

## Electronic Supporting Information for:

# Exothermic and Thermal Runaway Behaviour of Some Ionic Liquids at Elevated Temperatures

R. Vijayaraghavan<sup>a</sup>, M. Surianarayanan<sup>b</sup>, V. Armel<sup>a</sup> and D. R. MacFarlane<sup>a\*</sup>, and V. P. Sridhar<sup>b</sup>

### Instrumental techniques

The thermal behavior of the different ionic liquids (from room temperature to beyond decomposition temperature) was investigated by the Accelerated Rate Calorimeter (ARC) technique. This technique provides an intrinsic picture of the safety of compounds at elevated temperatures. The ARC works on a “heat-wait-measure” principle and has been widely employed to investigate thermal runaway of exothermic systems.<sup>10</sup> (References are to the reference list of the main paper). In order to compare the self-heat rates, the experiments were carried out with identical sample weights (in order to achieve similar thermal inertias,  $\Phi$ ). The self heat rate vs temperature, time vs temperature and pressure vs temperature profiles were recorded using the ARC software. The instrument also records the maximum pressure in the head-space above the reaction medium in the calorimeter that is reached during each temperature step of the calorimeter.

### Adiabatic thermo-kinetics<sup>10</sup>

The ARC instrument maintains the sample under adiabatic conditions. Under such conditions it can be assumed that the extent of reaction is directly proportional to the amount of heat produced. The thermodynamic relationship between the initial concentration,  $C_0$  and the remaining concentration,  $C$ , at any given time,  $t$ , in an adiabatic process, can then be related to the temperature reached via:

$$C / C_0 = (T_F - T) / (T_F - T_0) = (T_F - T) / \Delta T \quad (1)$$

where  $C$  is the concentration of the substance and  $T$  is the temperature. The subscript ‘0’ indicates the initial condition and  $F$  is a final state in which the substance has been completely consumed;  $\Delta T = T_F - T_0$  is the temperature rise for the reaction. It is also equal to the ratio of enthalpy to average specific heat; thus  $\Delta H$  can be calculated for the process from:

$$\Delta H = m C_p \Delta T$$

where  $C_p$  is the average heat capacity and  $m$  is the mass of the sample.

The heat generated in an exothermic reaction is consumed in three ways; to increase the temperature of the material, the container or sample bomb and the surroundings. The thermal inertia ( $\phi$ ), is expressed as follows:

$$\begin{aligned}\phi &= (m_s C_{ps} + m_b C_{pb}) / m_s C_{ps} \\ \phi &= 1 + m_b C_{pb} / m_s C_{ps}\end{aligned}\quad (2)$$

Here  $m_s$ ,  $C_{ps}$ ,  $m_b$ ,  $C_{pb}$  are respectively the mass of the sample, the heat capacity of the sample, the mass of the sample bomb and the heat capacity of the bomb. By incorporating the effects of thermal inertia, the corrected heat of reaction  $\Delta H_r$  is calculated using (3)

$$\Delta H_r = \phi m C_{ps} \Delta T \quad (3)$$

Figure S-1 : [C<sub>2</sub>mim][(BCN)<sub>4</sub>] - Temperature vs Time

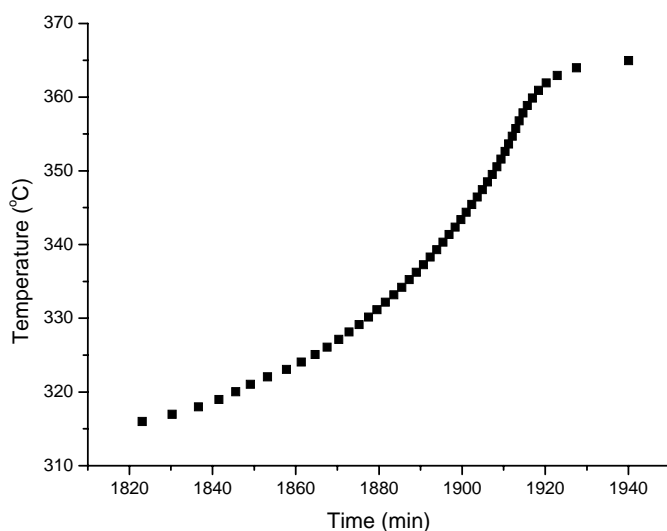


Figure S-2: [C<sub>2</sub>mim)][FSI] - Time vs Temperature

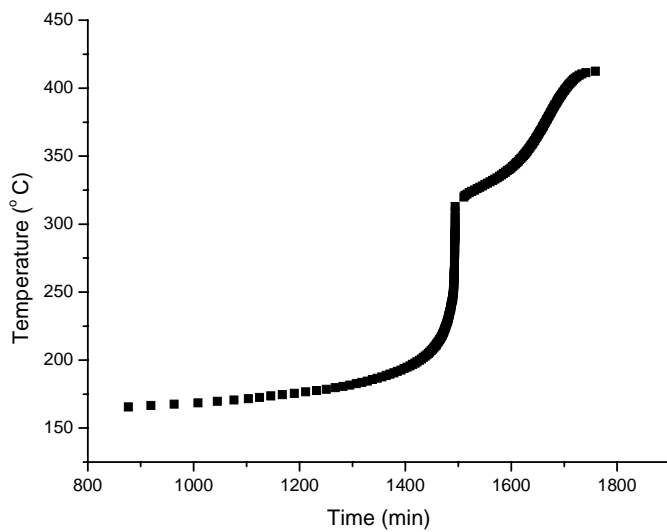


Figure S-3 : [C<sub>2</sub>mim)][TCM]- Temperature vs time

