Supplementary NMR data

The ^{1}H NMR spectra were used to determine the concentration of the 1-alkyl-3-methylimidazolium salts in the upper phosphonium phase.

Effect of alkyl group

Representative examples of the change in solubility of 1,3-dimethylimidazolium, 1-methyl-3-ethylimidazolium, 1-methyl-3-propylimidazolium, 1-methyl-3-butylimidazolium, 1-methyl-3-(1-methylpropyl)-imidazolium, and 1-methyl-3-pentylimidazolium chlorides in trihexyltetradecylphosphonium chloride are shown in Figures 1-6 respectively. The solubility was determined by comparing the integration of the imidazolium peaks at 10.7 (1H), 7-7-7.6 (1H + 1H), 4.4 (quartet or triplet – 2H {not dimethylimidazolium}), 4.1 (3H {or 6H for dimethylimidazolium}) with the phosphonium multiplet at 2.4-2.5 ppm (8H). From this a mol % composition of the two salts was determined and used in further calculations.

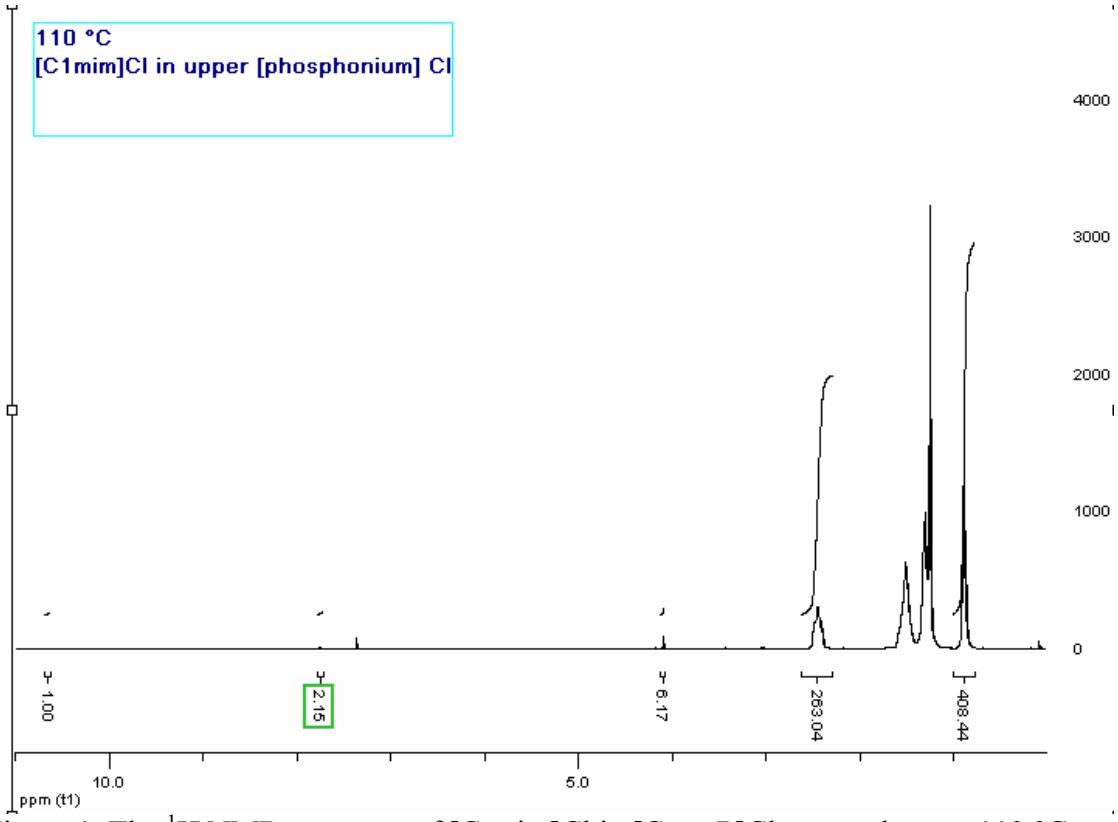

Figure 1. The ^{1}H NMR spectrum of [C_1mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

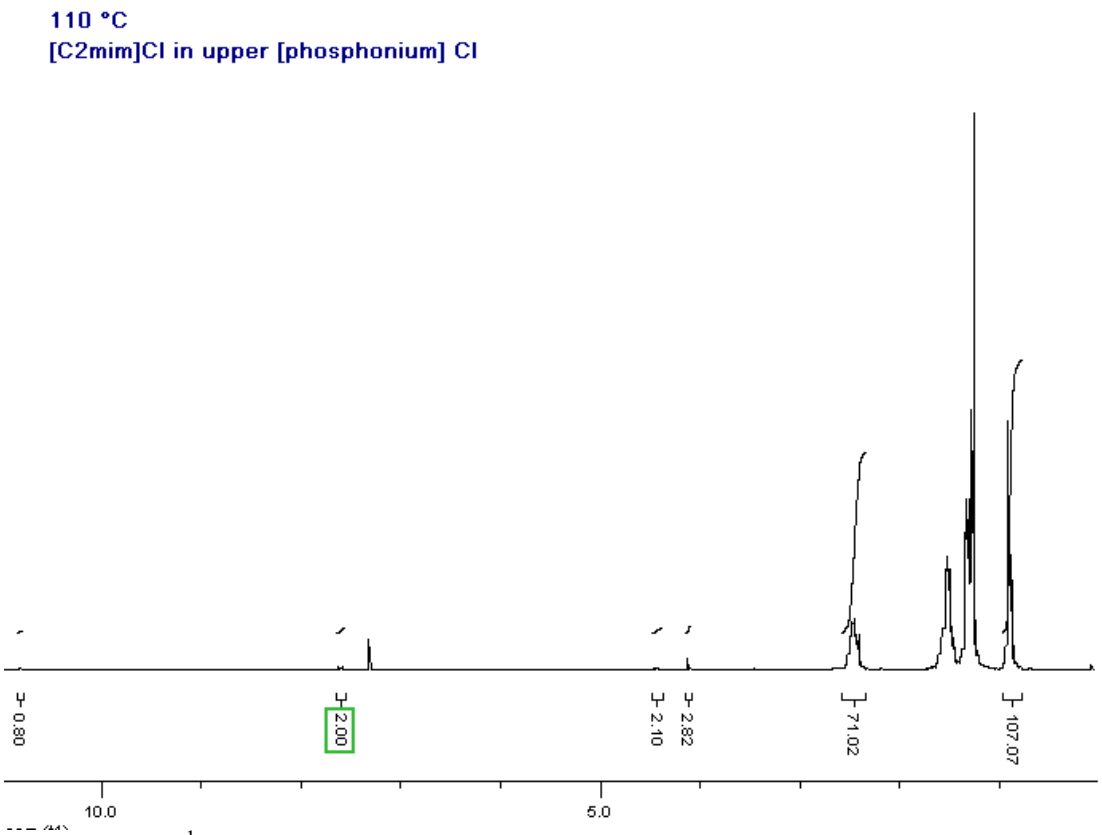

Figure 2. The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

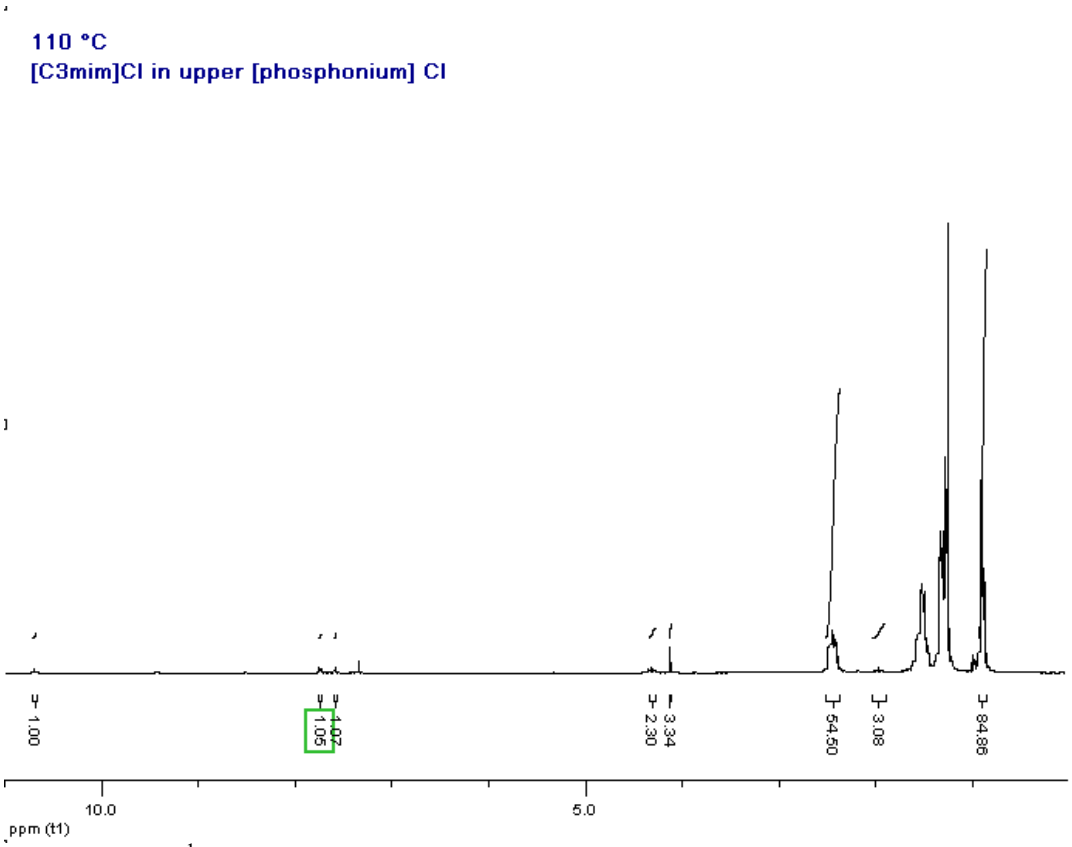

Figure 3. The ^{1}H NMR spectrum of [C_3mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

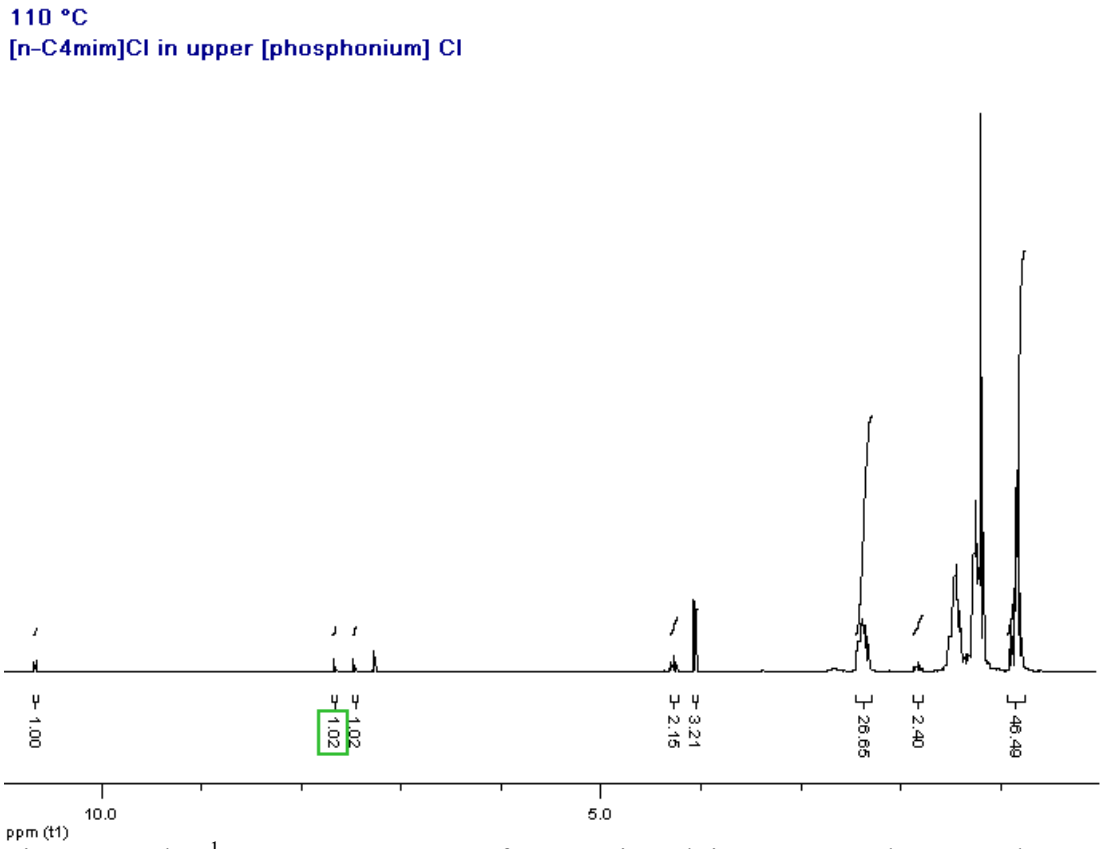

Figure 4. The ^{1}H NMR spectrum of [n-C_4mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

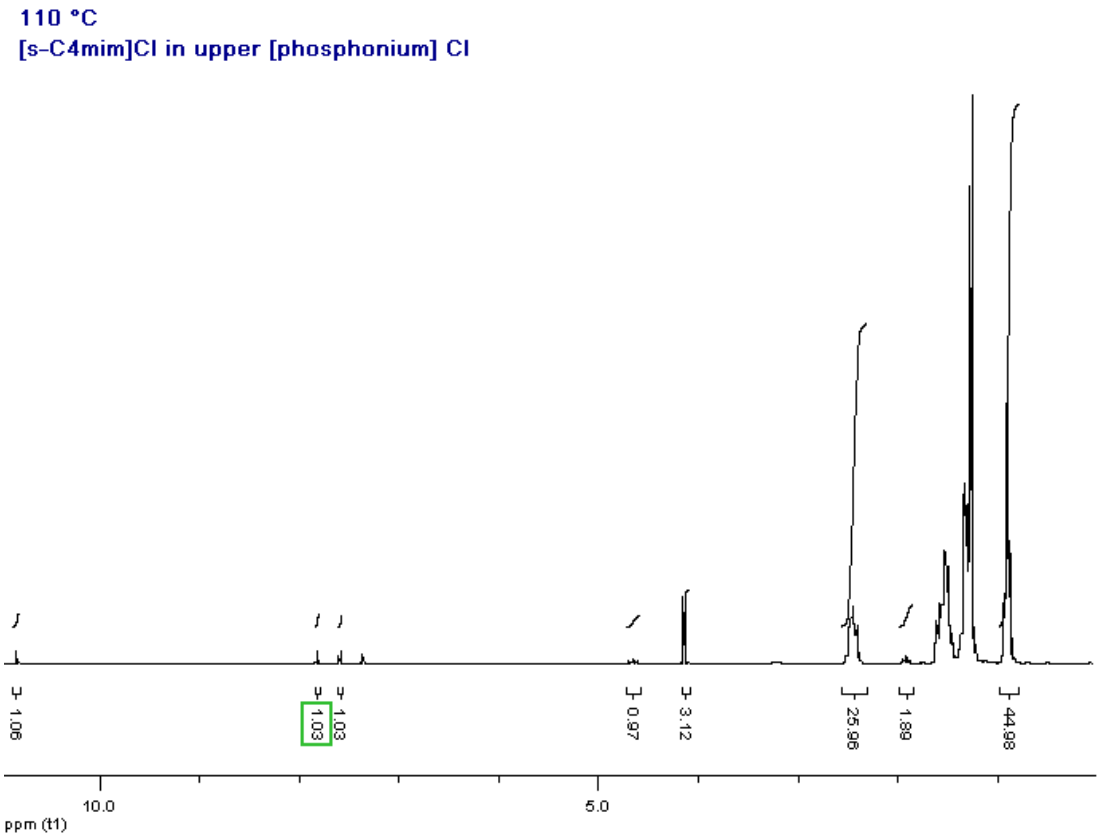

Figure 5. The ^{1}H NMR spectrum of [s-C_4mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

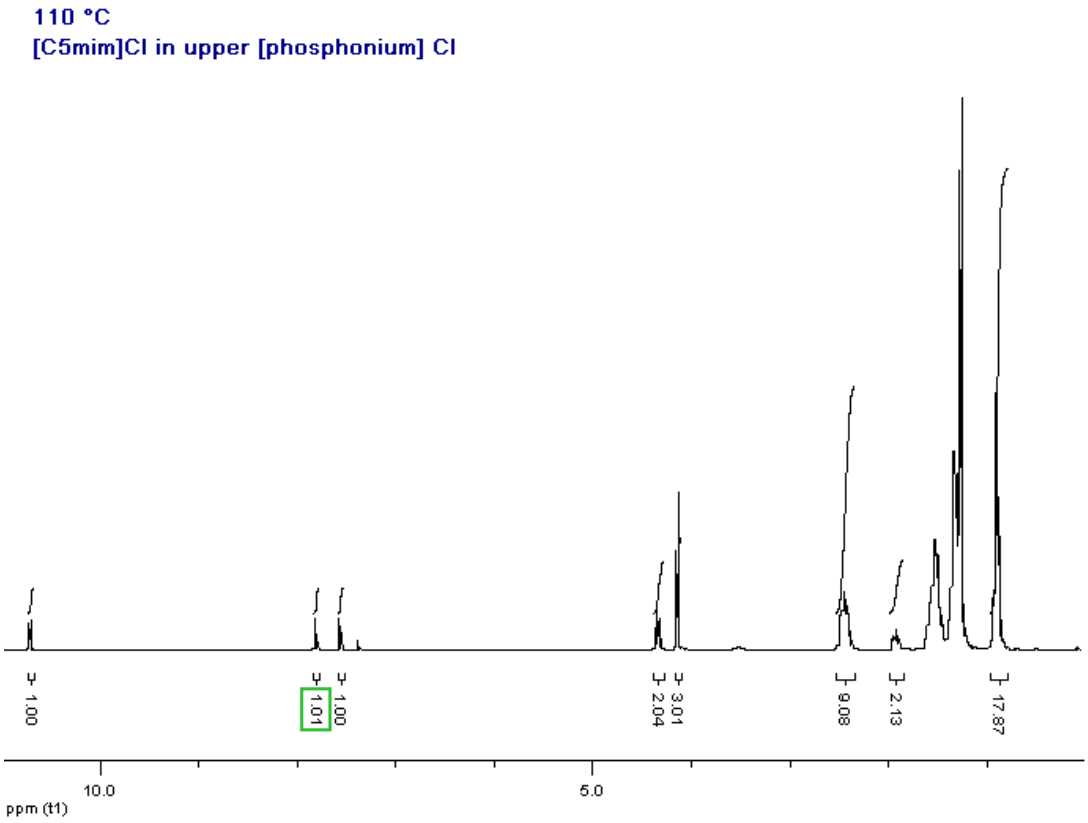

Figure 6. The ^{1}H NMR spectrum of [C_5mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

Effect of temperature

The NMR data for the solubility of 1-methyl-3-ethylimidazolium chloride in trihexyltetradecylphosphonium chloride at 50, 80, 110, 140, 160 and 170 °C are shown in Figures 7-12 respectively. The solubility was determined by comparing the integration of the imidazolium peaks at 10.7 (1H), 7-7-7.6 (1H + 1H), 4.4 (quartet), 4.1 (3H) with the phosphonium multiplet at 2.4-2.5 ppm (8H). From this a mol % composition of the two salts was determined and used in further calculations.

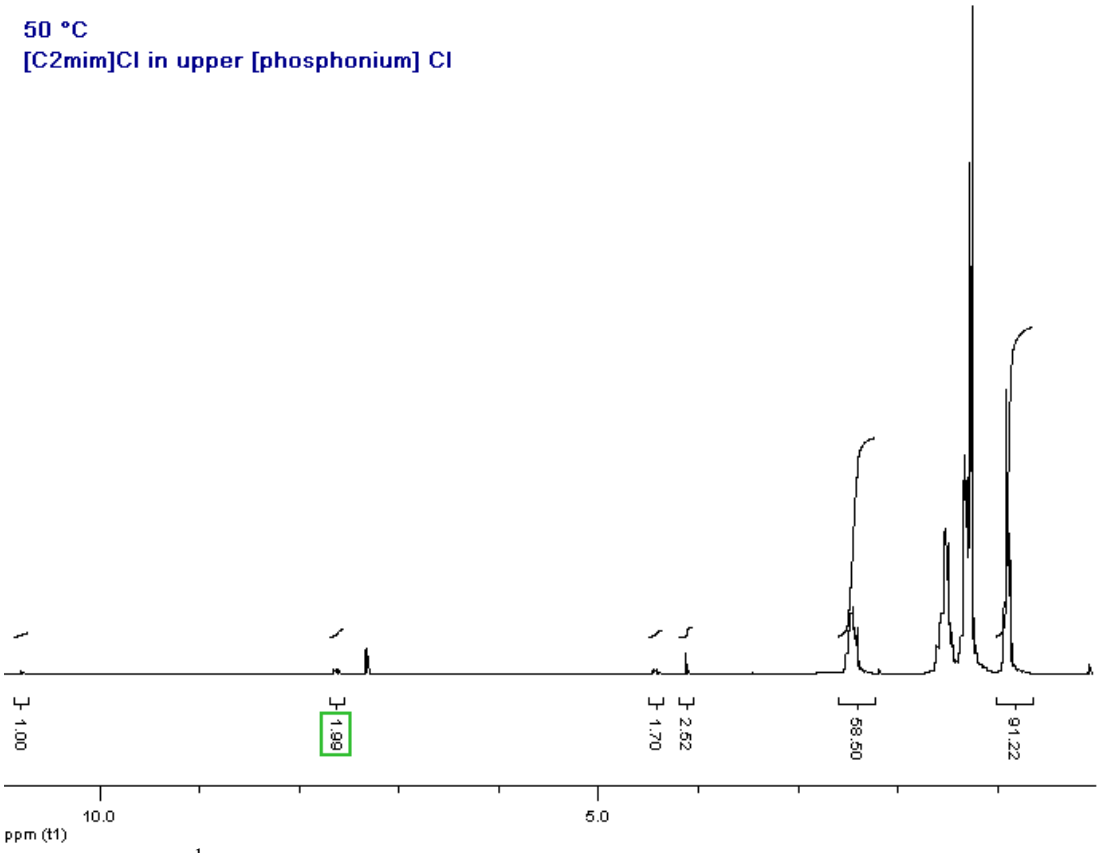

Figure 7. The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 50 °C

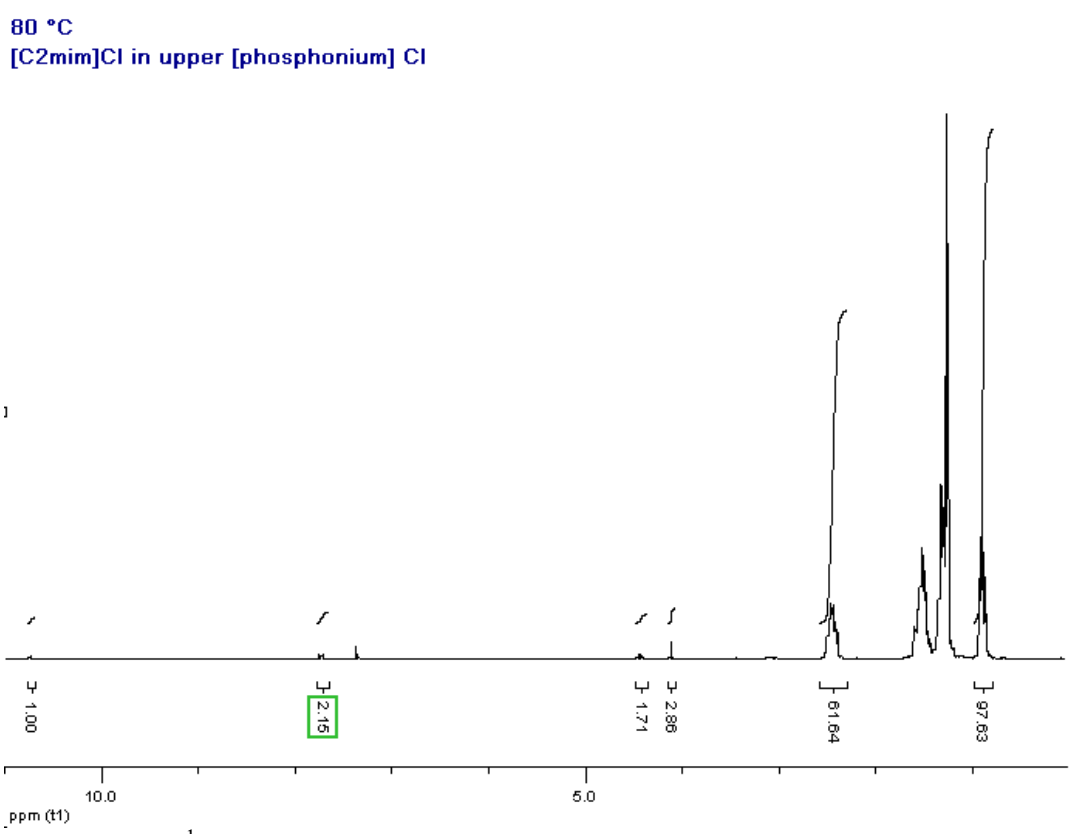

Figure 8. The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 80 °C

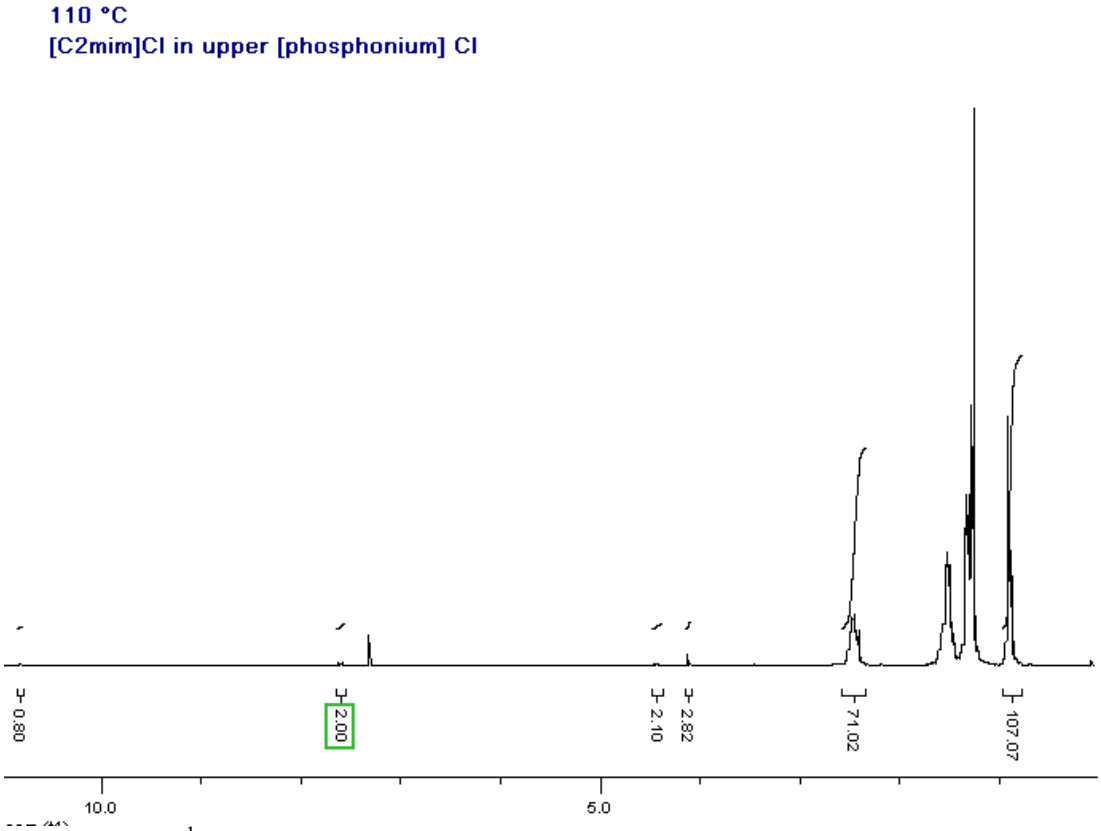

Figure 9. The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 110 °C

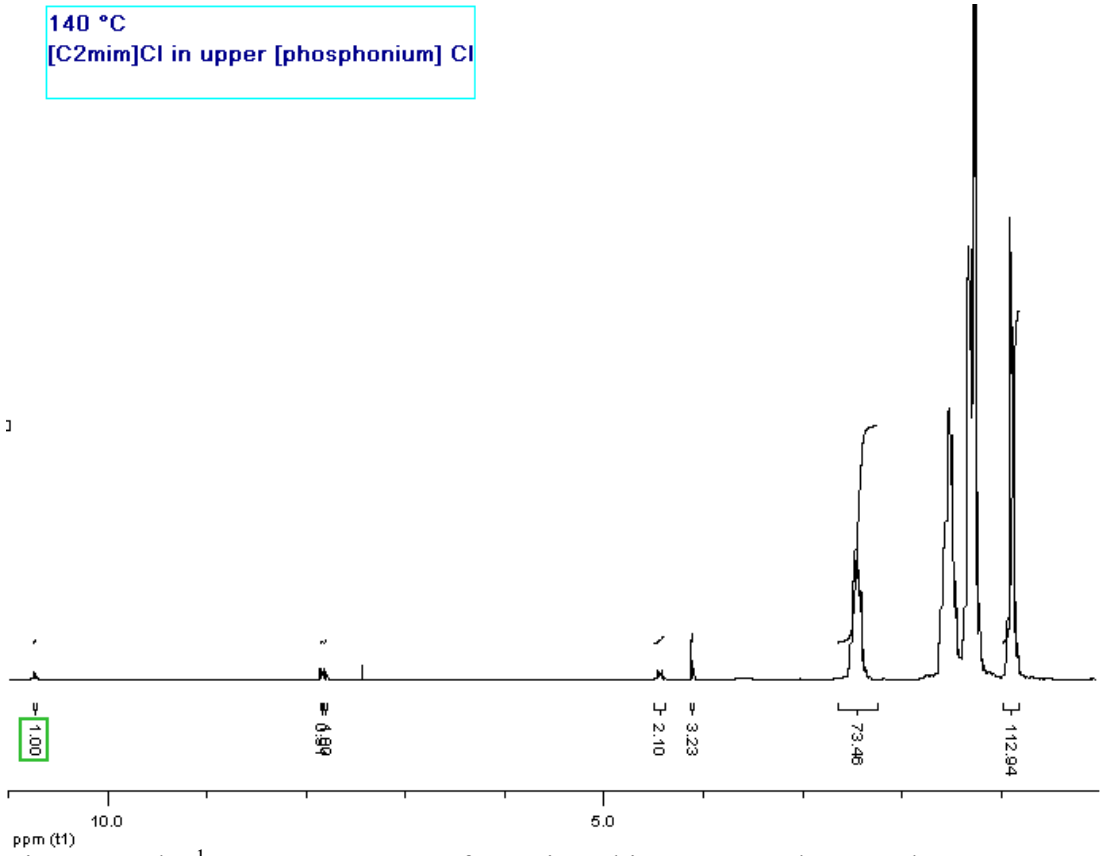

Figure 10 The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 140 °C

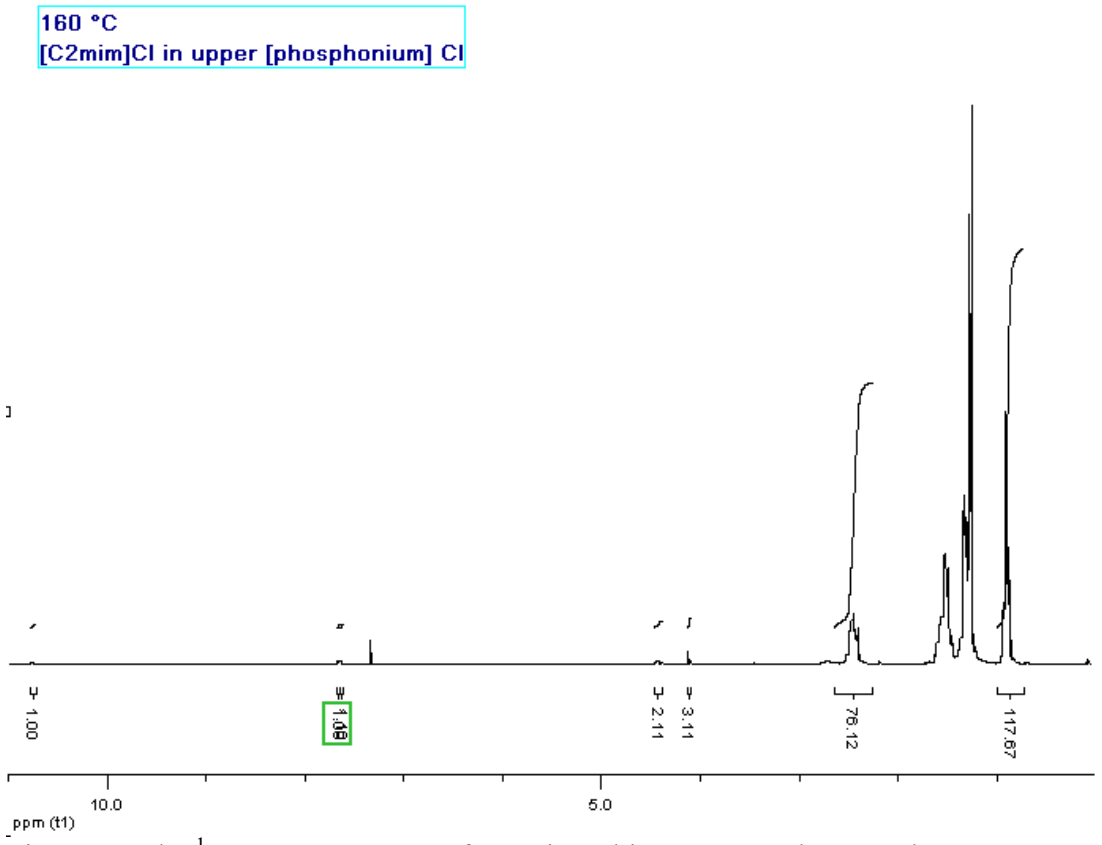

Figure 11 The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 160 °C

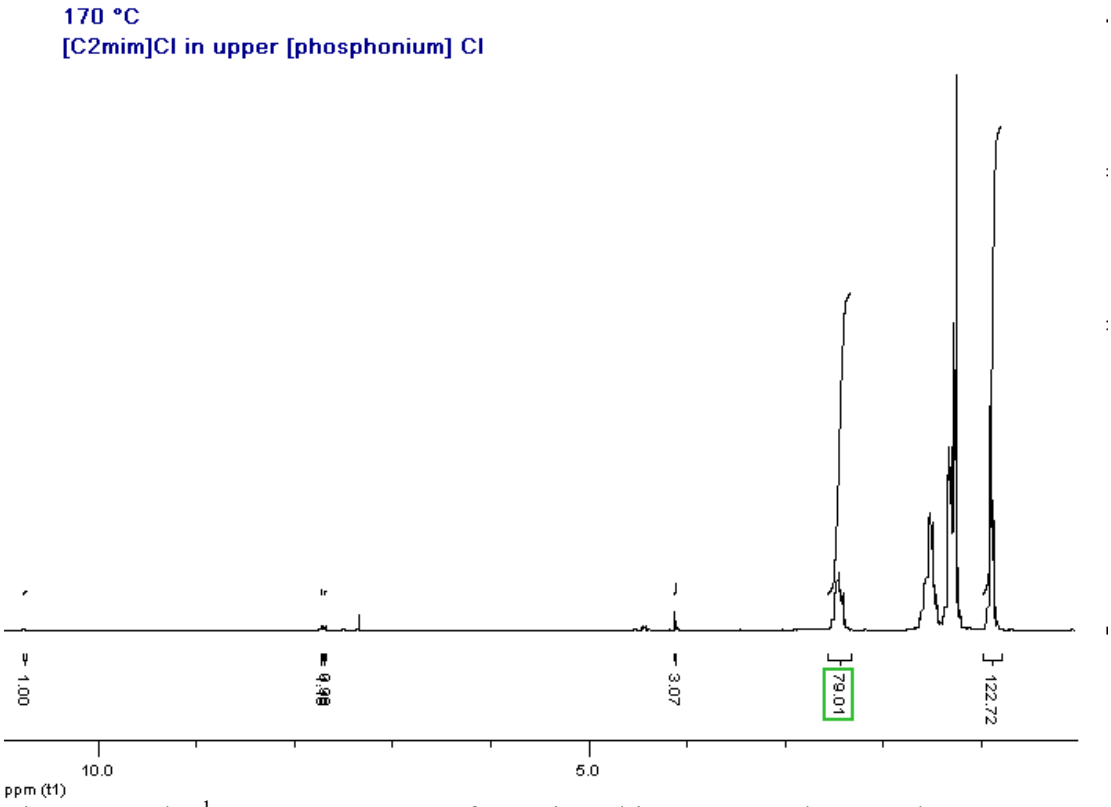

Figure 12. The ^{1}H NMR spectrum of [C_2mim]Cl in [C_{66614}P]Cl upper phase at 170 °C

Lower phase solubilities

The lower phases were also analysed by ^{1}H NMR, by comparing the phosphonium multiplet (8H) at 2.4-2.5 ppm with the imidazolium peaks at 4.0-4.5 ppm (3H and 2H). Two examples are given, showing the extremely low solubility of the [C_{66614}P]Cl in 1-ethyl-3-methylimidazolium chloride (Figure 13) and 1-butyl-3-methylimidazolium chloride (Figure 14). These values are typically 10-50 lower that the solubility of the imidazolium chlorides in the phosphonium layer. The solubilities are so low that it is not possible to obtain meaningful data to calculate solubility trends.

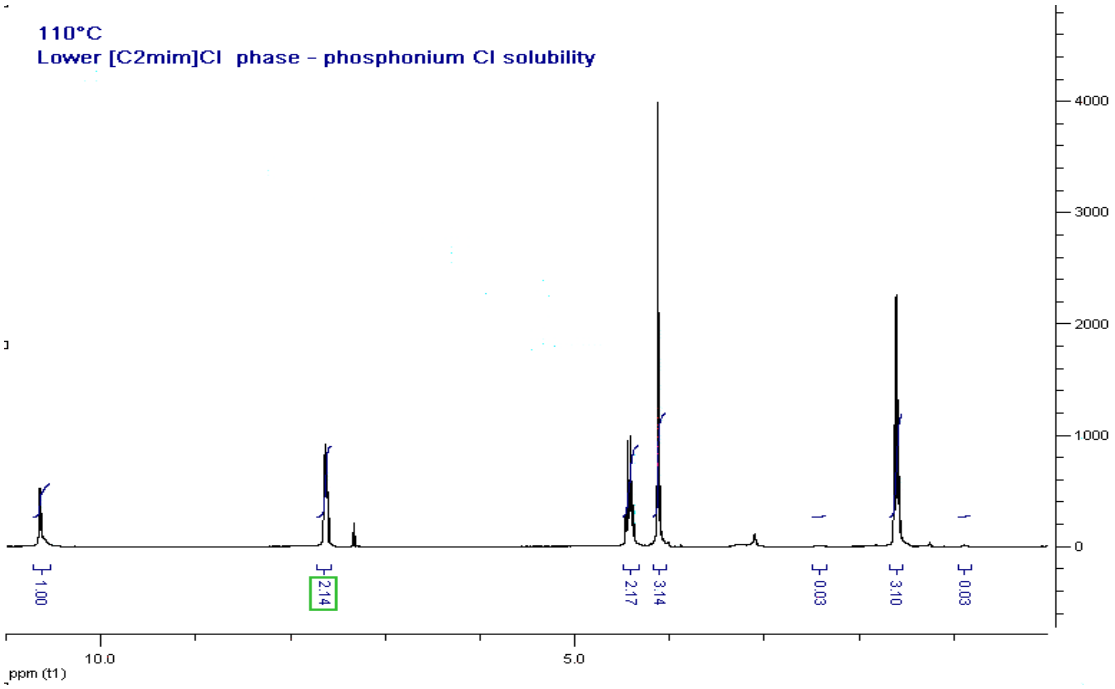

Figure 13. The solubility of $[C_{66614}P]Cl$ in [*n*-C_2mim]Cl at 110 °C (solvent = $CDCl_3$ / CD_3OD). Solubility = 0.34 mol %.

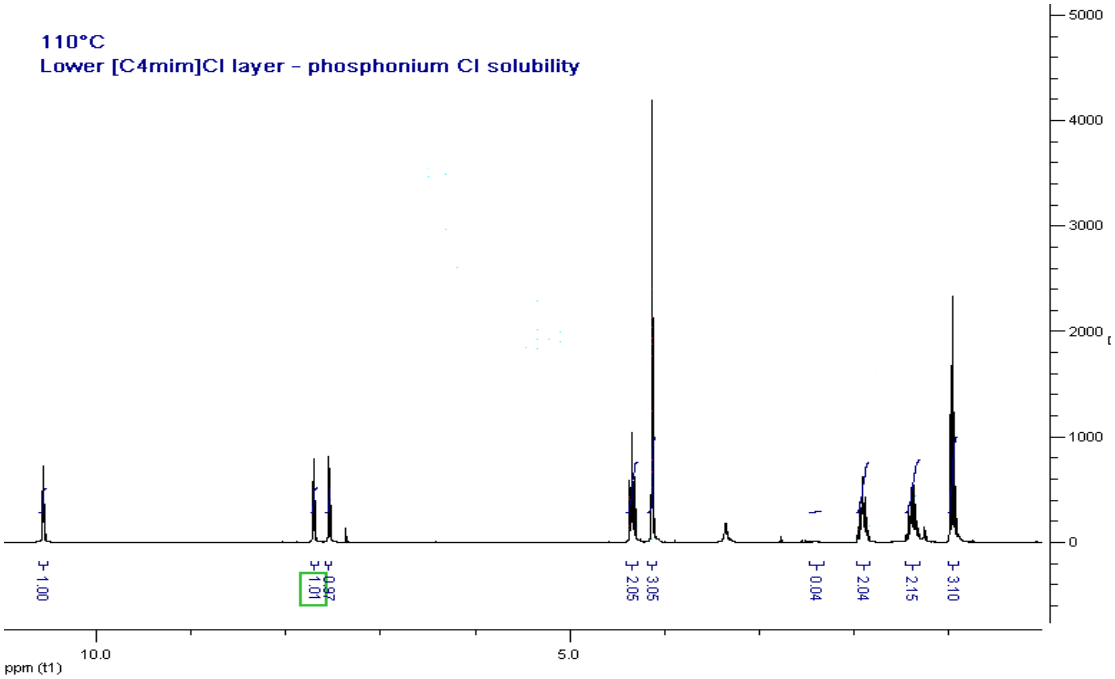

Figure 14. The solubility of $[C_{66614}P]Cl$ in [*n*-C_4mim]Cl at 110 °C (solvent = $CDCl_3$ / CD_3OD). Solubility = 0.48 mol %.