



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



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ARTICLE INFO

Article history:

Received 16 April 2015

Received in revised form 21 September 2015

Accepted 26 September 2015

Available online 9 October 2015

This paper is dedicated to the memory of Alexander “Xander D. Stanton, a talented and promising young researcher and friend who passed away during the course of this project.

Keywords:

Ionic liquid

Enthalpy of vaporization

Quartz-crystal microbalance

Prediction

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

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