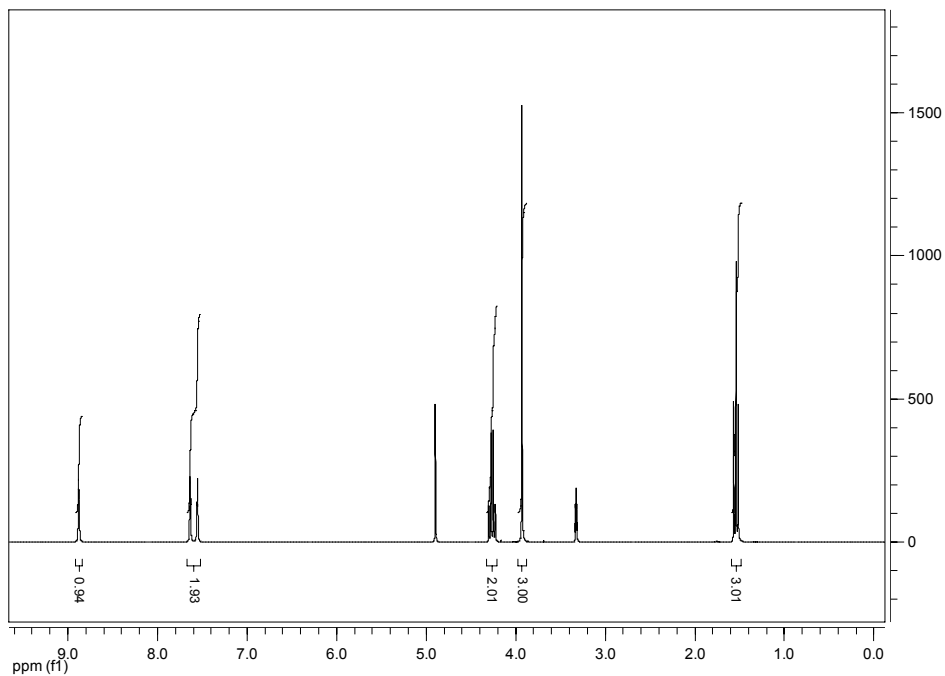


Supplementary Information

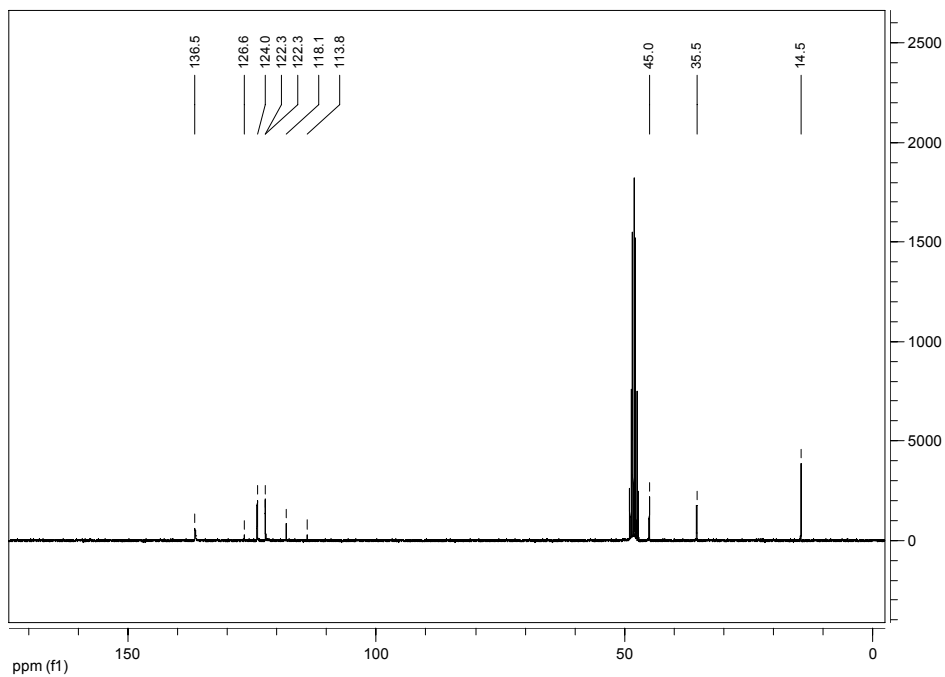
Details on the synthesis of the ionic liquids

Synthesis of 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C₂mim][NTf₂):

Alkylation of 1-methylimidazolium with chloroethane was carried out as described elsewhere (J. D. Holbrey et al., *Green Chem.*, 2001, **3**, 33-36) forming 1-ethyl-3-methylimidazolium chloride ([C₂mim]Cl). The latter was mixed in deionised water with lithium bis{(trifluoromethyl)sulfonyl}amide (Li[NTf₂]), in slight excess, thus obtaining the hydrophobic [C₂mim][NTf₂] by a metathetic reaction, which generated a denser non-aqueous phase. After the addition of dichloromethane, the organic phase was extracted and washed several times with fresh water, until no precipitation was observed by addition of silver nitrate to the residual aqueous phase, thus suggesting the absence of significant levels of chloride ions. The dichloromethane was removed in a rotary evaporator, and the purification process was completed by heating the ionic liquid at 70 °C for 24 h under high vacuum. A liquid with a slightly yellowish coloration was obtained. The structure of the desired product was confirmed by ¹H NMR and ¹³C NMR spectroscopy (see below). A water content of 150 ppm in the final product was measured by Karl Fischer titration.



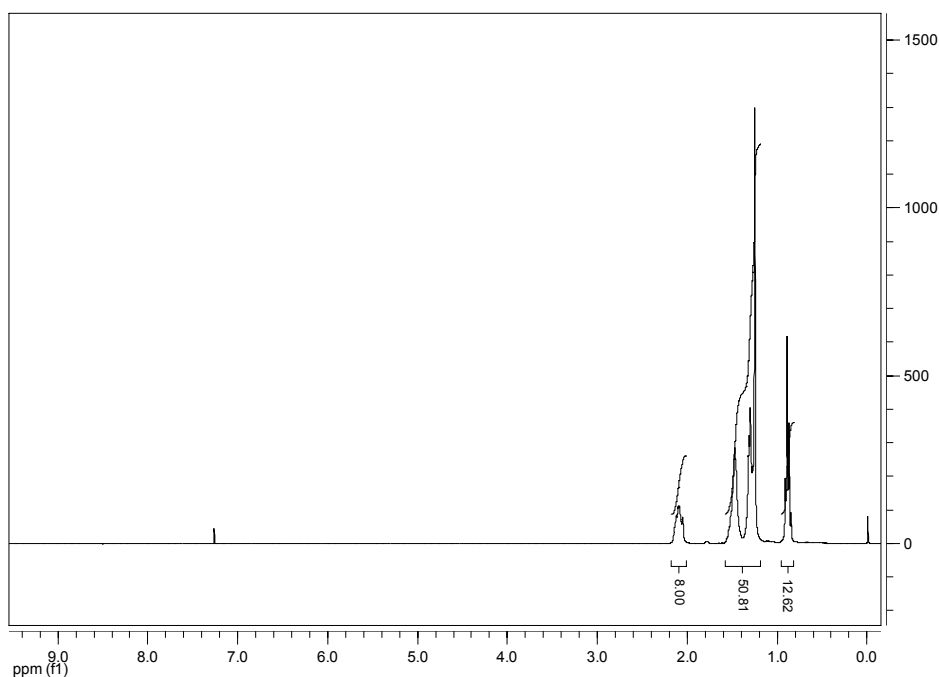
^1H NMR, δ_{H} (CD_3OD , 300 MHz): 1.54 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 3.93 (s, 3H, NCH_3), 4.26 (q, $J = 7.3$ Hz, 2H, NCH_2), 7.52-7.67 (m, unresolved, 2H, C(5)H and C(4)H), 8.88 (s, 1H, C(2)H).



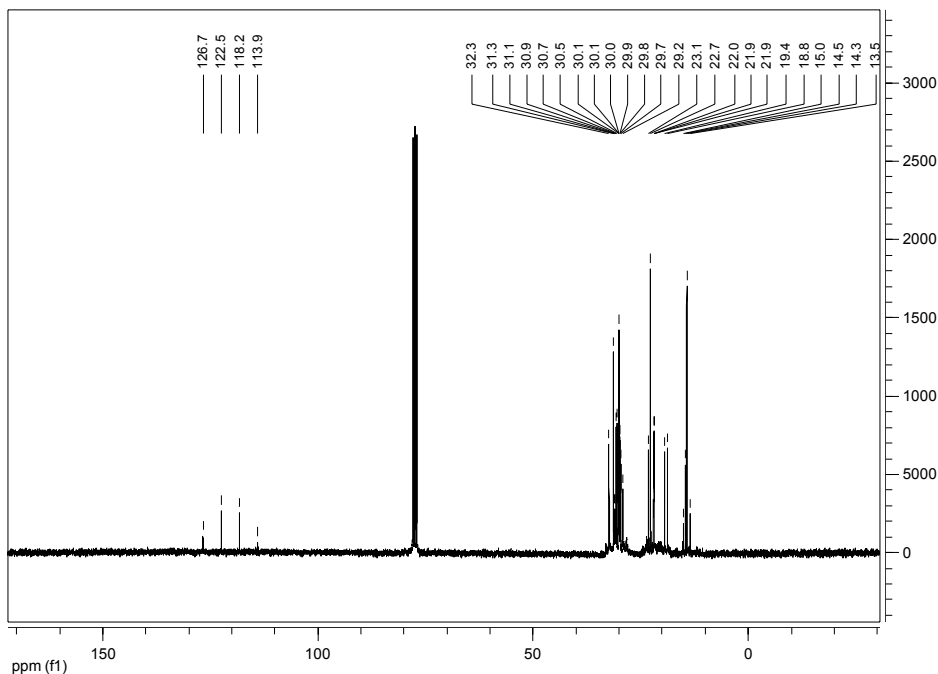
^{13}C NMR, δ_{C} (CD_3OD , 75.4 MHz): 14.5 (CH_2CH_3), 35.5 (NCH_3), 45.0 (NCH_2), 120.2 (q, $J_{\text{C-F}} = 321$ Hz, $2 \times \text{CF}_3$), 122.3 (C(4)H), 124.0 (C(5)H), 136.5 (C(2)H).

Synthesis of trihexyl(tetradecyl)phosphonium bis{(trifluoromethyl)sulfonyl}amide ([P_{6 6 6 14}][NTf₂]):

Trihexyl(tetradecyl)phosphonium chloride ([P_{6 6 6 14}]Cl), an ionic liquid itself, was supplied by Cytec. It was dissolved in dichloromethane and mixed with an aqueous solution of Li[NTf₂] in slight stoichiometric excess, stirring vigorously for several hours to get the desired [P_{6 6 6 14}][NTf₂] by ion metathesis. The resulting organic phase was isolated, and the dichloromethane was evaporated in a rotary evaporator. Final purification under high vacuum and spectroscopic characterisation of the ionic liquid were analogous to those described above for [C₂mim][NTf₂]. A viscous colourless ionic liquid was obtained. The water content of the final product was found to be less than 400 ppm, at its final structure was confirmed by ¹H NMR and ¹³C NMR (see below).



¹H NMR, δ_H (CDCl₃, 300 MHz): 0.82-0.95 (unresolved, 12H, 4 × CH₃), 1.19-1.58 (unresolved, 48H, PCH₂(CH₂)₁₂CH₃ and 3 × PCH₂(CH₂)₄CH₃), 2.01-2.18 (unresolved, 8H, 4 × PCH₂).

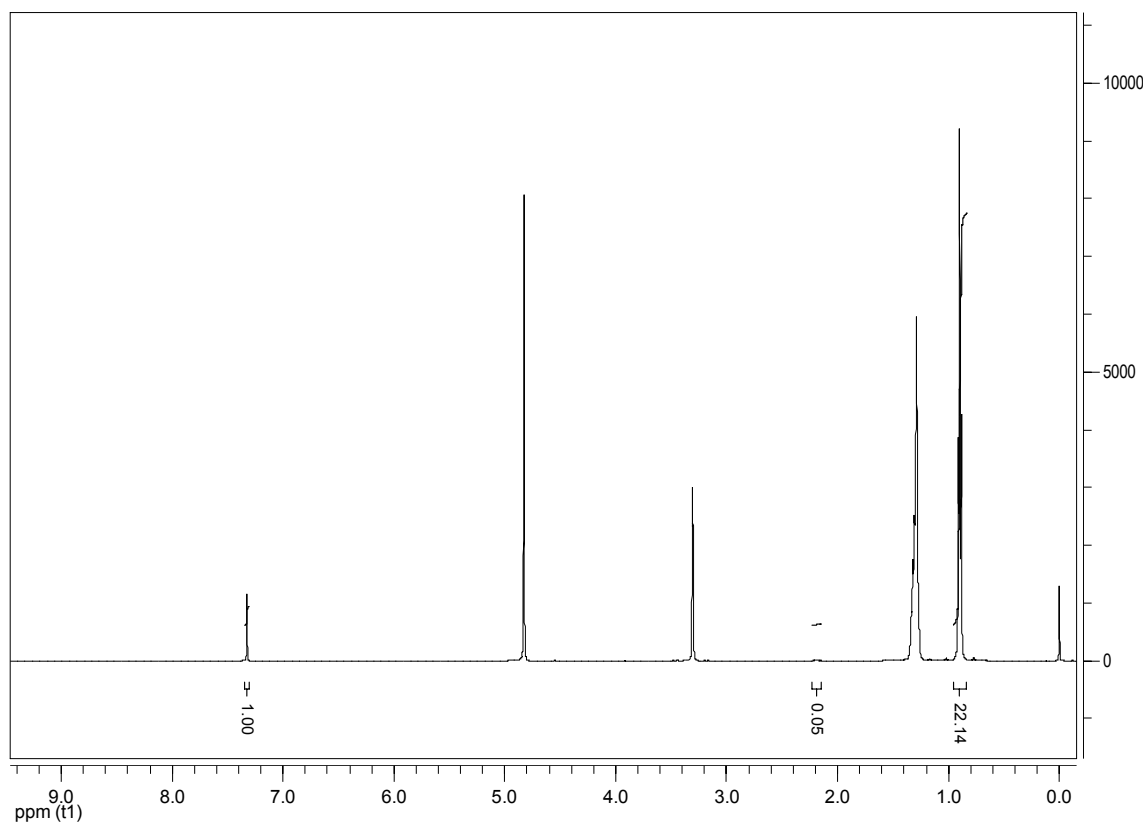


^{13}C NMR, δ_{C} (CDCl_3 , 75.4 MHz): 13-33 (unresolved, $\text{P}(\underline{\text{C}}\text{H}_2)_{13}\underline{\text{C}}\text{H}_3$ and $3 \times \text{P}(\underline{\text{C}}\text{H}_2)_5\underline{\text{C}}\text{H}_3$),
120.4 (q, $J_{\text{C-F}} = 322$ Hz, $2 \times \text{CF}_3$).

Examples of ^1H NMR spectra used in determining the phase compositions in the LLE experiments, as well as details on the calculations carried out to obtain the mole fractions from them

Here are shown, as an example, the three ^1H NMR spectra obtained for samples taken from each phase of one of the 3-phase equilibrium systems. Only the peaks of interest were integrated. The calculations made for obtaining the equilibrium compositions from the areas in the spectra, according to the procedure indicated in the experimental section of the article, are detailed below for each phase. Methanol-d₄ (CD_3OD) was used as the deuterated solvent. Relaxation times of 30 s were set in every NMR run.

1) Top phase:



Areas of the selected peaks (from left to right):

- Benzene (6H): 18358.44
- [C₂mim][NTf₂] (2H): 0.00
- [C₂mim][NTf₂] (3H): 0.00
- [P_{6,6,6,14}][NTf₂] (8H): 935.37
- Hexane (6H) + [P_{6,6,6,14}][NTf₂] (12H): 406493.30

Area per proton for each compound:

- Benzene:

$$\frac{18358.44}{6} = 3059.74$$

- [C₂mim][NTf₂]:

$$0$$

- [P_{6,6,6,14}][NTf₂]:

$$\frac{935.37}{8} = 116.92$$

- Hexane:

$$\frac{406493.30 - \left(12.45 \frac{8}{8}\right) 935.37}{6} = 67506.27$$

Mole fractions:

- Benzene:

$$\frac{3059.74}{3059.74 + 0 + 116.92 + 67506.27} = 0.043$$

- [C₂mim][NTf₂]:

$$0.000$$

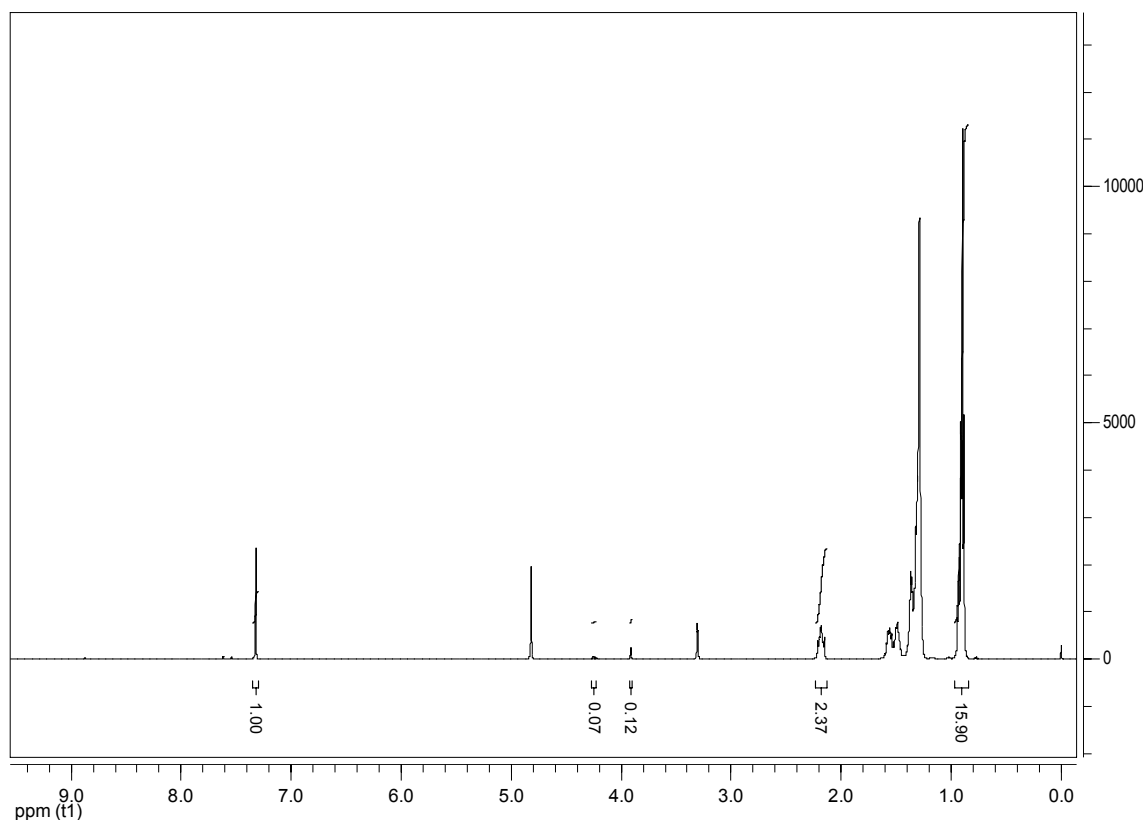
- [P_{6,6,6,14}][NTf₂]:

$$\frac{116.92}{3059.74 + 0 + 116.92 + 67506.27} = 0.002$$

- Hexane:

$$\frac{67506.27}{3059.74 + 0 + 116.92 + 67506.27} = 0.955$$

2) Medium phase:



Areas of the selected peaks (from left to right):

- Benzene (6H): 38782.67
- [C₂mim][NTf₂] (2H): 2685.16
- [C₂mim][NTf₂] (3H): 4774.28
- [P_{6,6,6,14}][NTf₂] (8H): 91792.25
- Hexane (6H) + [P_{6,6,6,14}][NTf₂] (12H): 616769.90

Area per proton for each compound:

- Benzene:

$$\frac{38782.67}{6} = 6463.78$$

- [C₂mim][NTf₂]:

$$\frac{1}{2} \left(\frac{2685.16}{2} + \frac{4774.28}{3} \right) = 1467.00$$

- [P_{6,6,6,14}][NTf₂]:

$$\frac{91792.25}{8} = 11474.03$$

- Hexane:

$$\frac{616769.90 - \left(12.45 \frac{8}{8}\right) 91792.25}{6} = 78986.37$$

Mole fractions:

- Benzene:

$$\frac{6463.78}{6463.78 + 1467.00 + 11474.03 + 78986.37} = 0.066$$

- [C₂mim][NTf₂]:

$$\frac{1467.00}{6463.78 + 1467.00 + 11474.03 + 78986.37} = 0.015$$

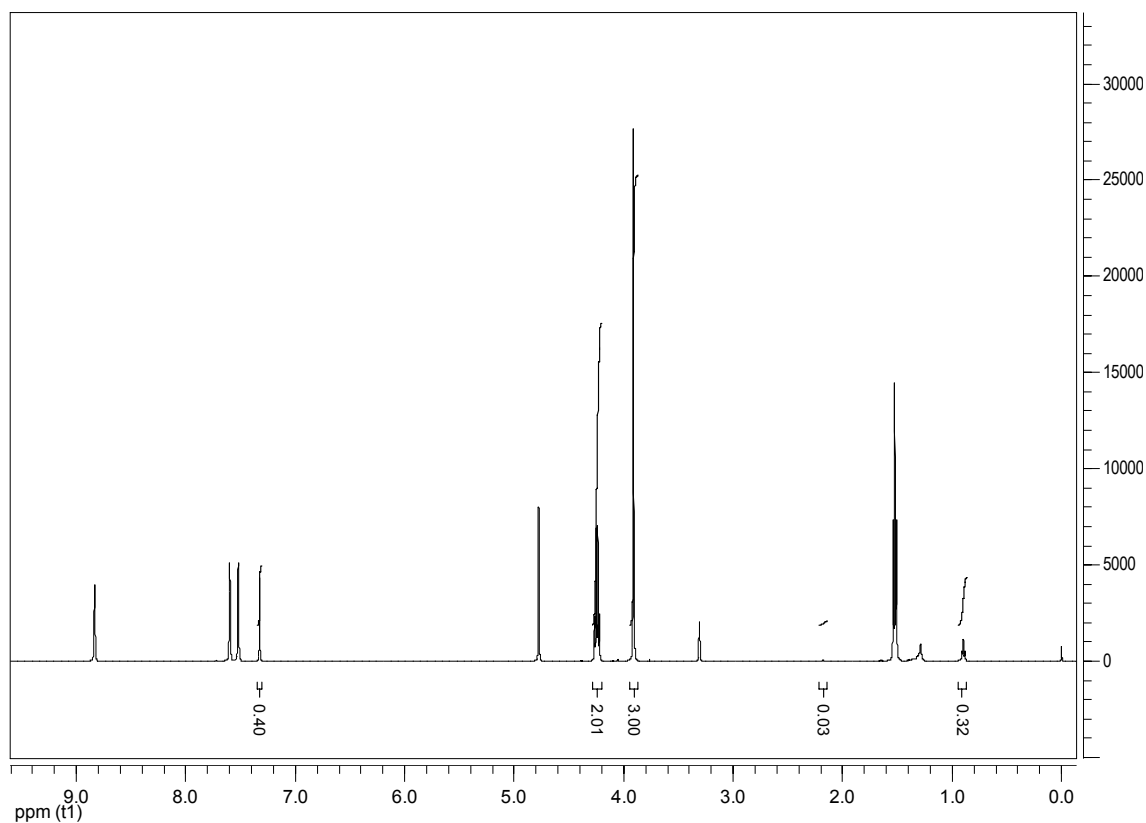
- [P_{6,6,6,14}][NTf₂]:

$$\frac{11474.03}{6463.78 + 1467.00 + 11474.03 + 78986.37} = 0.117$$

- Hexane:

$$\frac{78986.37}{6463.78 + 1467.00 + 11474.03 + 78986.37} = 0.803$$

3) Bottom phase:



Areas of the selected peaks (from left to right):

- Benzene (6H): 73760.27
- [C₂mim][NTf₂] (2H): 372650.00
- [C₂mim][NTf₂] (3H): 555884.50
- [P_{6,6,6,14}][NTf₂] (8H): 5438.26
- Hexane (6H) + [P_{6,6,6,14}][NTf₂] (12H): 58574.75

Area per proton for each compound:

- Benzene:

$$\frac{73760.27}{6} = 12293.38$$

- [C₂mim][NTf₂]:

$$\frac{1}{2} \left(\frac{372650.00}{2} + \frac{555884.50}{3} \right) = 185809.92$$

- [P_{6,6,6,14}][NTf₂]:

$$\frac{5438.26}{8} = 679.78$$

- Hexane:

$$\frac{58574.75 - \left(\frac{12.45}{8}\right)5438.26}{6} = 8351.91$$

Mole fractions:

- Benzene:

$$\frac{12293.38}{12293.38 + 185809.92 + 679.78 + 8351.91} = 0.059$$

- [C₂mim][NTf₂]:

$$\frac{185809.92}{12293.38 + 185809.92 + 679.78 + 8351.91} = 0.897$$

- [P_{6,6,6,14}][NTf₂]:

$$\frac{679.78}{12293.38 + 185809.92 + 679.78 + 8351.91} = 0.003$$

- Hexane:

$$\frac{8351.91}{12293.38 + 185809.92 + 679.78 + 8351.91} = 0.040$$