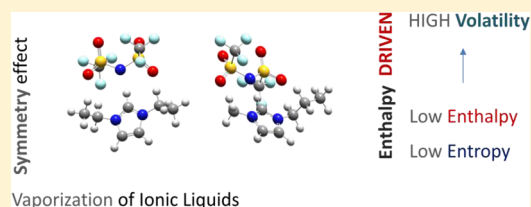


Cation Symmetry effect on the Volatility of Ionic Liquids

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S Supporting Information

ABSTRACT: This work reports the first data for the vapor pressures at several temperatures of the ionic liquids, $[C_{N/2}C_{N/2}im][NTf_2]$ ($N = 4, 6, 8, 10, 12$) measured using a Knudsen effusion apparatus combined with a quartz crystal microbalance. The morphology and the thermodynamic parameters of vaporization derived from the vapor pressures, are compared with those for the 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide series, $[C_{N-1}C_1im][NTf_2]$ ($N = 3 - 9, 11, \text{ and } 13$). It was found that the volatility of $[C_{N/2}C_{N/2}im][NTf_2]$ series is significantly higher than the asymmetric cation ILs with the same total number of carbons in the alkyl side chains, $[C_{N-1}C_1im][NTf_2]$. The observed higher volatility is related with the lower enthalpy of vaporization. The symmetric cation, $[C_{N/2}C_{N/2}im][NTf_2]$, presents lower entropies of vaporization compared with the asymmetric $[C_{N-1}C_1im][NTf_2]$, indicating an increase of the absolute liquid entropy in the symmetric cation ILs, being a reflection of a change of the ion dynamics in the IL liquid phase. Moreover both the enthalpy and entropy of vaporization of the $[C_{N/2}C_{N/2}im][NTf_2]$ ILs, present a clear odd–even effect with higher enthalpies/entropies of vaporization for the odd number of carbons in each alkyl chain ($[C_3C_3im][NTf_2]$ and $[C_5C_5im][NTf_2]$).



1. INTRODUCTION

Since 2001, room temperature ionic liquids, RTILs, have gained popularity, mainly because of their particular properties.¹ The research in these systems have been performed in a fundamental and applied way, contributing to a better understanding at a molecular level and consequently to an advance in the applied field of the ionic liquids.^{2–5} For the interpretation of their properties and a successful modeling of ionic liquids, highly accurate data regarding these physicochemical properties are needed, such as heat capacities, vapor pressures, viscosities, densities, refractive index, etc.

Volatility of ionic liquids has been a topic of several studies, to determine their vapor pressures or enthalpies of vaporization with accuracy. Accurate thermodynamic parameters, of liquid–vapor equilibrium, are not only important to provide information on the liquid phase structure and cohesive energy, and the nature of the vapor phase, but are also essential to validate force-fields models used in several simulation techniques to describe ionic liquids.^{2,3}

Earle et al. reported the first measurements of the volatility of some ILs, showing that many ionic liquids can be distilled at low pressure without decomposition.⁶ Since then, a number of works addressing vapor pressure measurements and measurements/predictions of enthalpies of vaporization have emerged. Several approaches to measuring and predicting these quantities have been proposed, including molecular dynamics simulations.⁷ Experimental determinations have been carried out by the integral Knudsen effusion method,^{8,9} Knudsen effusion method combined with a quartz crystal microbalance,¹⁰ quartz crystal microbalance method,¹¹ transpiration method,¹²

mass spectrometry,^{13–16} vacuum vaporization drop microcalorimetry,¹⁷ and thermogravimetry.¹⁸

Recently, we reported a thermodynamic study concerning the vaporization of the extended series of ILs $[C_{N-1}C_1im][NTf_2]$ (with $N = 3–9, 11, \text{ and } 13$), where the trends of the thermodynamic parameters of vaporization with the alkyl chain length were established.¹⁰ In this work it was shown that the enthalpy and entropy of vaporization presented trend shifts along the $[C_{N-1}C_1im][NTf_2]$ series, related to a change in the molecular structure of the liquid phase around $[C_6C_1im][NTf_2]$.^{10,19} It is well-known today that ILs are nanostructured fluids in which the ion pairs arrange themselves into polar and nonpolar domains. The structural segregation on these systems will depend on the size of the polar and nonpolar regions in each ion may exist as dispersed or continuous microphases. The transition between these two states depends on the relative size of the high-charge and low-charge regions in each ion and the size of the alkyl chain length.¹⁹ In this previous work, it was possible to highlight the effect of the nanoscale-organization of $[C_{N-1}C_1im][NTf_2]$ family, on the thermodynamic properties of vaporization and viscosity.^{10,20} On another recent work by us the effect of the nanoscale-organization on the heat capacities was also presented.²¹

The symmetry of the cation provides a different structural organization which can be used to tune the physicochemical properties of the ionic liquids. Xiao et al.,²² based on small-

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wide-angle X-ray scattering (SWAXS) data and optical Kerr effect (OKE) spectra, found that the symmetric ILs series, $[C_{N/2}C_{N/2}im][NTf_2]$, presents higher local order and higher intermolecular dynamics in frequency than the asymmetric series, $[C_{N-1}C_1im][NTf_2]$. SWAXS measurements provide information related with the structural heterogeneities in ILs. On the basis of this data, Zheng et al.²³ found that, for the asymmetric imidazolium based ILs, the structural heterogeneities take place over a large spatial scale, comparing with the results obtained for the symmetric ILs. In the same work, the authors observed that the densities for a symmetric/asymmetric IL pair, with a given total number carbons, are similar and the viscosity of the asymmetric IL is greater than the observed for the symmetric ILs. Also, it was observed an odd–even effect on the viscosity data, similar to what it was found in simulations of the ion diffusion coefficients.

In the present work, the thermodynamic properties of vaporization of 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide series, $[C_{N/2}C_{N/2}im][NTf_2]$ ($N = 4, 6, 8, 10, 12$) are compared to those of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide series, $[C_{N-1}C_1im][NTf_2]$ ($N = 3 - 9, 11$ and 13). The vapor pressures at several temperatures of the ILs series, $[C_{N/2}C_{N/2}im][NTf_2]$, were measured by the Knudsen effusion apparatus combined with a quartz crystal microbalance.²⁴ Based on the previous results, the standard molar enthalpies, entropies and Gibbs energies of vaporization were derived at the reference temperature, $T = 298.15$ K. This work aims to explore the enthalpic and entropic contribution to the volatility of the symmetric $[C_{N/2}C_{N/2}im][NTf_2]$ and to assess the effect of the cation topological symmetry on the liquid–vapor equilibrium. The schematic representation of the considered imidazolium based ionic liquids, are presented in Figure 1.

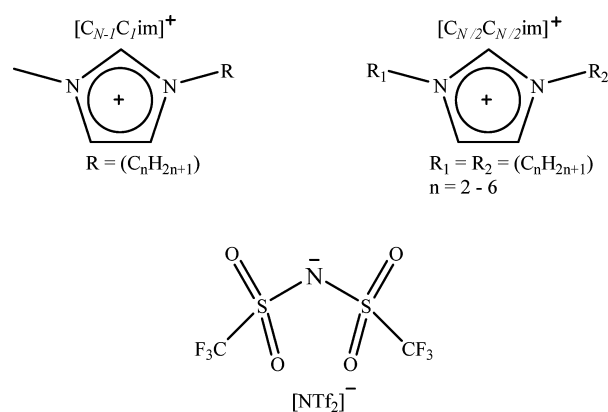


Figure 1. Schematic representation of the imidazolium based ionic liquids, where N corresponds to the total number of carbons in the two alkyl side chains in the cation.

2. EXPERIMENTAL SECTION

2.1. Purification and Characterization of Compounds.

The ionic liquids used in this work, the 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide series, $[C_{N/2}C_{N/2}im][NTf_2]$ ($N = 4, 6, 8, 10, 12$), were purchased from IOLITEC with a stated purity of better than 98%. All the ionic liquids were dried under reduced pressure (<10 Pa) and stirred constantly for a minimum of 72 h at 373 K, in order to reduce the presence of water or other volatile contents. Karl Fischer titration of the

degassed samples revealed less than 100 ppm of water. The purity of each ionic liquid after purification was further evaluated by 1H , ^{13}C , and ^{19}F NMR spectra and for all ionic liquids the mass fraction was found to be >0.99 .

2.2. Quartz Crystal Microbalance Knudsen Effusion Apparatus.

The vapor pressure of each ionic liquid was measured as a function of temperature using a new Knudsen effusion apparatus combined with a quartz crystal microbalance, KEQCM, recently described in the literature.²⁴ This apparatus comprises two mass loss detection techniques, gravimetric, and quartz crystal microbalance, which enables the decrease of effusion times and the sample size. Furthermore the combination of two mass loss determination techniques permits the instrument to measure vapor pressures from 0.005 Pa up to 1 Pa. For the measurements of pressures below 0.01 Pa, a flow-concentrator device, placed between the oven and the quartz crystal, was used.²⁵ The temperature step effusion procedure allows for vapor pressure measurements at different temperatures in a single experiment and it can reach temperatures up to 650 K. The temperature is controlled within a temperature fluctuation of $\pm (1 \times 10^{-2})$ K, measured with a resolution better than 1×10^{-3} K and with an overall uncertainty better than $\pm (2 \times 10^{-2})$ K along the entire working temperature range. The vapor pressure data obtained with this apparatus for the ionic liquid samples, presents a pressure dependent uncertainty between (1 and 5) %, that is the typical uncertainty obtained in this apparatus using this methodology.²⁴ Due to the low volatility of the ionic liquids, the vapor pressure range under 0.05 Pa was explored in some cases, but below this pressure and for a particular individual experimental point, the relative uncertainty increases dramatically exceeding the indicated interval. The claimed uncertainty is done based on the overall results obtained from the fitting of the Clarke and Glew equation and is valid for the middle of the experimental pT region.

Like a typical Knudsen effusion experiment, the system is kept at high vacuum, allowing free effusion of the vapor from the cell, and at a fixed temperature, T . During an effusion experiment, the mass loss rate from the effusion cell, $dm(\text{cell})/dt$, is proportional to the rate of change of the mass deposited on the quartz crystal, dm/dt , according to eq 1

$$\frac{dm(\text{cell})}{dt} = -g \times \frac{dm}{dt} = -g \times \frac{A_q}{S_q} \times \left(\frac{df}{dt}\right) \quad (1)$$

where g is a geometric factor of the mass detection, A_q is the area of the quartz crystal, S_q is the mass sensitivity of the crystal, and (df/dt) is the rate of change of the resonance frequency of the quartz crystal. Taking into account that

$$W = -\frac{S_q}{A_q \times g} \quad (2)$$

where, W , is the effective mass sensitivity coefficient, the eq 1 becomes

$$\left(\frac{df}{dt}\right) = W \times \left(\frac{dm(\text{cell})}{dt}\right) \quad (3)$$

To derive the vapor pressure, the value, W , must be known for each studied compound. The value can be determined by weighing the total mass loss of the effusion cell, $\Delta m(\text{cell})$, during an independent experiment, and considering the integrated form of the eq 3

$$W = \frac{\Delta f}{\Delta m(\text{cell})} \quad (4)$$

where Δf is the total change in the crystal's resonance frequency during the experiment.

The equilibrium vapor pressure of the liquid compound is obtained using the following eq 5:

$$p = \left(\frac{df}{dt}\right) \times \left(\frac{1}{w_o A_o W}\right) \times \left(\frac{2\pi RT}{M}\right)^{1/2} \quad (5)$$

where M is the molar mass of the sample, R is the gas constant ($R = 8.3144621 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), A_o is the area of the orifice, and w_o is the transmission probability factor ($w_o = \{1 + (l/2r)\}^{-1}$). The relative atomic masses used were those recommended by the IUPAC Commission in 2007.²⁶

3. RESULTS AND DISCUSSION

The vapor pressures for the studied imidazolium based ionic liquids ($[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$, $N = 4, 6, 8, 10, 12$), were measured at several temperatures, using the Knudsen effusion apparatus combined with a quartz crystal microbalance. The experimental vapor pressures data for each IL, are listed in Table S1 of the Supporting Information.

Figure 2, presents the $\ln(p/\text{Pa}) = f(K/T)$ plots for the experimental results obtained for the studied ILs.

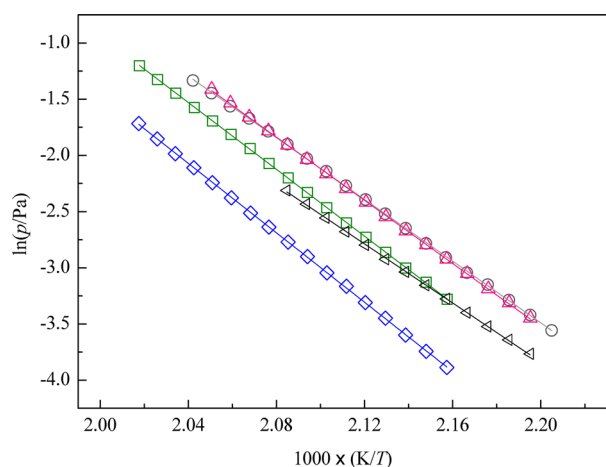


Figure 2. Plot of $\ln(p/\text{Pa}) = f(K/T)$ for each studied ionic liquid: black triangle, $[\text{C}_2\text{C}_2\text{im}][\text{NTf}_2]$; gray circle, $[\text{C}_3\text{C}_3\text{im}][\text{NTf}_2]$; pink triangle, $[\text{C}_4\text{C}_4\text{im}][\text{NTf}_2]$; green square, $[\text{C}_5\text{C}_5\text{im}][\text{NTf}_2]$; blue diamond, $[\text{C}_6\text{C}_6\text{im}][\text{NTf}_2]$.

The experimental results of the vapor pressures were fitted by the Clarke and Glew eq 6²⁷

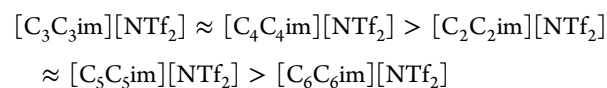
$$R \ln \frac{p}{p^\circ} = -\frac{\Delta_1^\ddagger G_m^\circ(\theta)}{\theta} + \Delta_1^\ddagger H_m^\circ(\theta) \left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_1^\ddagger C_{p,m}^\circ \left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (6)$$

where p is the vapor pressure, p° is a selected reference pressure ($p^\circ = 10^5 \text{ Pa}$), θ is a selected reference temperature, R is the gas constant ($R = 8.3144621 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), $\Delta_1^\ddagger G_m^\circ$ is the standard molar Gibbs energy of vaporization at the selected reference pressure, $\Delta_1^\ddagger H_m^\circ$ is the standard molar enthalpy of vaporization, and $\Delta_1^\ddagger C_{p,m}^\circ$ is the difference between the heat capacities of the gaseous and of the liquid phases [$\Delta_1^\ddagger G_{p,m}^\circ = C_{p,m}^\circ(\text{g}) - C_{p,m}^\circ(\text{l})$].

The values of $\Delta_1^\ddagger C_{p,m}^\circ$ were estimated considering the same temperature for all the ILs, $T = 388 \text{ K}$ (mean temperature between the average temperature and 298.15 K) using a procedure recently proposed in the literature.¹⁰ Table 1 presents the derived standard ($p^\circ = 10^5 \text{ Pa}$) molar enthalpies, entropies, and Gibbs energies of vaporization at the mean temperature, $\langle T \rangle$, at $T = 460.0 \text{ K}$ and at reference temperature, $T = 298.15 \text{ K}$, as derived from the fitting of eq 6 and related to each other by the following eq 7:

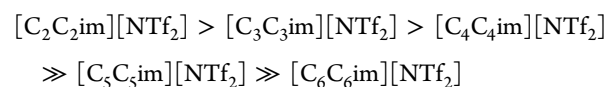
$$\Delta_1^\ddagger G_m^\circ(T) = -RT \ln \left[\frac{p(T)}{p^\circ} \right] = \Delta_1^\ddagger H_m^\circ(T) - T \Delta_1^\ddagger S_m^\circ(T) \quad (7)$$

The graphic representations of standard molar Gibbs energy of vaporization at reference temperature (460 and 298.15 K) as a function of total number of carbon atoms in the two alkyl side chains of the cation, N are presented in figure 3. At the temperature of 460 K , the following order of volatility for the studied series was found:



The $[\text{C}_2\text{C}_2\text{im}][\text{NTf}_2]$ is an exception within this sequence, showing a lower volatility than $[\text{C}_3\text{C}_3\text{im}][\text{NTf}_2]$ and $[\text{C}_4\text{C}_4\text{im}][\text{NTf}_2]$. This is the typical outlier behavior observed before for the ILs with a short alkyl chain length (e.g., $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$),¹⁰ that can be explained based on the stronger polar interactions contribution observed in the border members (methyl, ethyl) of the alkyl series.

Taking into account the estimated volatility at 298.15 K depicted in Figure 3 panel II, a slightly change in the volatility order arising from the differentiation effect of the enthalpies of vaporization, and in smaller scale from the $\Delta_1^\ddagger C_{p,m}^\circ$ correction to the volatility, that leads to a crossover of the pressure to temperature dependence along the series was identified. At 298.15 K , the estimated following order of volatility was derived:



In Figure 3 panel II, the derived standard molar Gibbs energies of vaporization, at $T = 298.15 \text{ K}$, of the studied ILs and the asymmetric ILs, $[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$, are compared.¹⁰ It can be observed that the volatility of $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$ is significantly higher than the asymmetric cation ILs with the same total number of carbons in the alkyl side chains, $[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$. At reference temperature, 298.15 K , the $[\text{C}_2\text{C}_2\text{im}][\text{NTf}_2]$ presents the highest volatility ever observed for the alkyimidazolium bis(trifluoromethylsulfonyl)imide based ionic liquids.

Unlike what happens for the asymmetric ILs series, which presents in one of the nitrogens of the imidazolium a methyl group and in the other an alkyl side chain of increasing length, the symmetric ILs presents a simultaneous increase of the two alkyl side chains. The existence of a permanent methyl group in the imidazolium ring, in the asymmetric ILs series, enhances their electrostatic interactions between the cations and anions which affects the charge distribution and accessibility as well as the dynamics, increasing in this way their interaction potential. The standard molar enthalpies of vaporization, $\Delta_1^\ddagger H_m^\circ$ (298.15

Table 1. Parameters of Clarke and Glew Equation Fitted from the Vapor Pressure Results and the Derived Standard Molar Entropy of Vaporization for Each Studied IL at the Reference Temperature, θ , and at the Standard Pressure, $p^\circ = 10^5$ Pa

T interval/K	θ /K	$\Delta_f^\ddagger C_m^\circ(\theta)/\text{J}\cdot\text{mol}^{-1}$	$\Delta_f^\ddagger H_m^\circ(\theta)/\text{J}\cdot\text{mol}^{-1}$	$\Delta_f^\ddagger S_m^\circ(\theta)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	r^2	$\Delta_f^\ddagger C_{p,m}^\circ(T = 388 \text{ K})/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
[C ₂ C ₂ im][NTf ₂]						
455–480	467.61 ^a	56539 ± 654	109212 ± 462	111.7 ± 1.0	0.9998	−117 ^b
	460.00	57404 ± 651	110102 ± 464	114.6 ± 1.0		
	298.15	79755 ± 1212	129038 ± 965	165.3 ± 2.5		
[C ₃ C ₃ im][NTf ₂]						
453–490	471.60 ^a	54529 ± 444	114013 ± 314	126.1 ± 0.7	0.9999	−127 ^b
	460.00	56010 ± 446	115487 ± 319	129.3 ± 0.7		
	298.15	81073 ± 1165	136041 ± 922	184.4 ± 2.4		
[C ₄ C ₄ im][NTf ₂]						
455–488	471.58 ^a	54564 ± 529	116836 ± 374	132.0 ± 0.8	0.9998	−138 ^b
	460.00	56113 ± 529	118434 ± 378	135.5 ± 0.8		
	298.15	82534 ± 1189	140769 ± 944	195.3 ± 2.4		
[C ₅ C ₅ im][NTf ₂]						
463–496	479.54 ^a	54675 ± 290	123575 ± 205	143.7 ± 0.4	0.9999	−149 ^b
	460.00	57543 ± 316	126486 ± 227	149.9 ± 0.5		
	298.15	86652 ± 1176	150602 ± 930	214.5 ± 2.4		
[C ₆ C ₆ im][NTf ₂]						
463–496	479.60 ^a	56928 ± 354	138362 ± 250	148.9 ± 0.5	0.9999	−160 ^b
	460.00	59912 ± 373	131498 ± 269	155.6 ± 0.6		
	298.15	90310 ± 1188	157394 ± 941	225.0 ± 2.4		

^aMean experimental temperature. r^2 is the linear regression coefficient. ^b $\Delta_f^\ddagger C_{p,m}^\circ(388 \text{ K})$ estimated using the linear fitted function ($\Delta_f^\ddagger C_{p,m}^\circ/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = -5.40 n(\text{C}) - 100.47$). ¹⁰ An uncertainty of $\pm 5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was considered for the $\Delta_f^\ddagger C_{p,m}^\circ$.

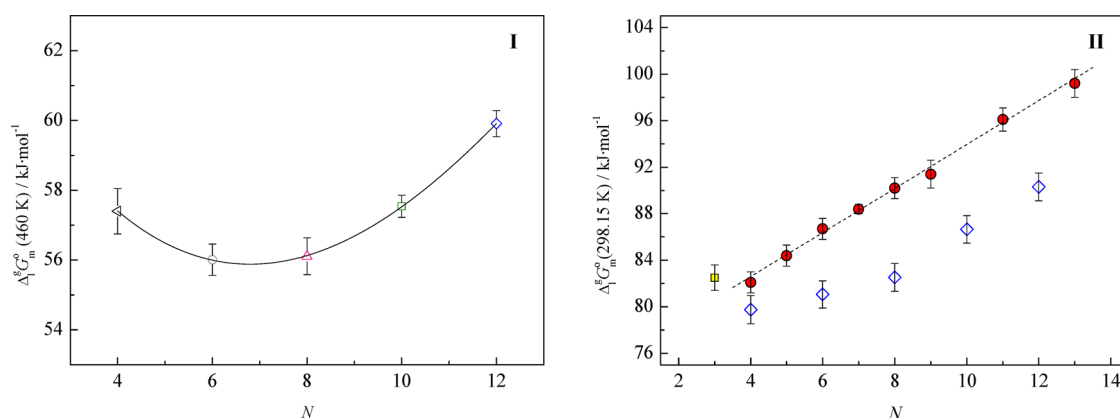


Figure 3. Graphic representation of standard molar Gibbs energy of vaporization at reference temperature as a function of total number of carbon atoms in the two alkyl side chains of the cation, N . (I) $\Delta_f^\ddagger G_m^\circ(460 \text{ K})$: black triangle, [C₂C₂im][NTf₂]; gray circle, [C₃C₃im][NTf₂]; pink triangle, [C₄C₄im][NTf₂]; green square, [C₅C₅im][NTf₂]; blue diamond, [C₆C₆im][NTf₂]; (II) $\Delta_f^\ddagger G_m^\circ(298.15 \text{ K})$: yellow square and red circle, [C_{*N*-1}C_{*i*}im][NTf₂];¹⁰ blue diamond, [C_{*N*/2}C_{*N*/2}im][NTf₂].

K), as a function of the total number of the alkyl side chains of the cation, N , for the studied compounds ([C_{*N*/2}C_{*N*/2}im][NTf₂]) is presented in Figure 4 and compared with the previous data for the [C_{*N*-1}C_{*i*}im][NTf₂] series.

In the previous work on the asymmetric imidazolium ILs series, [C_{*N*-1}C_{*i*}im][NTf₂], an enthalpic and entropic trend shift was observed with the increase of the cation alkyl chain length, is related to a change in the molecular structure of the liquid phase around [C₆C_{*i*}im][NTf₂].^{10,19} The symmetry of the IL cation changes dramatically the thermodynamic vaporization parameters. The enthalpies of vaporization are lower for the symmetric [C_{*N*/2}C_{*N*/2}im][NTf₂] than for the asymmetric imidazolium ILs, [C_{*N*-1}C_{*i*}im][NTf₂], indicating a decrease of the polar interactions in the symmetric imidazolium ILs. Moreover the vaporization results of the [C_{*N*/2}C_{*N*/2}im][NTf₂] ILs, show an enthalpic differentiation with a clearly discernible odd–even effect with higher enthalpies of vaporization for the

odd numbered [C₃C₃im][NTf₂] and [C₅C₅im][NTf₂]. An odd–even effect was also reported in the viscosity data for the same ILs series and is also consistent with the solid phase crystallization behavior, recently published.²³ The odd numbered ILs, which presents higher enthalpies of vaporization, show also higher viscosities in agreement with the observed increase of their cohesive energies.²³

The standard molar entropies of vaporization, $\Delta_f^\ddagger S_m^\circ(298.15 \text{ K})$, as a function of the total number of the alkyl side chains of the cation, N , for the studied compounds ([C_{*N*/2}C_{*N*/2}im][NTf₂]) is presented in figure 5 and compared with the data for the [C_{*N*-1}C_{*i*}im][NTf₂] series.

Similarly to what was observed for the enthalpies of vaporization, a differentiation between the asymmetric and symmetric ILs series, was found. The ILs with symmetric cations, [C_{*N*/2}C_{*N*/2}im][NTf₂], present lower entropies of vaporization compared with the asymmetric imidazolium,

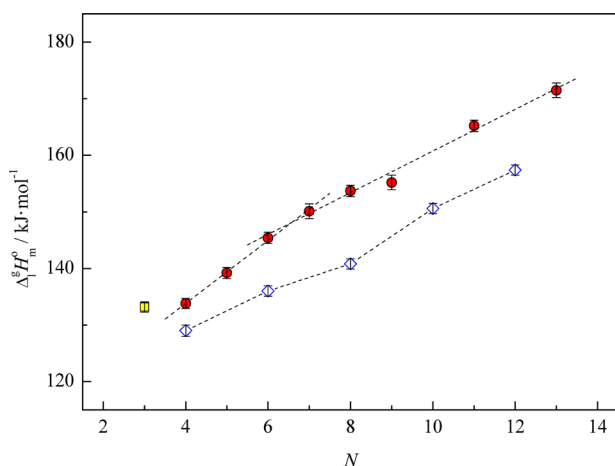


Figure 4. Graphic representation of standard molar enthalpy of vaporization at reference temperature ($T = 298.15\text{K}$) as a function of the total number of carbon atoms in the alkyl side chains of the cation, N . Yellow square and red circle $[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$;¹⁰ blue diamond, $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$.

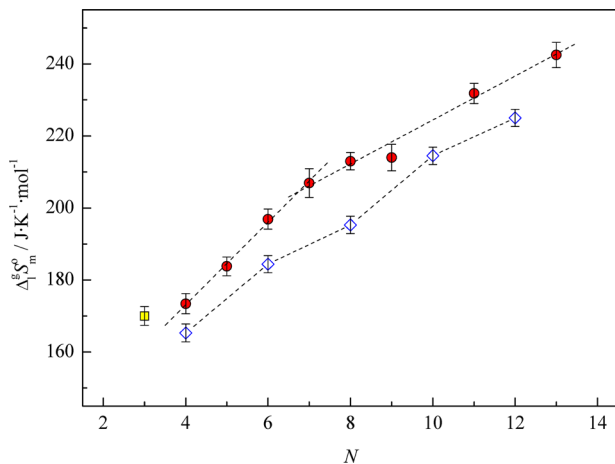


Figure 5. Graphic representation of standard molar entropy of vaporization at reference temperature ($T = 298.15\text{K}$) as a function of the total number of carbon atoms in the alkyl side chains of the cation, N . Yellow square and red circle, $[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$;¹⁰ blue diamond, $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$.

$[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$, indicating an entropic increase of the absolute liquid entropy for the symmetric cation ILs, that could be related with a molecular entropy increase as well as being a reflection of the change of the ion dynamics in the IL liquid phase.

The observed lower entropies of vaporization are in opposition with the higher volatility observed for the symmetric ILs series, which shows that the higher volatility of the symmetric ILs, when compared with the asymmetric series, is ruled by their enthalpy of vaporization.

The odd–even effect is also clearly discernible in the entropies of vaporization of the $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$ ILs, with higher entropies of vaporization for the odd numbered $[\text{C}_3\text{C}_3\text{im}][\text{NTf}_2]$ and $[\text{C}_5\text{C}_5\text{im}][\text{NTf}_2]$, indicating a decrease in the absolute entropies of the liquid for the odd numbers.

The observed odd–even effect in the entropy and enthalpy of vaporization in the symmetrical series are attenuated in the volatility because of an entropic–enthalpic compensation.

4. FINAL REMARKS

The study of the five symmetric imidazolium based ionic liquids, $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$, enabled the evaluation the effect of the symmetry of the cation on the thermodynamic parameters of vaporization, taking into account the previous results for the $[\text{C}_{N-1}\text{C}_1\text{im}][\text{NTf}_2]$ series. The volatility of $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$ series is significantly higher than the asymmetric cation ILs. It was found that the higher volatility is ruled by the enthalpy of vaporization. The symmetric ILs show lower entropies of vaporization compared with the asymmetric, indicating an increase of the absolute liquid entropy in the symmetric cation ILs. The obtained vaporization results of the $[\text{C}_{N/2}\text{C}_{N/2}\text{im}][\text{NTf}_2]$ ILs, shows an enthalpic and entropic differentiation with a clearly discernible odd–even effect, with higher enthalpies and entropies of vaporization for the odd numbered $[\text{C}_3\text{C}_3\text{im}][\text{NTf}_2]$ and $[\text{C}_5\text{C}_5\text{im}][\text{NTf}_2]$.

■ ASSOCIATED CONTENT

📄 Supporting Information

This section presents the experimental vapor pressures for the five studied imidazolium based ILs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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