SUPPORTING INFORMATION

Solid-Liquid Equilibria for Hexafluorophosphate-Based Ionic Liquid Quaternary Mixtures and Their Corresponding Subsystems

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Composition variables relevant for the present work :

The composition variables χ_{AB} that are relevant for the present work are given by :

$$\chi_{[C_3mpy][C_3mim]} = x_{[C_3mpy][C_3mpy]} / \left(x_{[C_3mpy][C_3mpy]} + x_{[C_3mim][C_3mim]} + x_{[C_3mpy][C_3mim]} \right) \quad \text{(S1)}$$

$$\chi_{[C_3mpip][C_3mim]} = \chi_{[C_3mpyrr][C_3mim]} \quad \text{(S2)}$$

$$= \left(x_{[C_3mpip][C_3mpip]} + x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mpyrr]} \right)$$

$$/ \left(x_{[C_3mpip][C_3mpip]} + x_{[C_3mim][C_3mim]} + x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mim]} \right.$$

$$\left. + x_{[C_3mpip][C_3mpyrr]} + x_{[C_3mim][C_3mpyrr]} \right)$$

$$\chi_{[C_3mim][C_3mpip]} = \chi_{[C_3mim][C_3mpyrr]} \quad \text{(S3)}$$

$$= x_{[C_3mim][C_3mim]}$$

$$/ \left(x_{[C_3mpip][C_3mpip]} + x_{[C_3mim][C_3mim]} + x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mim]} \right.$$

$$\left. + x_{[C_3mpip][C_3mpyrr]} + x_{[C_3mim][C_3mpyrr]} \right)$$

$$\chi_{[C_3mpy][C_3mpyrr]} \quad \text{(S4)}$$

$$= x_{[C_3mpy][C_3mpy]}$$

$$/ \left(x_{[C_3mpy][C_3mpy]} + x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mpip]} + x_{[C_3mpy][C_3mpyrr]} \right.$$

$$\left. + x_{[C_3mpy][C_3mpip]} + x_{[C_3mpyrr][C_3mpip]} \right)$$

$$\chi_{[C_3mpyrr][C_3mpy]} = \chi_{[C_3mpip][C_3mpy]} \quad \text{(S5)}$$

$$= \left(x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mpip]} + x_{[C_3mpyrr][C_3mpip]} \right)$$

$$/ \left(x_{[C_3mpy][C_3mpy]} + x_{[C_3mpyrr][C_3mpyrr]} + x_{[C_3mpip][C_3mpip]} + x_{[C_3mpy][C_3mpyrr]} \right.$$

$$\left. + x_{[C_3mpy][C_3mpip]} + x_{[C_3mpyrr][C_3mpip]} \right)$$

where x_{AB} is the mole fraction of second-nearest-neighbor (*A*-[PF_6]-*B*) pairs. Note that, for any binary system *A*[PF_6]-*B*[PF_6] (where *A*, *B* = [C_3mim], [C_3mpy], [C_3mpip], [C_3mpyrr]), Equations (S1-S5) reduce to:

$$\chi_{AB} = x_{AA} \qquad \text{(S6)}$$

Table S1 : Experimental DSC data for the ternary mixtures of ionic liquids, for mole fraction *x*, transition temperature *T* and pressure *p* = 102.0 kPa :

For most DSC measurements, one cooling run was followed by one heating run, and only the thermal transitions of the heating run are reported. For a few ternary mixtures (identified with *), three consecutive heating/cooling cycles were used, and only the thermal transitions of the last two heating runs are reported. The following notations are used : [C_3mim][PF_6] (1), [C_3mpy][PF_6] (2), [C_3mpip][PF_6] (3), and [C_3mpyrr][PF_6] (4).

Ternary system (1) + (3) + (4)				Ternary system (2) + (3) + (4)			
Isoplethal section $x_1 = 0.4$		Isoplethal section $x_4 / (x_3 + x_4) = 0.6$		Isoplethal section $x_2 = 0.4$		Isoplethal section $x_4 / (x_3 + x_4) = 0.6$	
x_4	T (°C)	x_1	T (°C)	x_4	T (°C)	x_2	T (°C)
0.100	32.2	0.251	6.6	0.103	24.6	0.166	62.9
0.200	40.6	0.251	40.8	0.103	25.5	0.166	64.3
0.201	20.3	0.375	7.1	0.300	23.9	0.418	-0.8
0.300	32.6	0.749	0.0	0.300	37.2	0.418	25.5
0.401	31.3	0.749	5.0	0.501	1.3	0.666	0.8
0.500	33.1	0.749	23.7	0.501	10.8	0.666	10.1
0.550	26.5	0.874	-0.3	0.501	29.9	0.666	19.5
		0.874	7.3				
0.100	25.9	0.874	29.4				
0.201	9.6						
0.201	27.7	0.122*	69.6*				
0.401	4.2	0.122*	69.9*				
0.500	16.2						
0.552	8.6						
0.552	23.7						

Ternary system (1) + (2) + (3)				Ternary system (1) + (2) + (4)			
Isoplethal section $x_2 = 0.4$		Isoplethal section $x_2 / (x_1 + x_2) = 0.6$		Isoplethal section $x_2 = 0.4$		Isoplethal section $x_2 / (x_1 + x_2) = 0.6$	
x_3	T (°C)	x_3	T (°C)	x_4	T (°C)	x_4	T (°C)
0.099	-10.2	0.123	13.2	0.102	-12.9	0.139	13.1
0.099	2.3	0.255	13.2	0.102	4.1	0.415	-26.9
0.498	39.5	0.379	24.0	0.298	-4.0	0.660	41.1
0.498	42.3	0.505	-23.3	0.492	7.9		
0.519	39.9	0.505	40.8				
0.519	42.4	0.619	39.9				
		0.619	53.0				
0.059*	-9.4*	0.751	41.4				
0.059*	8.3*	0.751	56.2				
0.059*	-8.8*	0.868	40.6				
0.059*	0.6*	0.868	70.8				
0.059*	9.6*						

Discussion of the first and second scenarios for the [C_3mim][PF_6] - [C_3mpip][PF_6] - [C_3mpyrr][PF_6] system : Figures S1 and S2 display the calculated liquidus projections of the [C_3mim][PF_6] - [C_3mpip][PF_6] - [C_3mpyrr][PF_6] system corresponding to the first and second scenarios, respectively. As reported previously, [C_3mpyrr][PF_6] and [C_3mpip][PF_6] both have three allotropes (s_1, s_2, s_3). The first scenario assumes a negligible solid solubility between the low-temperature allotropes (s_1-s_1) and also between the intermediate-temperature allotropes (s_2-s_2) whereas the second scenario assumes a continuous solid solution between the low-temperature allotropes (s_1-s_1) and also between the intermediate-temperature allotropes (s_2-s_2). The calculated liquidus projection with the first scenario exhibits a ternary eutectic reaction at -9 °C (see Figure S1), while the one with the second scenario displays no ternary invariant reaction (see Figure S2).

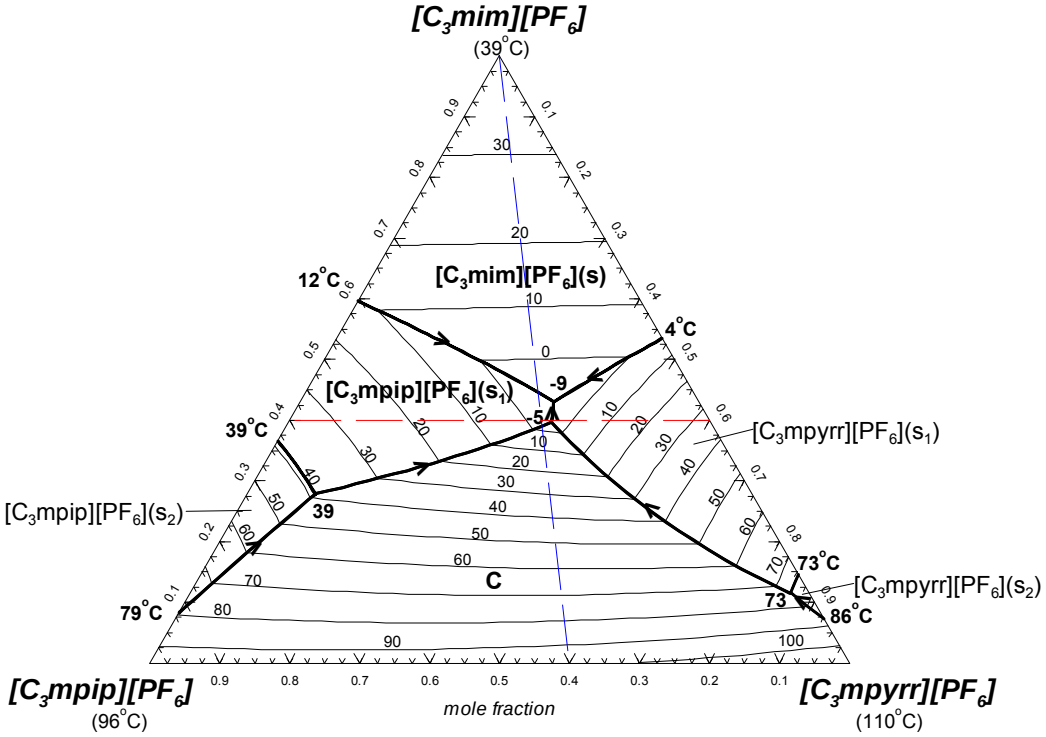


Figure S1 : Calculated liquidus projection of the $[C_3mim][PF_6]$ - $[C_3mpip][PF_6]$ – $[C_3mpyrr][PF_6]$ system with the first scenario. Notations : C = {$[C_3mpip][PF_6](s_3)$ – $[C_3mpyrr][PF_6](s_3)$}(ss). The isoplethal sections at constant 40 mol% $[C_3mim][PF_6]$ (red dashed line) and at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60 (blue dashed line) are shown schematically.

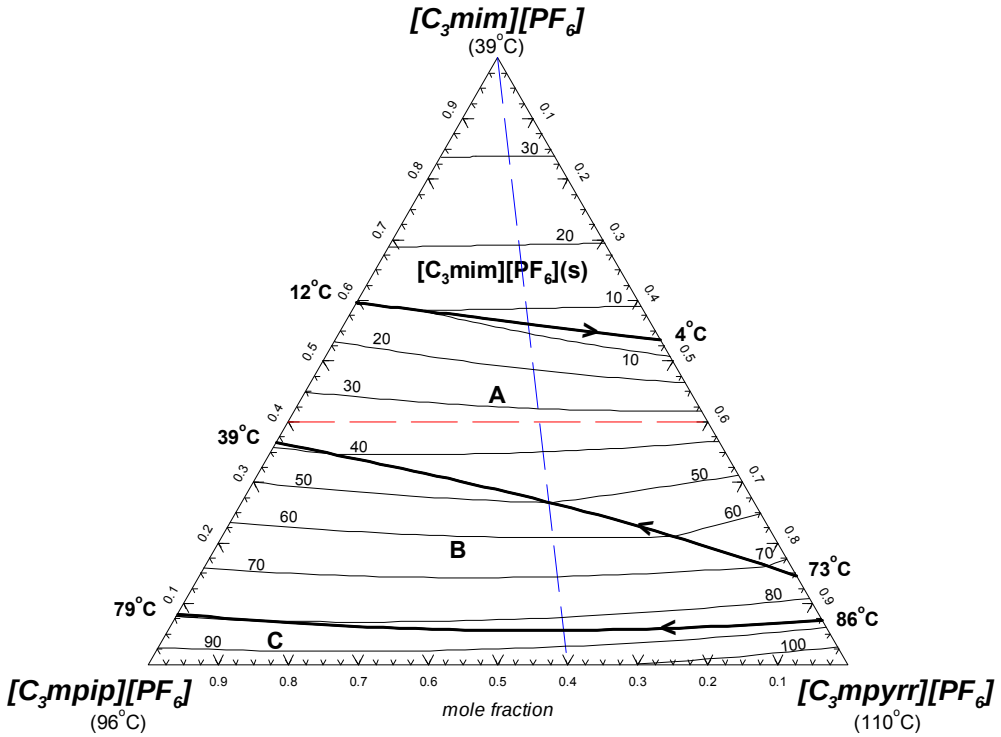


Figure S2 : Calculated liquidus projection of the $[C_3mim][PF_6]$ - $[C_3mpip][PF_6]$ - $[C_3mpyrr][PF_6]$ system with the second scenario. Notations : A={$[C_3mpip][PF_6](s_1)$ – $[C_3mpyrr][PF_6](s_1)$}(ss); B={$[C_3mpip][PF_6](s_2)$ – $[C_3mpyrr][PF_6](s_2)$}(ss); C={$[C_3mpip][PF_6](s_3)$ – $[C_3mpyrr][PF_6](s_3)$}(ss). The isoplethal sections at constant 40 mol% $[C_3mim][PF_6]$ (red dashed line) and at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60 (blue dashed line) are shown schematically.

As explained in the main article, in order to identify the most probable scenario, the isoplethal sections at constant 40 mol% $[C_3mim][PF_6]$ (red dashed line in Figures S1 and S2) and at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60 (blue dashed line in Figures S1 and S2) were measured using DSC. The liquidus lines of both isoplethal sections according to the two scenarios were also calculated.

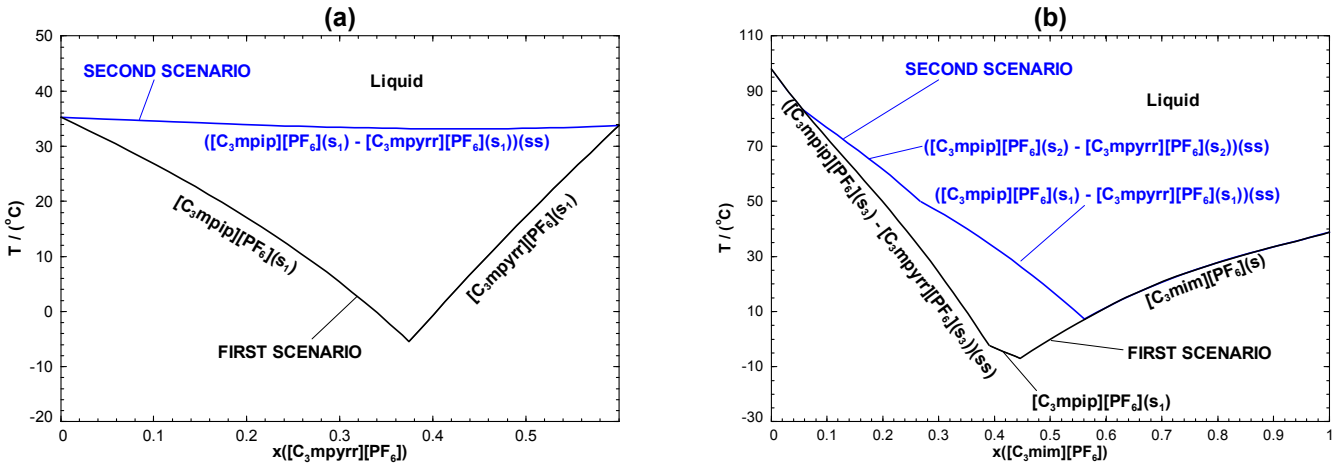


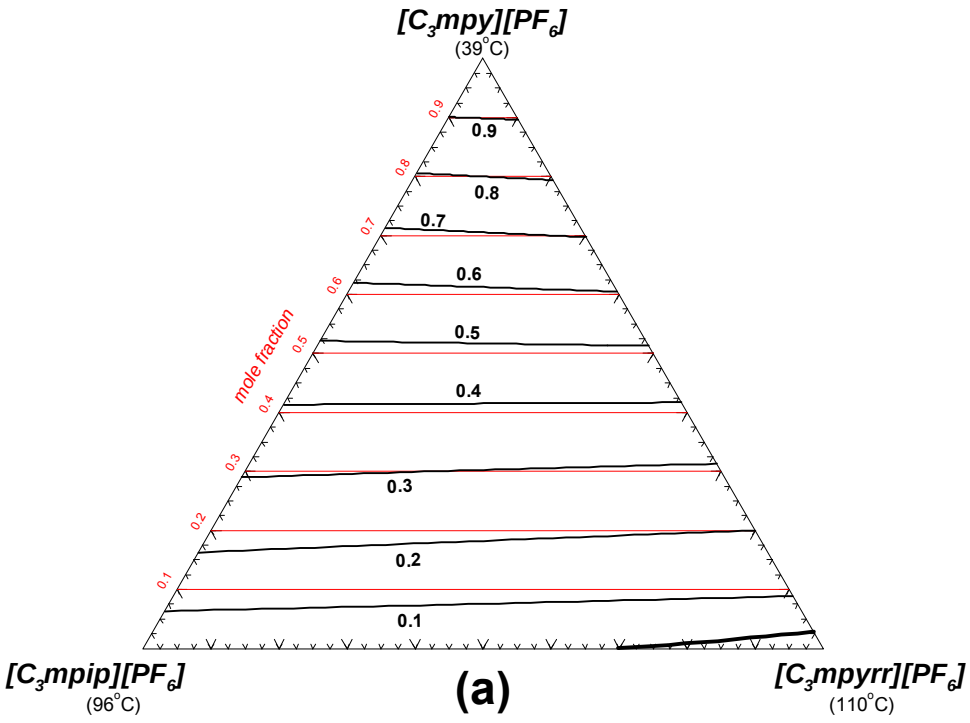
Figure S3 : Calculated liquidus lines for the isoplethal sections at constant 40 mol% $[C_3mim][PF_6]$ {**(a)**} and at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60 {**(b)**} in the $[C_3mim][PF_6]$ - $[C_3mpip][PF_6]$ - $[C_3mpyrr][PF_6]$ system with the first (black line) and second (blue line) scenarios.

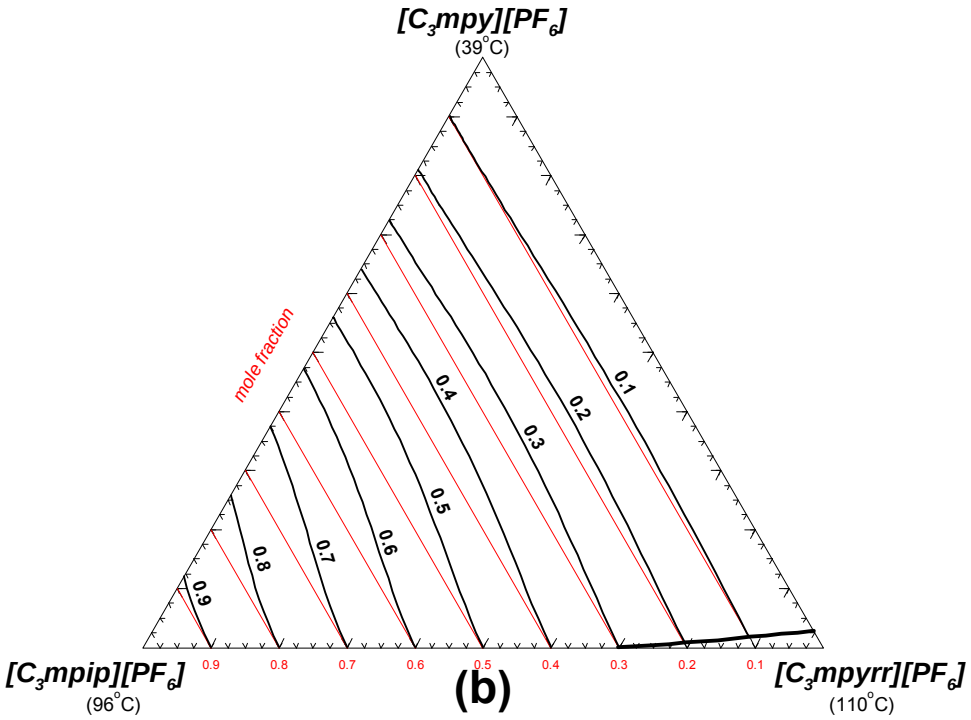
For the isoplethal section at constant 40 mol% $[C_3mim][PF_6]$ (see Figure S3(a)), the first scenario gives two liquidus lines (in black), corresponding to the precipitation of the low-temperature allotropes $[C_3mpip][PF_6](s_1)$ or $[C_3mpyrr][PF_6](s_1)$, while there is an almost flat liquidus line corresponding to the precipitation of the $[C_3mpip][PF_6](s_1)$ - $[C_3mpyrr][PF_6](s_1)$ low-temperature solid solution for the second scenario (blue line). For the isoplethal section at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60 (see Figure S3(b)), the first scenario (in black) gives a liquidus line corresponding to the successive precipitation of {$[C_3mpip][PF_6](s_3)$ - $[C_3mpyrr][PF_6](s_3)$}(ss), $[C_3mpip][PF_6](s_1)$ and $[C_3mim][PF_6]$. For the second scenario (in blue), the solid phases precipitating are successively {$[C_3mpip][PF_6](s_3)$ - $[C_3mpyrr][PF_6](s_3)$}(ss), {$[C_3mpip][PF_6](s_2)$ - $[C_3mpyrr][PF_6](s_2)$}(ss), {$[C_3mpip][PF_6](s_1)$ - $[C_3mpyrr][PF_6](s_1)$}(ss) and $[C_3mim][PF_6]$. Figures 6(a) and 6(b) (in the main article) display the measured and calculated isoplethal sections at constant 40 mol% $[C_3mim][PF_6]$ and at a constant molar ratio $[C_3mpyrr][PF_6]$ / ($[C_3mpyrr][PF_6]$ + $[C_3mpip][PF_6]$) of 0.60, respectively. The second scenario has finally been favored based on the available ternary experimental data. As seen in zone 1 in Figure 6(a), the measured liquidus temperatures virtually do not change as a function of the mole fraction of $[C_3mpyrr][PF_6]$ in the ternary mixture. This is consistent with the second scenario (see Figure S3(a)). As reported previously, no ternary excess parameter was included for the liquid phase, and the excess Gibbs energies of the low temperature (s_1-s_1) and intermediate-temperature (s_2-s_2) $[C_3mpip][PF_6]$ – $[C_3mpyrr][PF_6]$ binary solid solutions were adjusted (see Table 3 in the main article) in

order to best reproduce the ternary data. The final calculated liquidus projection of the [C_3mim][PF_6] - [C_3mpip][PF_6] - [C_3mpyrr][PF_6] system is shown in Figure 5 (main article).

Deviations from ideality in the {[C_3mpy], [C_3mpip], [C_3mpyrr]}[PF_6], {[C_3mpip], [C_3mpy], [C_3mim]}[PF_6] and {[C_3mpyrr], [C_3mpy], [C_3mim]}[PF_6] ternary liquids :

The iso-activity lines (relative to liquid standard state) of the three components in the {[C_3mpy], [C_3mpip], [C_3mpyrr]}[PF_6], {[C_3mpip], [C_3mpy], [C_3mim]}[PF_6] and {[C_3mpyrr], [C_3mpy], [C_3mim]}[PF_6] common-anion ternary liquids calculated at 100 °C are shown in Figures S4, S6 and S8, respectively. The ideal case is represented by the thin red lines, which correspond to a constant mole fraction of the investigated component. For each of the three ternary liquids, the activity coefficients of all three components were calculated at 100 °C along the two isoplethal sections investigated by DSC. These calculations are displayed in Figures S5, S7 and S9, respectively.





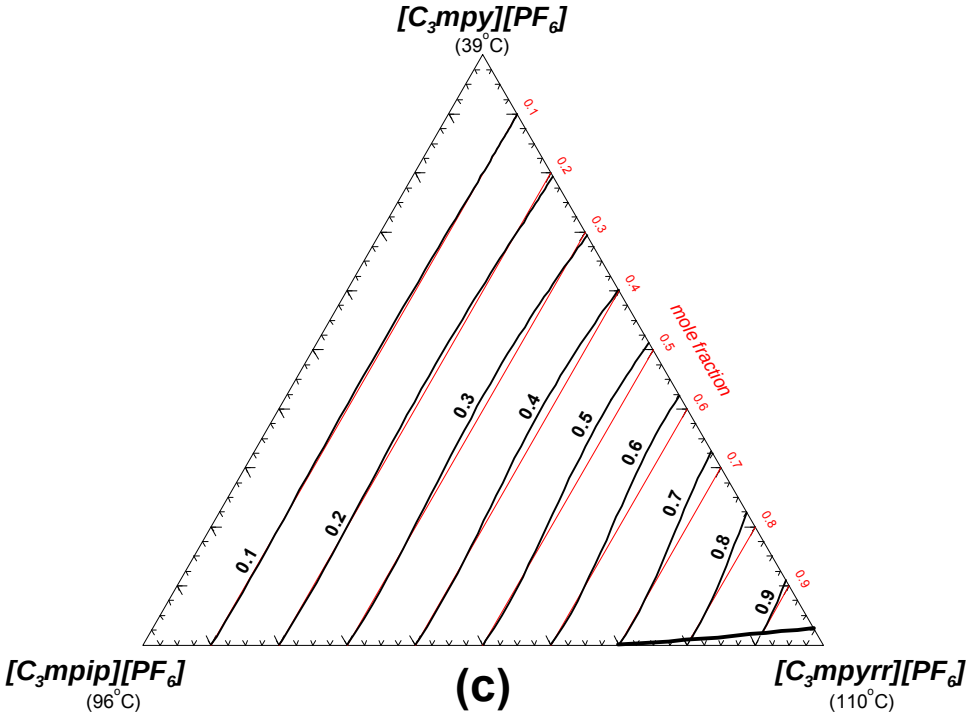


Figure S4 : Calculated iso-activity lines (liquid standard state) at 100 °C in the [C3mpy][PF6] - [C3mpip][PF6] - [C3mpyrr][PF6] ternary liquid for : **(a)** [C3mpy][PF6]; **(b)** [C3mpip][PF6]; and **(c)** [C3mpyrr][PF6]. The ideal case is represented by the thin red lines, which correspond to a constant mole fraction of the investigated component.

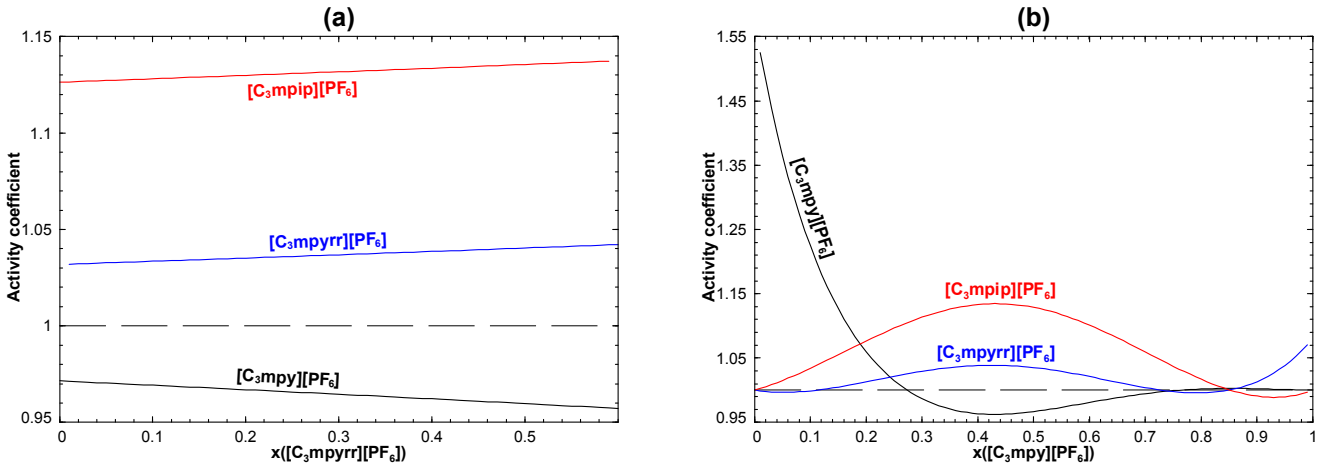
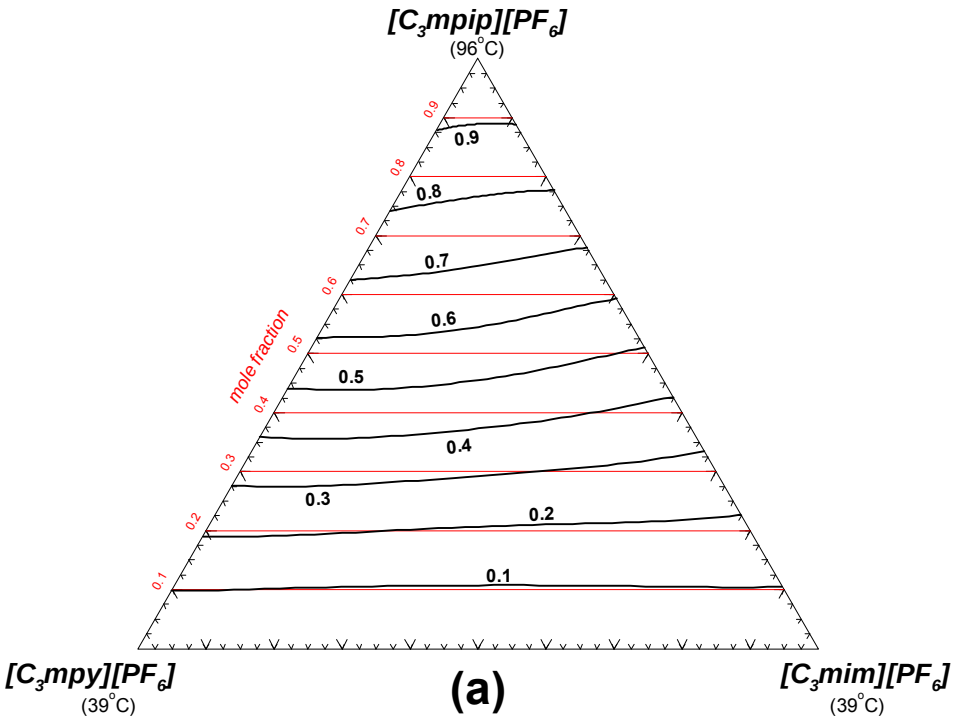
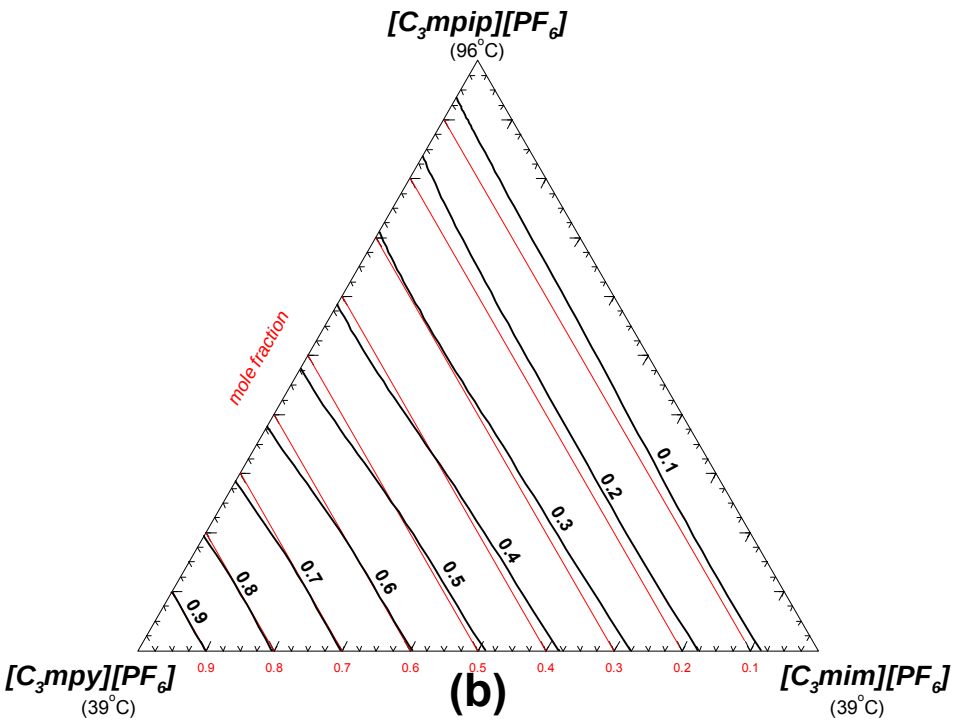


Figure S5 : Calculated activity coefficients at 100 °C of the components (liquid standard state) in the [C3mpy][PF6] - [C3mpip][PF6] - [C3mpyrr][PF6] ternary liquid along the isoplethal sections at : **(a)** constant 40 mol% [C3mpy][PF6], and **(b)** a constant molar ratio [C3mpyrr][PF6] / ([C3mpyrr][PF6] + [C3mpip][PF6]) of 0.60.





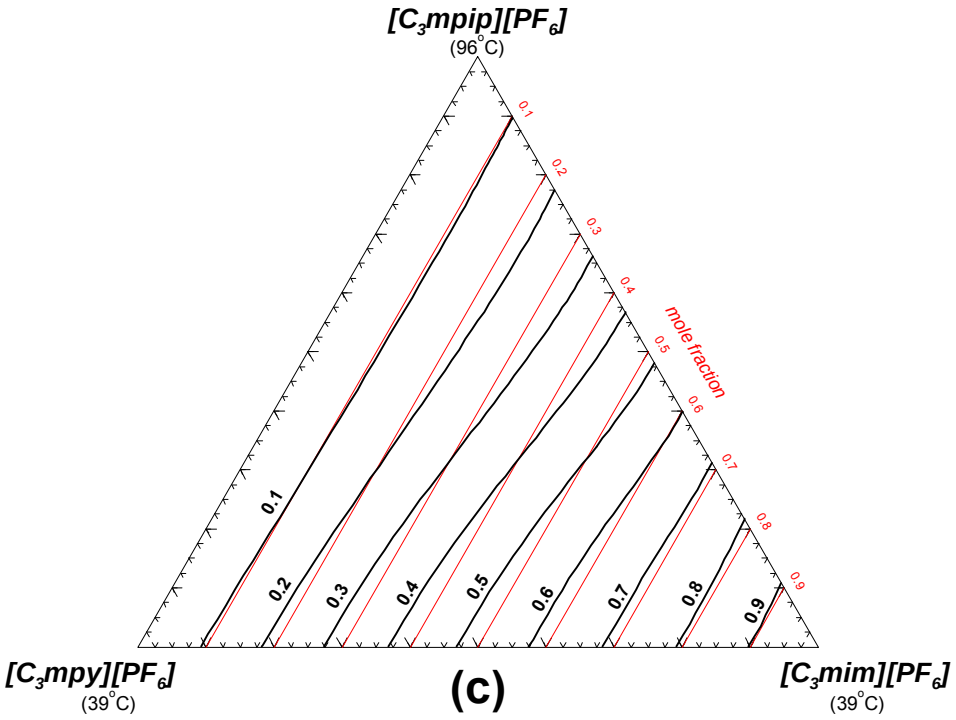


Figure S6 : Calculated iso-activity lines (liquid standard state) at 100 °C in the [C3mpip][PF6] - [C3mpy][PF6] - [C3mim][PF6] ternary liquid for : **(a)** [C3mpip][PF6]; **(b)** [C3mpy][PF6]; and **(c)** [C3mim][PF6]. The ideal case is represented by the thin red lines, which correspond to a constant mole fraction of the investigated component.

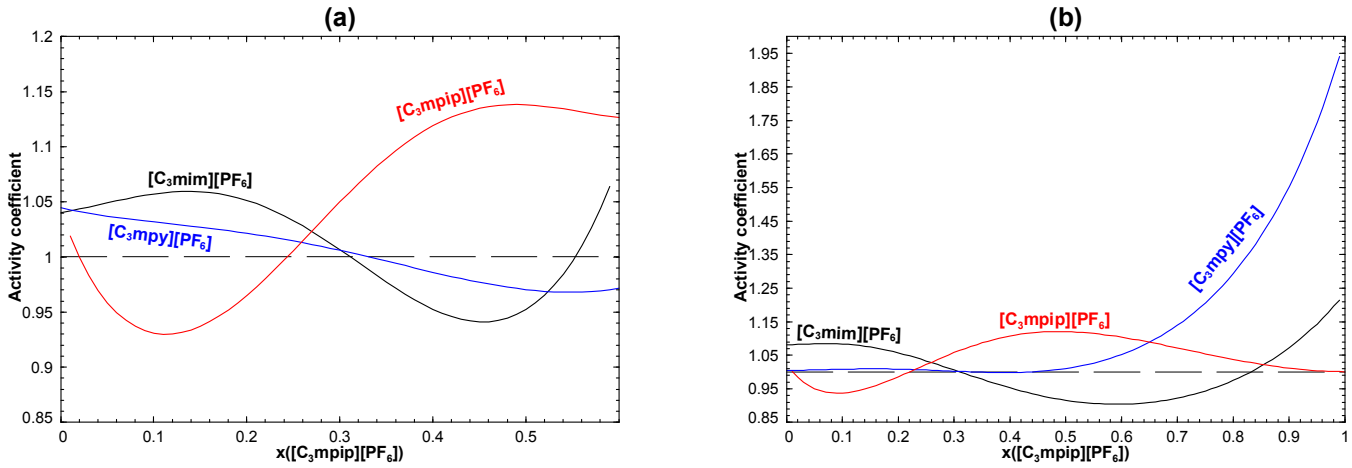
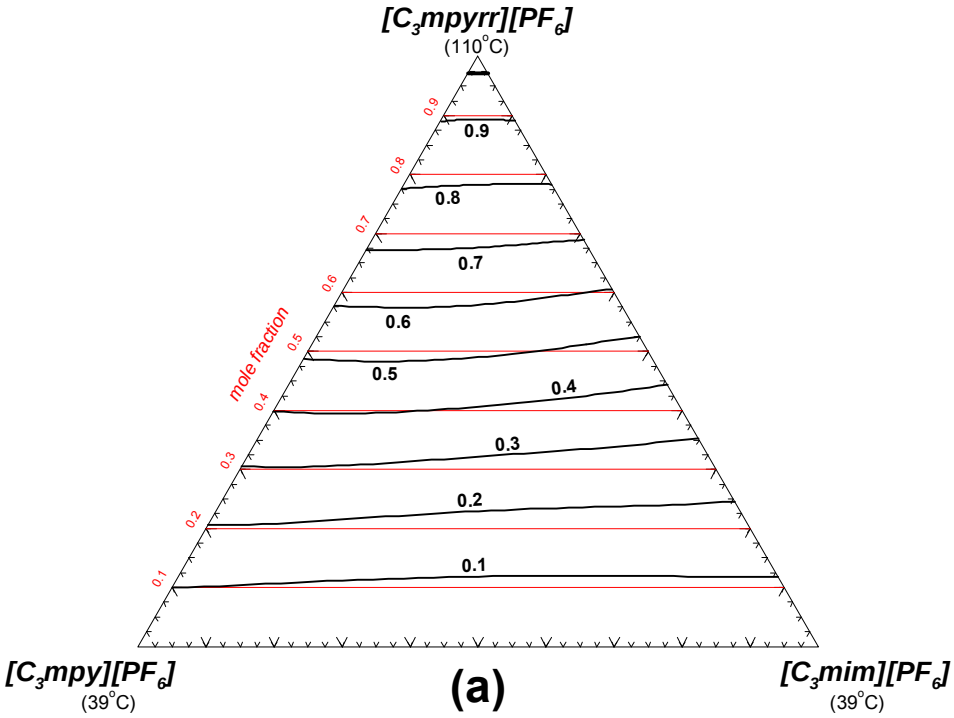
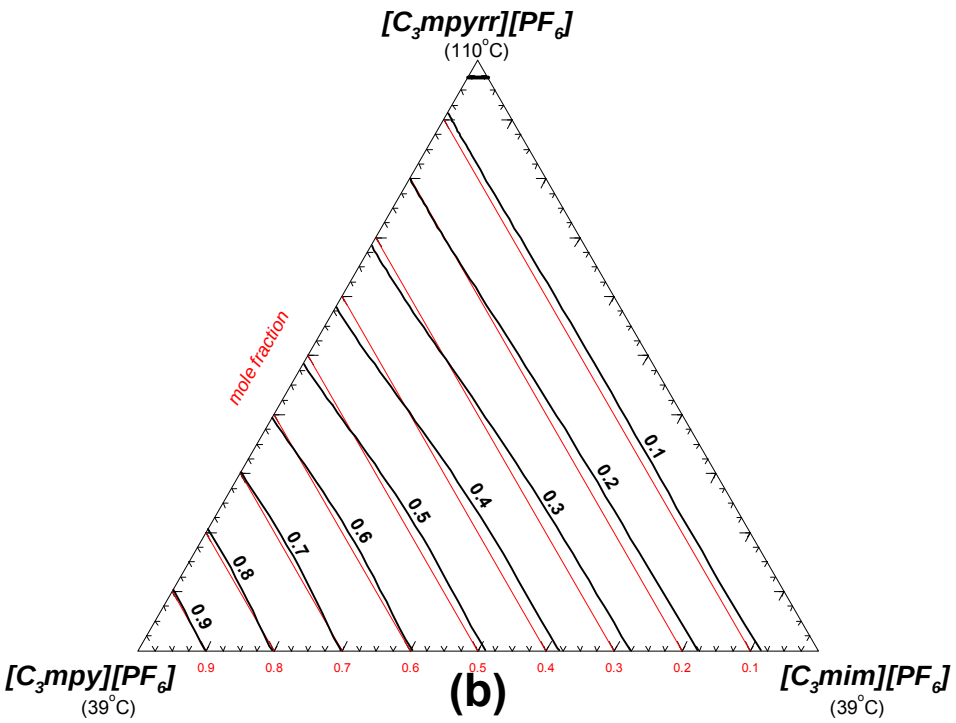


Figure S7 : Calculated activity coefficients at 100 °C of the components (liquid standard state) in the [C3mpip][PF6] - [C3mpy][PF6] - [C3mim][PF6] ternary liquid along the isoplethal sections at : **(a)** constant 40 mol% [C3mpy][PF6], and **(b)** a constant molar ratio [C3mpy][PF6] / ([C3mpy][PF6] + [C3mim][PF6]) of 0.60.





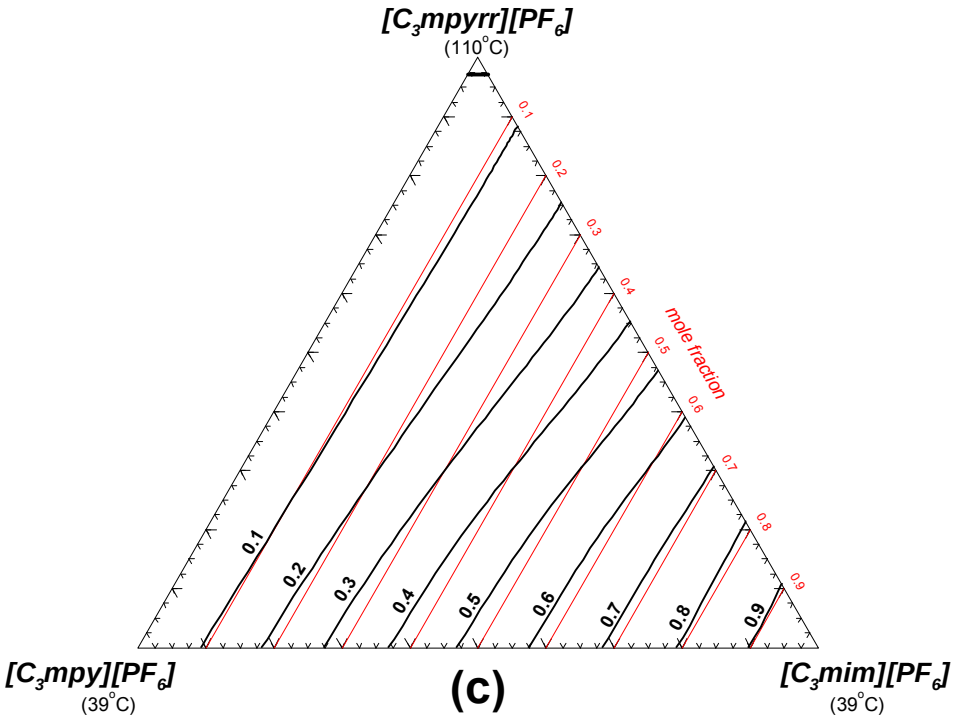


Figure S8 : Calculated iso-activity lines (liquid standard state) at 100 °C in the [C3mpyrr][PF6] - [C3mpy][PF6] - [C3mim][PF6] ternary liquid for : **(a)** [C3mpyrr][PF6]; **(b)** [C3mpy][PF6]; and **(c)** [C3mim][PF6]. The ideal case is represented by the thin red lines, which correspond to a constant mole fraction of the investigated component.

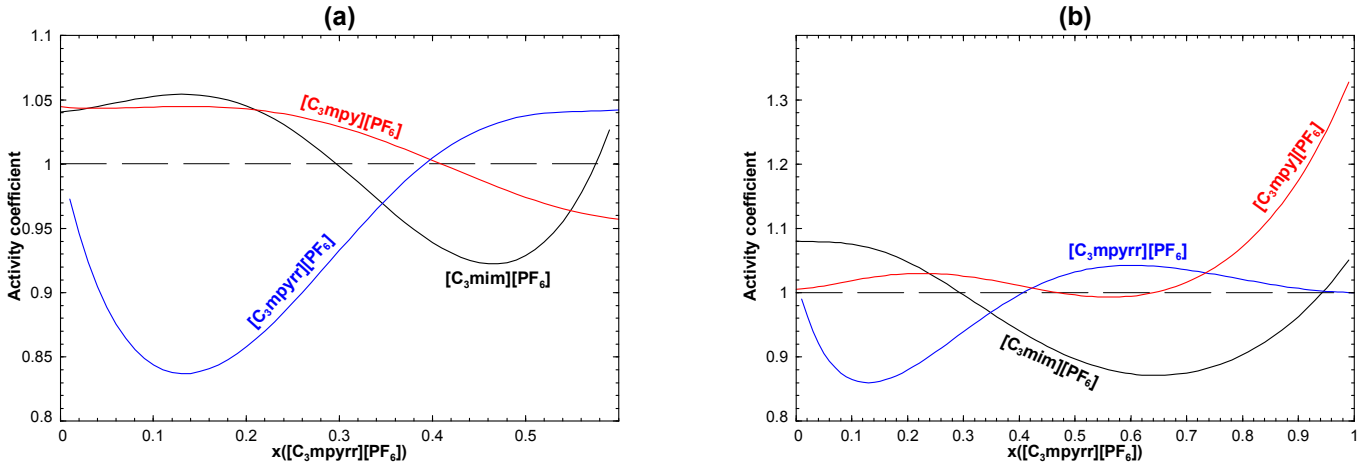


Figure S9 : Calculated activity coefficients at 100 °C of the components (liquid standard state) in the $[C_3mpyrr][PF_6]$ - $[C_3mpy][PF_6]$ - $[C_3mim][PF_6]$ ternary liquid along the isoplethal sections at : **(a)** constant 40 mol% $[C_3mpy][PF_6]$, and **(b)** a constant molar ratio $[C_3mpy][PF_6]$ / ($[C_3mpy][PF_6]$ + $[C_3mim][PF_6]$) of 0.60.