

SUPPLEMENTARY MATERIAL

Benchmark values: thermochemistry of the ionic liquid [C₄Py][Cl]

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TABLE S1. Experimental results for measurements of reaction enthalpies, $\Delta_r H_m(\text{liq})$, using DSC for reaction Pyridine (*liq*) + C₄H₉Cl (*liq*) = [C₄Py][Cl] (*liq*)

Molar ratio	Solvent % wt.	T_{max} K	$\Delta_r H_m(\text{liq})$ kJ mol ⁻¹
0.50	70	445±5	-76.8
0.54	68	443±5	-77.6
0.55	71	444±2	-75.2
			-76.5±1.4 ^a

^a Uncertainties are twice the standard deviations of the mean value

Quantum Chemical Calculations. Calculation of the Gas Phase Enthalpy of Reaction and Formation.

Standard first-principles molecular orbital calculations were performed using the Gaussian 03 Rev.04 program package¹. Conformation analysis of the IL was performed using B3LYP/6-31+G(d,p) with help of the procedure developed in our previous work². Optimized structure, and energy of the most stable conformer of the ionic pair was further obtained using the CBS-QB3 composite method. CBS-QB3 theory uses geometries from B3LYP/6-311G(2d,d,p) calculation, scaled zero-point energies from B3LYP/6-311G(2d,d,p) calculation followed by a series of single-point energy calculations at the MP2/6-311G(3df,2df,2p), MP4(SDQ)/6-31G(d(f),p) and CCSD(T)/6-31G† levels of theory.³ Calculated values of the enthalpy of reaction are based on the electronic energy calculations obtained using standard procedures of statistical thermodynamics.⁴

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Table S2 Calculated liquid internal energy, vapor internal energy, and enthalpy of vaporization of [C₄Py][Cl] obtained from MD simulations. Note that the results at 298K were obtained by direct simulation of the (metastable) liquid phase. If the 413K results are adjusted as are the experimental data, then $\Delta_l^g H_m^\circ = 167.2 \pm 0.2 \text{ kJ}\cdot\text{mol}^{-1}$. Uncertainties in the last digit are shown as subscripts.

Temperature, K	u_{liq} , $\text{kJ}\cdot\text{mol}^{-1}$	u_{vap} , $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_l^g H_m^\circ$, $\text{kJ}\cdot\text{mol}^{-1}$
298	-87.28 ₄	75.7 ₂	165.4 ₂
413	-6.44 ₈	145.8 ₂	155.7 ₂

Force Field and Molecular Dynamics Methodology

Briefly, the molar enthalpy of vaporization was computed as

$$\Delta_l^g H_m^\circ(T,P) = \langle h_{\text{vap}}(T,P) \rangle - \langle h_{\text{liq}}(T,P) \rangle \quad (1)$$

where $\langle h_{\text{vap}}(T,P) \rangle$ and $\langle h_{\text{liq}}(T,P) \rangle$ are the molar average enthalpies of an ideal gas and the condensed phase, respectively, at T and P. The individual components are computed as

$$\langle h_{\text{vap}}(T,P) \rangle = \langle u_{\text{vap}}(T) \rangle + RT \quad (2)$$

$$\langle h_{\text{liq}}(T,P) \rangle = \langle u_{\text{liq}}(T,P) \rangle + Pv \quad (3)$$

where u is the internal energy, R is the gas constant, P and v are the pressure and molar volumes of the liquid phase, respectively. The gas phase was assumed to be ideal. The magnitude of the Pv term was negligible in Eq. (3) and was neglected.

A standard Class I force field was used to model [Nbupy][Cl]. The atoms were represented as Lennard-Jones spheres with formal partial charges placed at the atomic centres. For the [Nbupy][Cl] simulations, the intra-molecular parameters, and the inter-molecular Lennard-Jones parameters for the [Nbupy] cation were obtained from our earlier work¹. The Lennard-Jones parameters for [Cl] were taken from Jensen and Jorgensen².

For computing the liquid phase internal energy, simulations were conducted in the isothermal-isobaric ensemble at the temperature and pressure of interest on 216 ion pairs for 500 ps using the Nosé-Hoover thermostat and barostat³. Then, simulations were performed on the resulting

equilibrated structure in the canonical ensemble for 1 ns using the Nosé-Hoover temperature thermostat⁴, and the internal energy was accumulated. For the ideal gas phase, one ion pair was simulated in the NVT ensemble in a large, non-periodic box to prevent edge effects. For all simulations, a timestep of 1 fs was used, and for all thermostats, a thermostat time constant of 0.1 ps was used, while for the barostat, a time constant of 0.5 ps was used. The Lennard-Jones and Coulombic interactions were truncated at 11 Å, with long-range corrections being applied for the Lennard-Jones interactions. The Particle-Particle-Particle-Mesh⁵ algorithm was used for the Coulombic interactions in the liquid phase. For the vapor phase, a large cutoff (50 Å) was used for both the Lennard-Jones and Coulombic interactions. All simulations were conducted using LAMMPS⁶.

To obtain the partial charges on the atoms, an ab initio calculation was conducted on the [Nbupy] cation in the gas phase at the B3LYP/6-311++g(2d,p) level of theory using Gaussian. The partial charge assignment was computed using the CHELPG algorithm. It is known that the use of full (+/- 1) charges on the ions neglects charge transfer and leads to enthalpies of vaporization that are too high⁷⁻⁹. We therefore followed the practice used in our previous work and uniformly scaled the charge on the cation by 0.8. To maintain charge neutrality, the chloride ion was given a charge of -0.8.

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Enthalpy of Fusion of [C₄Py][Cl] from DSC Measurements.

The thermal behavior of [C₄Py][Cl] including melting temperature and enthalpy of fusion were determined with a computer controlled Perkin-Elmer DSC-2. For all measurements an empty pan run was subtracted and specific heat capacity was calculated. The fusion

temperatures and enthalpies were determined at the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_0 = 429.8$ K and $\Delta H_{\text{ref}} = 28.5$ J·g⁻¹). The uncertainty for temperature is ± 0.5 K and for enthalpy of fusion ± 1 J·g⁻¹.

The melting temperature $T_{\text{fus}} = 393.3$ K and the enthalpy of fusion $\Delta_{\text{cr}}^l H_m = 20.7 \pm 0.8$ kJ·mol⁻¹ (average of 3 experiments) have been measured for [C₄Py][Cl] in the present study using DSC. No phase transitions other than melting have been detected. In general, experimental enthalpy of fusion measured by DSC are obtained at the melting temperature T_{fus} . Because of the difference in the reference temperatures, the experimental enthalpy of fusion have to be adjusted to $T = 298$ K. The adjustment was calculated from the equation:

$$\Delta_{\text{cr}}^l H_m (298 \text{ K}) / (\text{J} \cdot \text{mol}^{-1}) = \Delta_{\text{cr}}^l H_m (T_{\text{fus}}/\text{K}) + \Delta C_p [(T_{\text{fus}}/\text{K}) - 298 \text{ K}]$$

where the average value $\Delta C_p = (85 \pm 6)$ J·mol⁻¹·K⁻¹ is the isobaric molar heat capacities, C_p^{cr} and C_p^l of the solid and the liquid imidazolium based ionic liquids reported in the literature [1,2].

With this adjustment the molar enthalpies of fusion, $\Delta_{\text{cr}}^l H_m (298 \text{ K}) = 12.6 \pm 0.8$ kJ·mol⁻¹ was calculated.

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