Supporting Information

Ionic Liquids: First Direct Determination of their Cohesive Energy

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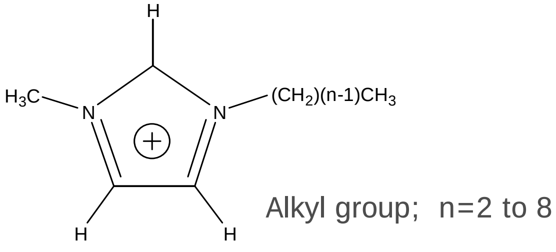
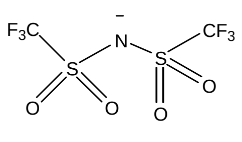
1. Experimental

1.1. Chemicals. 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, [C$_n$mim][NTf$_2$], with *n* ranging from 2 to 8, were synthesized at QUILL (The Queen's University Ionic Liquid Laboratories, Belfast) according to methods found elsewhere,[1] where they underwent first-stage purification.





The ionic liquids were washed several times with water to decrease the chloride content. It was confirmed that no precipitation (of AgCl) would occur by adding $AgNO_3$ to the wash water. NMR and ESI-MS analyses showed no major impurities in the untreated, original samples, except for the presence of water. Proton spectra were recorded on a BRUKER AMX300 spectrometer, operating at 300 MHz. The electro-spray mass spectra were performed on an ion trap instrument (Brucker, model Esquire 3000+) in the positive and negative modes using acetonitrile as the solvent at an approximate dilution of 1:10000, flow rate of 100 μL/h, and source temperatures of 100-150 ºC. See Figures S1 and S2 as examples of the NMR and MS performed for [C_4MIM][NTf_2]. Spectra taken on original samples and those on used ones (after microcalorimetric vaporization) showed no detectable differences. All original samples were thoroughly degassed, dried, and freed from any small traces of volatile compounds by applying vacuum (0.1 Pa) at moderate temperatures (60 - 80ºC) for typically 48 h. Then, both the water and chloride contents were analysed. Coulometric Karl-Fischer titrations revealed very low levels of water (below 100 ppm) for all treated ILs to be compared with values of 2500 – 5500 ppm of water for untreated samples. The Cl^- specific electrode using the standard addition method has generally shown chloride contents in the range of 20-150 ppm.

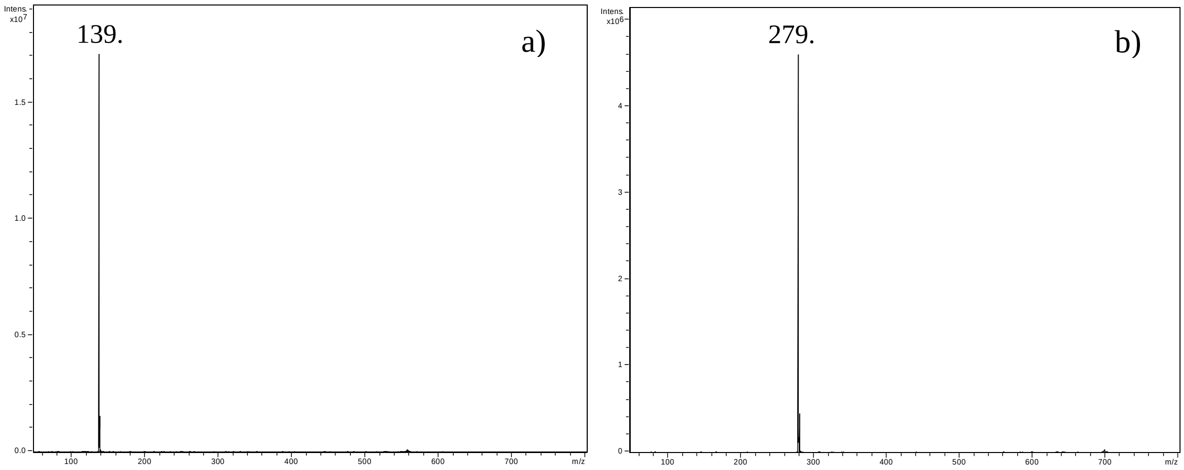


Figure S1. ESI-MS spectra of [C_4MIM][NTf_2] in acetonitrile at an approximate dilution of 1:10,000 as an example of the purity assessment performed for the ionic liquids used in this work. Intensity versus (*m/z*). a) Positive mode b) Negative mode.

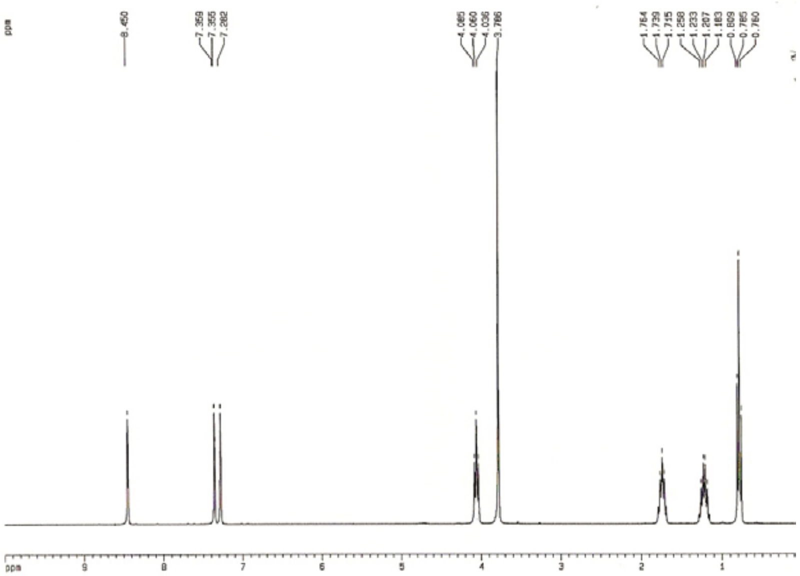


Figure S2. ^{1}H NMR spectra of [C_4MIM][NTf_2] as an example of the purity assessment performed for the ionic liquids used in this work.

1.2. Calorimetry.

1.2.1. *Instrumentation*

A Calvet type microcalorimeter (Setaram, model HT1000D) with a sensitivity of 3 $\mu V \cdot mW^{-1}$ was used in this work (the apparatus is represented in Figure S3.). The sensitive part of this calorimeter is the conduction device, which connects the outer wall of the measuring chamber to the isothermal block, with heaters placed under the base and on top of the block to archive a uniform temperature distribution in this high-temperature version of the calorimeter.

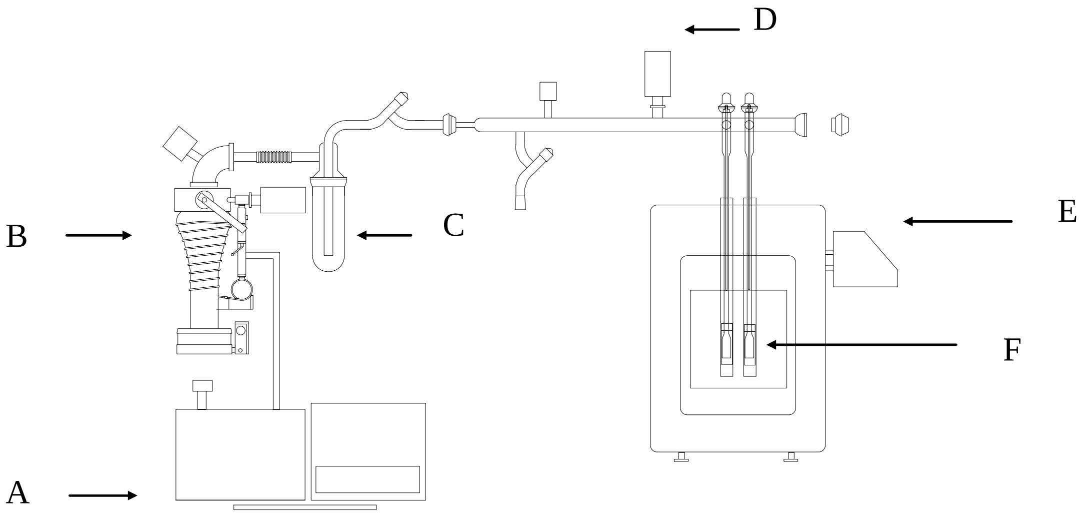


Figure S3. Schematic view of the Calvet drop method assembly, consisting of the vacuum line and a Calvet microcalorimeter Setaram, model HT1000D: A (rotary vacuum pump); B (diffusion pump); C (liquid nitrogen glass trap); D (Pirani and Penning gauges); E (HT1000D calorimeter block); F (calorimetric cells).

The G11 system controller is used as a temperature controller, for temperature monitoring and for thermopile sign amplification and digitalization. Data acquisition and analysis (Setaram 3.20) is done through an interface connected to a computer.

Vacuum line system

The pumping system (10^{-2} Pa) consists of a rotary vacuum pump (Edwards, model RV5), which is used both for pre-evacuating the system and for backing the vapor diffusion pump (Edwards, model Diffstak 63). A Pirani gauge (Edwards, model APG-M) is used to measure the vacuum in the system during the pre-evacuation process. A Penning gauge (Edwards, model AIM-S) is used to measure the vacuum maintained in the system throughout the sublimation process. The vacuum line is connected to the pumping system through a glass cold trap, which can be filled with liquid nitrogen. All glass connections in the system are made of greaseless spherical joints from Young.

Calorimetric cells

The calorimetric cells are Pyrex glass cylinders of internal diameter 12 mm and depth 50 mm. They are embedded in identical cylinders made of Kanthal, thus providing good thermal contact in the hot-zone. Rejuvenated prolongations of the glass cylinders are leaving the hot-zone and assure the connection to the vacuum line; tunneling tubes allow repeating the measurements without removing the cells from the hot-zone (less volatile compounds tend to condense on the walls of cooler sections of the prolongation tube, thus making multiple measurements impossible). The tunneling tubes are easy removed and cleaned, without disturbing the thermal equilibrium of the cells.

1.2.2. Calvet microcalorimetry

The standard molar enthalpies of vaporization have been measured using a Calvet microcalorimetry drop-method as described in detail by Adedeji *et al.*[2] and Santos *et al.*[3]. In order to measure the heat of vaporization of the ionic liquids, method was slightly modified: the calorimeter cells (sample and reference) were purged with ultra pure (99.999%) N_2 and the sample drop procedure was done under inert atmosphere.

Samples of about 10 mg of ionic liquid were inserted in thin glass capillary tubes (25 to 30 mg each) sealed at one end. Then, they were dropped at 298.15 K, into the hot reaction vessel of the Calvet High Temperature Microcalorimeter held at the temperature T= 577.8 K and, when the heat flow signal reached around 5% of the peak heat flow signal, the liquid was completely removed from the hot zone by vacuum vaporization. For the determination of enthalpies of vaporization in the Calvet microcalorimetry drop-technique a capillary tube containing the sample and a capillary blank tube are simultaneously dropped into the hot-zone of the calorimeter. When the tubes have reached thermostability the sample is evacuated from the hot-zone.

The calorimeter was calibrated, making use of the reported molar enthalpy exchange corresponding to the heating of solid sapphire, and the hot-zone temperature was calibrated *in situ*, using a miniature Pt100 temperature sensor, class1/10, (Labfacility). This sensor had been previously calibrated against a SPRT (25 ohms; Tinsley, 5187A) temperature probe using an ASL bridge model F26, in accordance to the International Temperature Scale of 1990, ITS-90.

Thermal corrections for the glass capillaries were made by dropping tubes of near equal mass into each of the twin cells.

2. Calculations

2.1. Enthalpies of vaporization

The total measure enthalpy change for the process, $\Delta_{\mathrm{l},\,298.15}^{\mathrm{g},\,T} H_m^0$,

$$\begin{tikzcd}
\textbf{IL}\ (\mathrm{l},\ T) \arrow[r, dotted, "\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(T)"] & \textbf{IL}\ (\mathrm{g},\ T) \\
\textbf{IL}\ (\mathrm{l},\ T = 298.15\ \mathrm{K}) \arrow[u, dotted, "\int_{298.15}^{T} C_p(l)dT"] \arrow[ur, "\Delta_{\mathrm{l},\,298.15}^{\mathrm{g},\,T} H_{\mathrm{m}}^0"] \arrow[r, dotted, "\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^0(298.15\ \mathrm{K})"] & \textbf{IL}\ (\mathrm{g},\ T = 298.15\ \mathrm{K}) \arrow[u, dotted, "\int_{298.15}^{T} C_p(g)dT"']
\end{tikzcd}$$

can be subdivided in two main terms: i) the enthalpy change due to the heating of the sample in the liquid phase from T = 298.15 K to the hot-zone temperature T, $\Delta_{l,298.15}^{l,T} H_m^0$; ii) the enthalpy change corresponding to the vaporization of the sample at hot-zone temperature T, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(T)$. The first main term can be obtained, according to equation 1, from the integration of the experimental heat flow data, using the hypothetical exponential decay;

$$\Delta_{l,298.15}^{l,T} H_m^0 = \int_{298.15}^{T} C_p(l)dT \qquad (1)$$

The second term, the enthalpy change corresponding to the vaporization of the sample at hot-zone temperature, can be derived from the difference between the total enthalpy change $\Delta_{\mathrm{l},\,298.15}^{\mathrm{g},\,T} H_m^0$, and enthalpy change due to the heating of the sample in the liquid phase $\Delta_{l,298.15}^{l,T} H_m^0$, according the equation 2

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(T) = \Delta_{\mathrm{l},\,298.15}^{\mathrm{g},\,T} H_m^0 - \Delta_{l,298.15}^{l,T} H_m^0 \qquad (2)$$

The standard molar enthalpy of vaporization at T = 298.15 K, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(298.15\mathrm{K})$, may be derived from the total enthalpy change measured for the process using equations 3 or 4:

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(298.15\mathrm{K}) = \Delta_{\mathrm{l},\,298.15}^{\mathrm{g},\,T} H_m^0 - \int_{298.15}^{T} C_p(g)dT \qquad (3)$$

or,

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(298.15K) = \Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(T) + \int_{298.15}^{T} C_p(l)dT - \int_{298.15}^{T} C_p(g)dT \qquad (4)$$

where *Cp*(l) and *Cp*(g) stands for the liquid and gas heat capacity respectively. Usually the two heat capacity correction terms are condensed in a single term noted as $\int_{298.15}^{T} \Delta_l^g C_p dT = - [\int_{298.15}^{T} C_p(l)dT - \int_{298.15}^{T} C_p(g)dT]$, which, in turn, can be simplified using the mean value of $\Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}}$ in that temperature interval, $< \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} >$. The temperature correction becomes:

$$\Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(298.15K) = \Delta_{\mathrm{l}}^{\mathrm{g}} H_m^0(T) - < \Delta_{\mathrm{l}}^{\mathrm{g}} C_{\mathrm{p}} > . (T - 298.15) \qquad (5)$$

The heat capacities differences at constant pressure between the gas and liquid phases were estimated using the energy equipartition principle and the difference between isochoric and isobaric heat capacities in the liquid and gas phases,

$$\Delta_l^g C_p \approx -2R - \frac{\alpha_p^2}{\kappa_T} V_m T \qquad (6)$$

Table S1. Average heat capacity difference between the gas an liquid phases, $\Delta_l^g C_p$ = Cp(g) - Cp(l).

Ionic Liquid	$<\Delta_l^g C_p>$ / J·K^{-1}·mol^{-1}
C2mimTf2N	-90.7
C3mimTf2N	-93.1
C4mimTf2N	-95.5
C5mimTf2N	-97.9
C6mimTf2N	-100.3
C7mimTf2N	-102.7
C8mimTf2N	-105.0

References

[1] Bonhôte, P.; Dias. A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K. *Gratzel Inorg. Chem.* **1996**, *35*, 1168-1178.

[2] Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. J. *Organometallic Chem.* **1975**, *97*, 221-228.

[3] Santos, L.M.B.F.; Schröder, B.; Fernandes; O.O.P.; Ribeiro da Silva, M.A.V. *Thermochimica Acta* **2004**, *415*, 15-20.