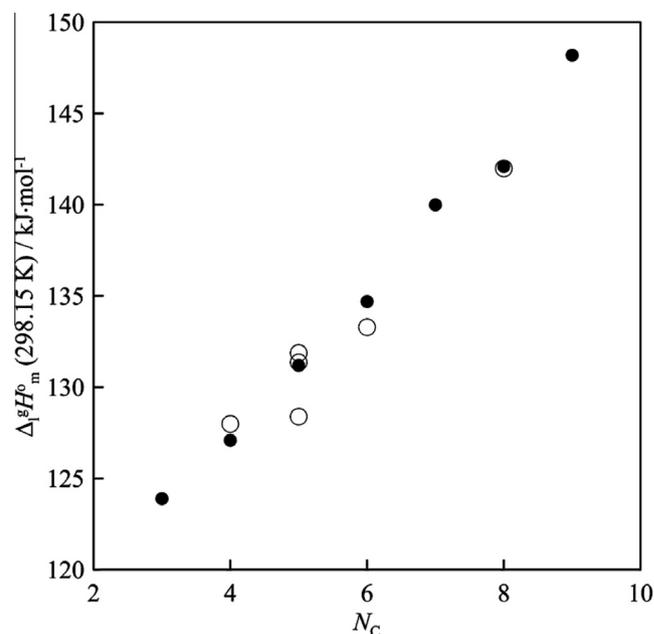
**FIGURE 2.** Vaporization enthalpies for the family [C_nmim][NTf₂] as the chain length dependence (N_C is the total number of all C-containing units present in the imidazolium cation in the 1 and 3 positions) ● – series with the straight chain [20], ○ – series with the branched chain.

TABLE 4

Experimental vaporization enthalpies of selected alkanes and alkylbenzenes, used as homomorphs for comparison with ILs (in $\text{kJ} \cdot \text{mol}^{-1}$).

	Reference [13]	$\Delta_1^{\text{g}}H_m^{\circ}$ (T = 298.15 K)	Reference [26]	$\Delta_1^{\text{g}}H_m^{\circ}$ (T = 298.15 K)
1	Isobutane	20.0 ± 0.2	Iso-propylbenzene	45.2 ± 0.2
2	2-methylbutane	25.2 ± 0.2	Iso-butylbenzene	47.9 ± 0.2
3	2-methylbutane	25.2 ± 0.2	Sec-butylbenzene	48.5 ± 0.2
4	Ethyl-cyclopropane	26.2 ± 0.5	Cyclo-propyl-methylbenzene [1667-00-1]	52.4 ± 0.5
5	Methyl-cyclopentane	31.8 ± 0.2	Cyclo-pentylbenzene [700-88-9]	56.3 ± 0.5
6	Ethyl-cyclohexane	40.6 ± 0.4	Cyclo-hexyl-methylbenzene [4410-75-7]	67.4 ± 0.5

^a Uncertainties of vaporization enthalpies are presented as standard deviations.

TABLE 5

Experimental vaporization enthalpies of selected alkylimidazoles, used as homomorphs for comparison with ILs (in $\text{kJ} \cdot \text{mol}^{-1}$).

	Reference [25]	$\Delta_1^{\text{g}}H_m^{\circ}$ (T = 298.15 K)
1	N-iso-propylimidazole [4532-96-1]	58.4 ± 0.3
2	N-iso-butylimidazole [16245-89-9]	62.2 ± 0.3
3	N-sec-butylimidazole [20075-29-0]	64.6 ± 0.3
4	N-cyclo-propyl-methylimidazole [717908-74-2]	59.8 ± 0.3
5	N-cyclo-pentylimidazole [71614-58-9]	70.6 ± 0.5
6	N-cyclo-hexyl-methylimidazole [71621-00-6]	77.5 ± 0.4

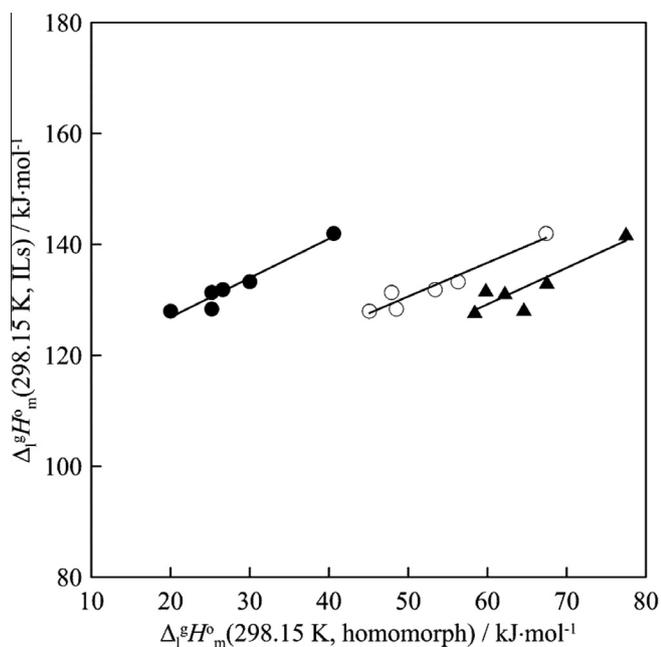
^a Uncertainties of vaporization enthalpies are presented as standard deviations.

FIGURE 3. Comparison of vaporization enthalpies for branched substituted ILs $[\text{C}_n\text{mim}][\text{NTf}_2]$ (y-axis) with the vaporization enthalpies of the homomorph series (x-axis): ● – branched alkanes (see table 3); ○ – branched alkyl-benzenes (see table 3); ▲ – branched alkyl-imidazoles (see table 4).

below $2 \text{ kJ} \cdot \text{mol}^{-1}$. Especially interesting correlation between enthalpies of vaporization of alkyl-imidazoles served as precursors for synthesis of ILs (**1** to **6**) and those for ILs themselves. The correlation (see figure 3) is not perfect with ($R^2 = 0.93$), but such correlation is sufficiently good to suggest similarity of group-contributions required for prediction vaporization enthalpy in the alkyl-imidazoles and in the similarly shaped branched ILs [25].

Summing up, for technically important rough calculations $\Delta_1^{\text{g}}H_m^{\circ}$ (T = 298.15 K) – values of the branched ILs similar to those studied in this work could be assessed within (2 to 3) $\text{kJ} \cdot \text{mol}^{-1}$ with help of general equation (5). More detailed understanding of structure

property relationship in branched ILs can be achieved with help of experimental data measured in this work (see table 3). This knowledge could be useful for quick appraisal of vaporization enthalpies for pyrrolidinium, pyridinium, and ammonium based ILs with linear and branched alkyl chains.

4. Conclusions

New experimental vaporization enthalpies of six ILs with branched/cyclic functionalities from the $[\text{Rmim}][\text{NTf}_2]$ family were measured by the QCM method. The enthalpies of vaporization measured for these ILs with branched/cyclic functionalities are nearly identical to those previously measured for analogous $[\text{C}_n\text{-mim}][\text{NTf}_2]$ ILs with the same number of carbon in the side group. These results were adjusted to the reference temperature 298.15 K and tested for consistency. New experimental data are useful for the quick estimation of vaporization enthalpies of ILs with branching of the alkyl chain. It seems to be that similarity of vaporization enthalpies between branched and not branched ILs (except for quaternary branching) could be expected for various substituted IL cations (e.g. pyrrolidinium, ammonium, pyridinium, etc.) connected to another anions (e.g. sulfates, triflates, halides, dicyanoamide, etc.)

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Appendix A. Supplementary data

¹H NMR data and spectra for **1** to **6**. Table with the primary QCM data. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2015.09.033>.

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