Electronic Supplementary Information†

The impact of ionic liquids fluorinated moieties on their thermophysical properties and aqueous phase behaviour

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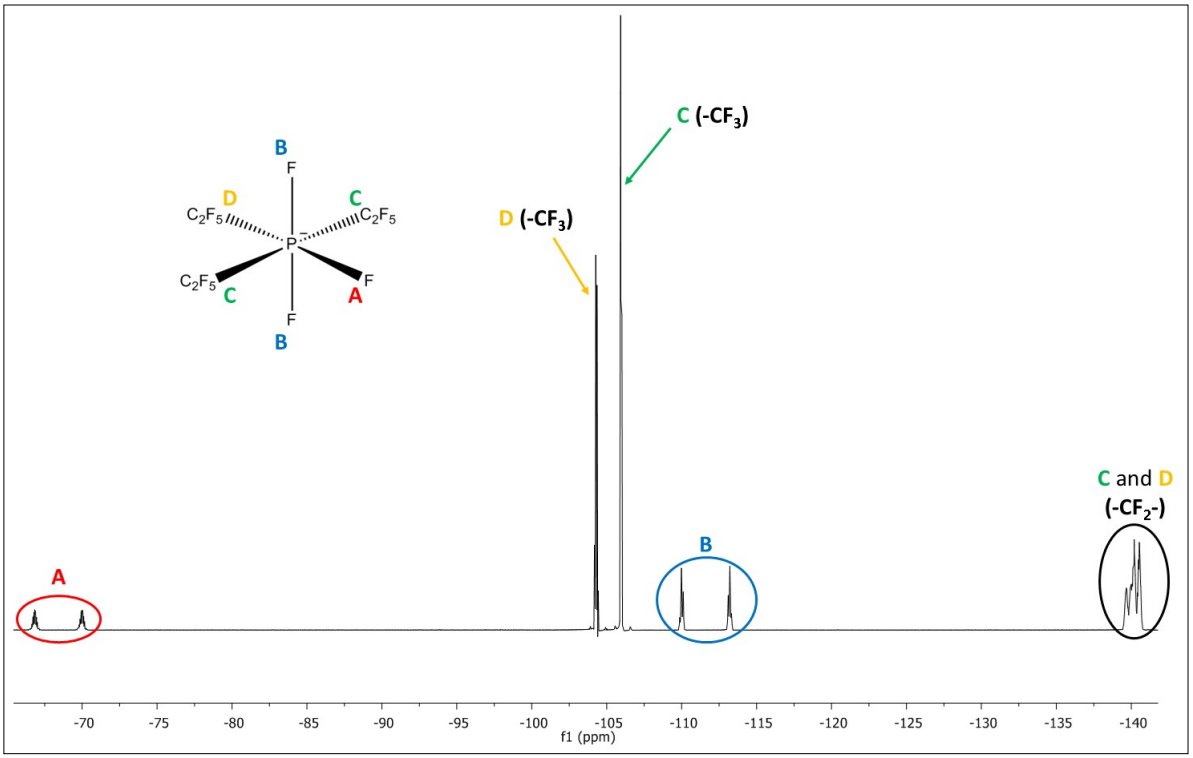

Fig. S1. ^{19}F NMR spectra of [C_2C_1im][FAP].

Table S1. Experimental density, ρ, and viscosity, η, for pure ILs as function of temperature and at 0.1 MPa.

T / K	ρ / (kg·m^{-3})		η / (mPa·s)	
	[C_2C_1im][FAP]	[C_2C_1im][PF_6]	[C_2C_1im][FAP]	[C_2C_1im][PF_6]
278.15	1726.7	---	168.750	---
283.15	1720.6	---	126.710	---
288.15	1714.5	---	97.357	---
293.15	1708.1	---	76.410	---
298.15	1701.6	---	61.022	---
303.15	1695.0	---	49.617	---
308.15	1688.3	---	40.934	---
313.15	1681.6	---	34.213	---
318.15	1674.9	---	28.934	---
323.15	1668.2	---	24.722	---
328.15	1661.5	---	21.327	---
333.15	1654.8	---	18.552	---
338.15	1648.4	1437.6	16.263	26.830
343.15	1641.9	1433.3	14.355	23.296
348.15	1635.4	1429.1	12.726	20.330
353.15	1629.1	1424.8	11.371	17.920
358.15	1622.8	1420.6	10.216	15.810
363.15	1616.6	1416.4	9.223	14.075

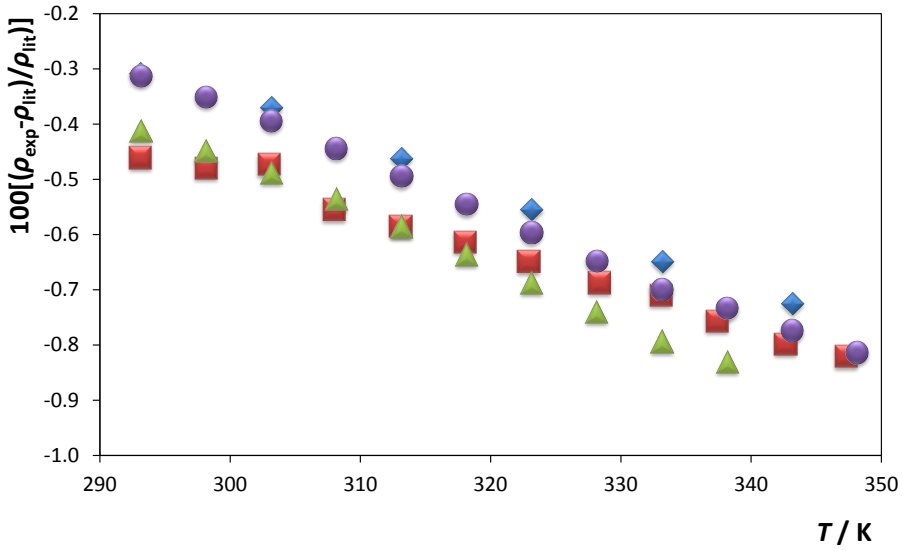

Fig. S2. Relative deviations between the experimental densities measured in this work (ρ_{exp}) and those reported in literature (ρ_{lit}) as a function of temperature for $[C_2C_1im][FAP]$: ∞, Seki et al.[1]; ◘, Liu et al.[2]; ◆, Almantariotis et al.[3]; O, Součková et al.[4].

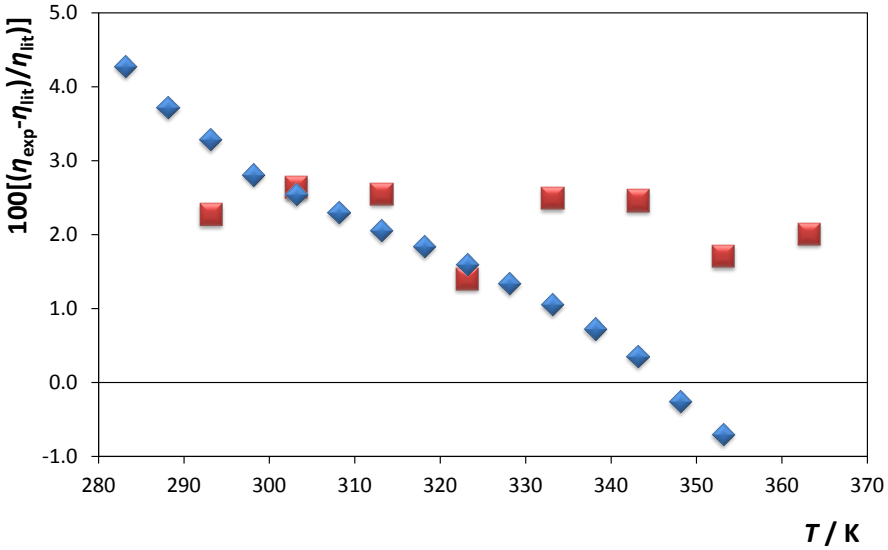

Fig. S3. Relative deviations between the experimental viscosities measured in this work (η_{exp}) and those reported in literature (η_{lit}) as a function of temperature for $[C_2C_1im][FAP]$: ◆, Seki et al.[1]; O, Almantariotis et al.[3].

Table S2. Experimental mole fraction solubility of water in ILs, x_w, and of ILs in water, x_{IL}, as a function of temperature and at 0.1 MPa.

	[C_2C_1im][FAP]		[C_2C_1im][PF_6]	
T / K	$10^5 \times (x_{IL} \pm \sigma^a)$	$10^1 \times (x_w \pm \sigma^a)$	$10^2 \times (x_{IL} \pm \sigma^a)$	$x_w \pm \sigma^a$
288.15	0.999 ± 0.014	0.577 ± 0.008	0.167 ± 0.003	---
293.15	1.325 ± 0.034	0.614 ± 0.021	0.260 ± 0.008	---
298.15	1.624 ± 0.024	0.682 ± 0.011	0.288 ± 0.002	---
303.15	1.805 ± 0.019	0.769 ± 0.006	0.567 ± 0.005	---
308.15	1.965 ± 0.238	0.835 ± 0.018	0.848 ± 0.006	---
313.15	2.164 ± 0.041	0.923 ± 0.022	1.027 ± 0.003	---
318.15	2.483 ± 0.009	1.010 ± 0.018	1.148 ± 0.004	---
333.15	3.011 ± 0.066	1.387 ± 0.001	1.785 ± 0.082	---
338.15	3.313 ± 0.007	1.541 ± 0.012	1.973 ± 0.072	---
343.15	3.643 ± 0.036	1.633 ± 0.070	2.191 ± 0.078	0.644 ± 0.015
348.15	3.845 ± 0.004	1.756 ± 0.018	2.365 ± 0.086	0.694 ± 0.024
353.15	4.070 ± 0.010	1.831 ± 0.006	2.529 ± 0.083	0.733 ± 0.011
358.15	4.499 ± 0.021	1.947 ± 0.007	2.712 ± 0.079	0.765 ± 0.004
363.15	4.753 ± 0.058	2.073 ± 0.024	2.934 ± 0.073	0.802 ± 0.074

[a] Standard deviation

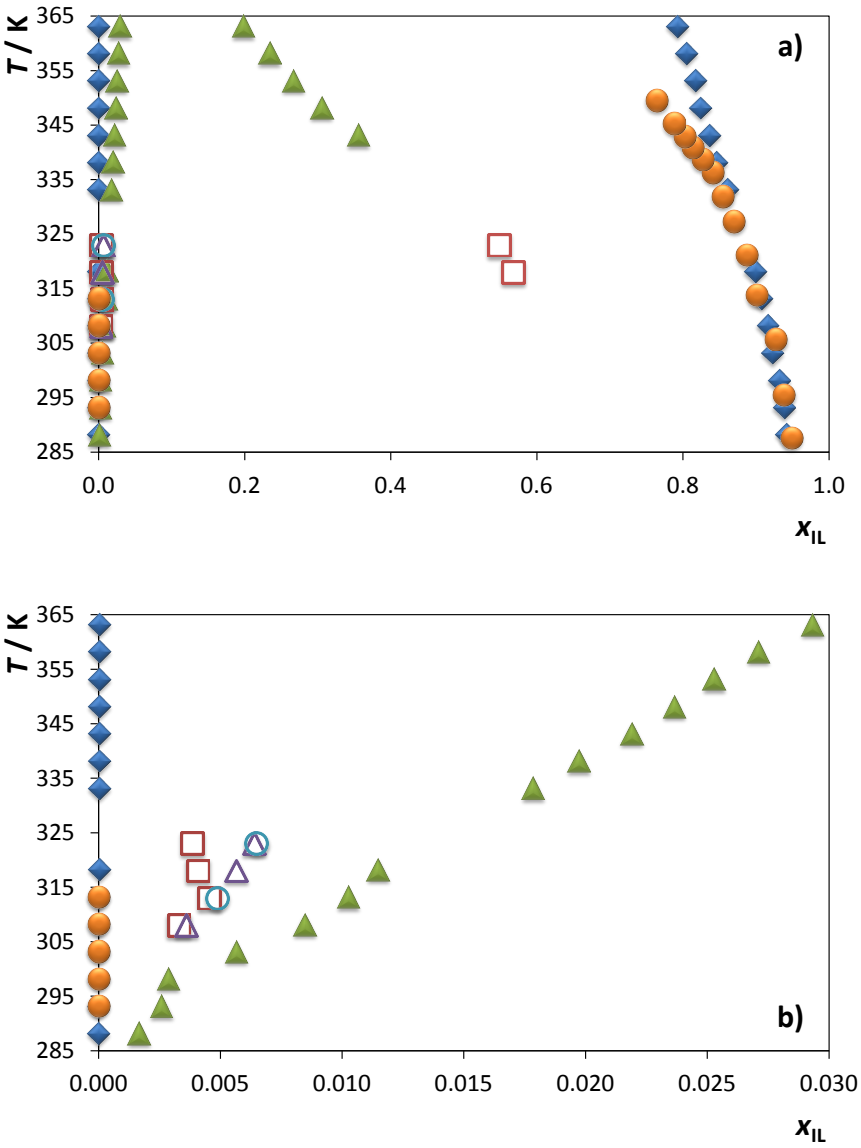

Fig. S4. LLE phase diagrams obtained in this work (□, $[C_2C_1im][PF_6]$; ◆, $[C_2C_1im][FAP]$) and those reported in literature: ○, Wong et al.[5] with values obtained by KF; ∽, Wong et al.[5] with values obtained by UV; ❒, Wong et al.[5] with values obtained by TGA; ∽, Domańska et al.[6] with values obtained by UV (solubility of IL in water) and dynamic (synthetic) method (solubility of water in IL).

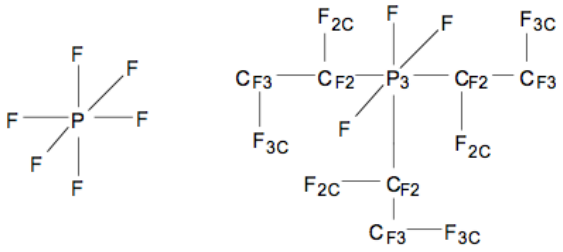

Fig. S4. Nomenclature adopted for the atomistic force-field modeling of the $[PF_6]^-$ (left) and $[FAP]^-$ (right) anions (equivalent atoms are not shown in the latter scheme for clarity reasons).

Table S1. Force field non-bonded parameters - atomic point charges (q), Lennard-Jones diameter and interaction parameters (σ_{LJ} and ε_{LJ}) - for the $[PF_6]^-$ and $[FAP]^-$ anions adopted in this work.[7-10] The different partial charges conferred to each type of atom in the two ions are highlighted in bold. These were calculated using quantum-mechanics methods described in literature.[8-10]

$[PF_6]^-$ [7-9]			
atom	q (a.c.u.)	σ_{LJ} (10^{-10}m)	ε_{LJ} / (kJ/mol)
P	**1.34**	3.74	0.8368
F	**-0.39**	3.12	0.2552
$[FAP]^-$ [10]			
P3	**0.62**	3.74	0.8368
CF2	**0.24**	3.50	0.27614
F2C	**-0.12**	3.12	0.2552
CF3	**0.42**	3.50	0.27614
F3C	**-0.19**	3.12	0.2552

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