**Supplementary Data**

Below is additional information on how the enthalpy and entropy values were obtained. The mol % of [Rmim]Cl in [$C_{66614}$P]Cl (upper phase) and the concentration of [Rmim]Cl in the lower phase (approximates to the molar volume of [Rmim]Cl since it is composed of > 98 % [Rmim]Cl) were converted to mol / litre values and the temperature, in deg. C was converted into deg. K. These values were used to create the Van't Hoff plot in Figure 2. The Table 1 data were in turn derived from the equation of the straight lines in Figure 2.

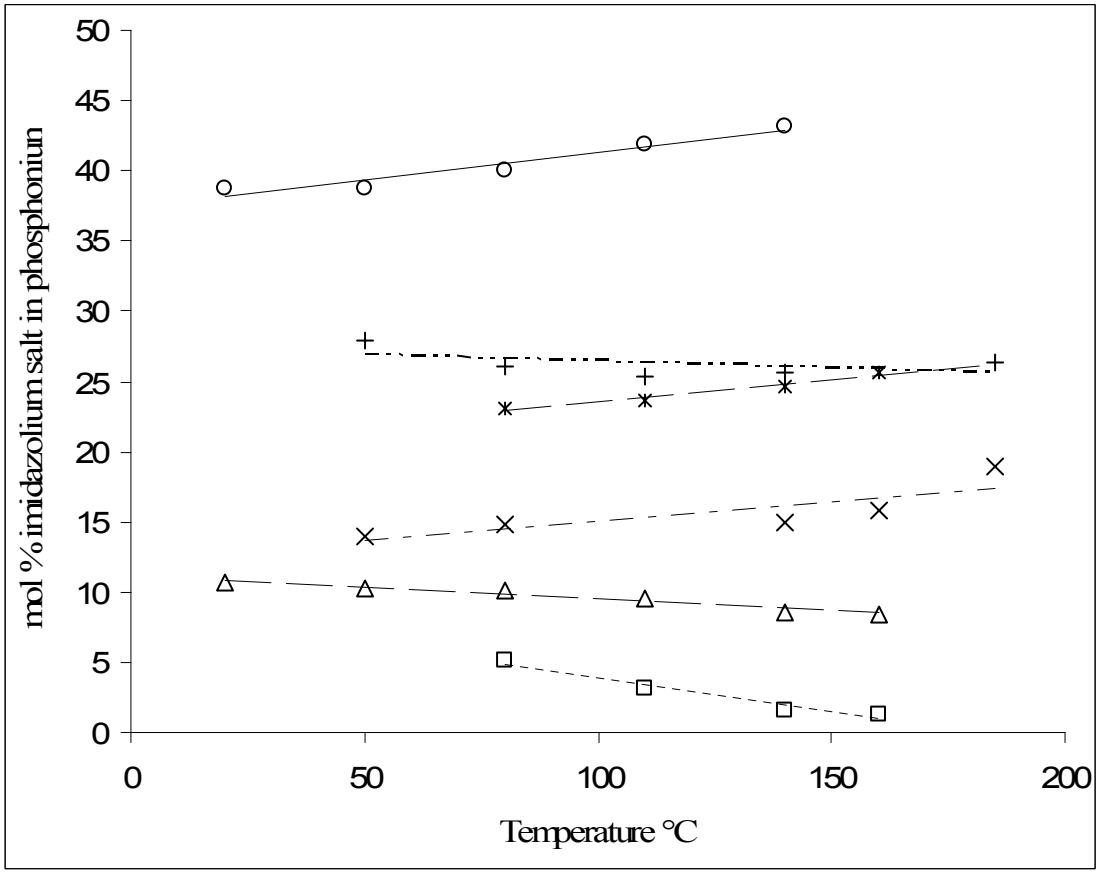


**Figure 1.** Concentration of 1-alkyl-3-methylimidazolium chlorides in the phosphonium rich phase. This was determined directly by NMR. From top to bottom, the lines represent [$C_5$mim]Cl - o; [*s*-$C_4$mim]Cl - +; [$C_4$mim]Cl - ∗; [$C_3$mim]Cl - ×; [$C_2$mim]Cl - △; and [$C_1$mim]Cl - □.

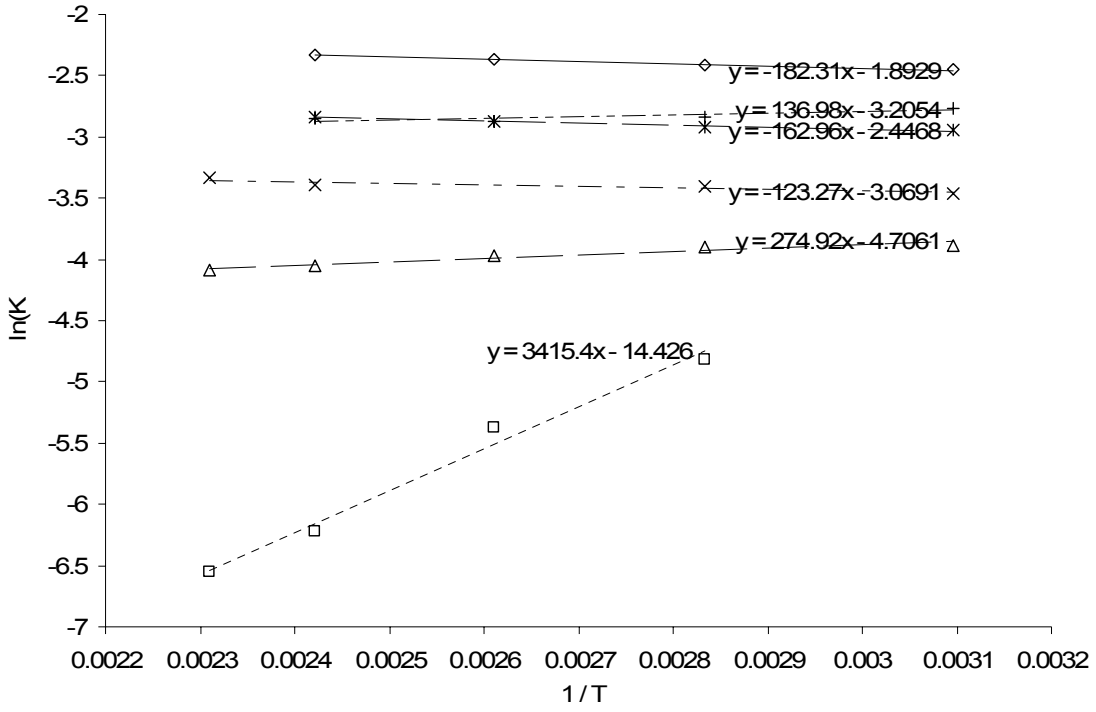


**Figure 2**. Van't Hoff plot of data derived from Figure 1. Gradient = -ΔH / R and Intercept = ΔS / R, where R = Universal Gas Constant. T = Temperature in Kelvin, and K = equilibrium constant (concentration of [Rmim]Cl upper / concentration of [Rmim]Cl lower {all mol $l^{-1}$}). From top to bottom, the lines represent [$C_5$mim]Cl - ◇; [*s*-$C_4$mim]Cl - +; [$C_4$mim]Cl - ✳; [$C_3$mim]Cl - ×; [$C_2$mim]Cl - △; and [$C_1$mim]Cl - □.

**Table 1.** The enthalpy and entropy of dissolving 1-alkyl-3-methylimidazolium chlorides in the [$P_{6\,6\,6\,14}$]Cl rich phase. The data is derived from the equations of the lines in Figure 2 of the form y = mx + c. Gradient (m) = -ΔH / R and intercept (c) = ΔS / R.

| Alkyl Group | ΔH / K J $mol^{-1}$ | ΔS / J $K^{-1}mol^{-1}$ |
|---|---|---|
| C1 | -21.7 | -100.3 |
| C2 | -2.29 | -39.1 |
| C3 | 1.03 | -25.5 |
| *s*-C4 | -1.14 | -26.7 |
| C4 | 1.35 | -20.3 |
| C5 | 1.51 | -15.7 |