High Nitrogen Gas Solubility and Physicochemical Properties of [C_4mpyr][eFAP]–Fluorinated Solvent Mixtures

*Colin S. M. Kang, Xinyi Zhang and Douglas R. MacFarlane**

ARC Centre of Excellence for Electromaterials Science, School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

SUPPORTING INFORMATION

Contents:

1. *Detailed experimental and calculations for N_2 solubility*

Details for the N_2 solubility apparatus, including instrument schematic and specifications, can be found in a previous publication.[1] The description and calculations for N_2 solubility are shown below:

(a) First, the number of moles of N_2 admitted into the equilibrium chamber Ec containing the degassed liquid sample is given by **equation 1**:

$$n_{N_2}^{admitted} = \frac{P_1 V_{Bc}}{RT_1 Z_1} - \frac{P_2 V_{Bc}}{RT_2 Z_2} \qquad (1)$$

Here, P_1 and T_1 are the initial pressure and temperature before N_2 is admitted, and P_2 and T_2 are the pressure and temperature after thermal equilibrium respectively. V_{Bc} is the volume of the ballast chamber Bc, R is the universal gas constant, and Z_1, Z_2 are the compressibility factors of N_2 at the given temperature and pressure.

(b) The number of moles of N_2 measured in the headspace of the equilibrium chamber Ec is determined by **equation 2**:

$$n_{N_2}^{headspace} = \frac{(P_3 - P_{sample})(V_{Ec} - V_{sample})}{RT_3 Z_{12}} \qquad (2)$$

Here, P_3 is the total pressure (N_2 and any vapor pressure exerted by the sample mixture) contained in the headspace of the equilibrium chamber volume V_{Ec}, V_{sample} is the volume of the sample mixture of which the N_2 solubility is measured at temperature T_3. P_{sample} is the vapor pressure exerted by the sample mixture that is measured before thermal equilibrium (which is usually negligible in a neat IL), Z_{12} is the compressibility factor of the vapor phase (that consists of N_2 and the vapor pressure exerted by the sample mixture) in equilibrium with the sample mixture, calculated by **equation 3**:[2]

$$Z_{12} = 1 + \frac{P}{RT}\ (y_1B_{22} + y_2B_{33} + y_1y_2\delta_{23}) \qquad (3)$$

Here, y_1 and y_2 are the mole fraction of N_2 and the mole fraction of solvent contained in the vapor phase respectively, B_{22} and B_{33} are the second virial coefficients of N_2 and the respective solvent. δ_{23} is calculated using the second virial coefficient of each pure component and the crossed virial coefficient B_{23}, taken as the average between B_{22} and B_{33} ($\delta_{23} = 2B_{22} - B_{33} - B_{23}$).[2-3]

Although measurements of N_2 solubility in this study are conducted near atmospheric pressure, where such compressibility factors are not likely to be a large correction, it is still important to account for such non–ideality of gases. The final volume of sample mixture, upon mixing the IL and solvent together, is known by the exact mass and measuring the density of the final binary mixture. Furthermore, the amount of solvent that is present in the vapor phase is subtracted from the total volume of the liquid phase, although such values are substantially lower than the volume of sample mixture and hardly affects measurement accuracy.

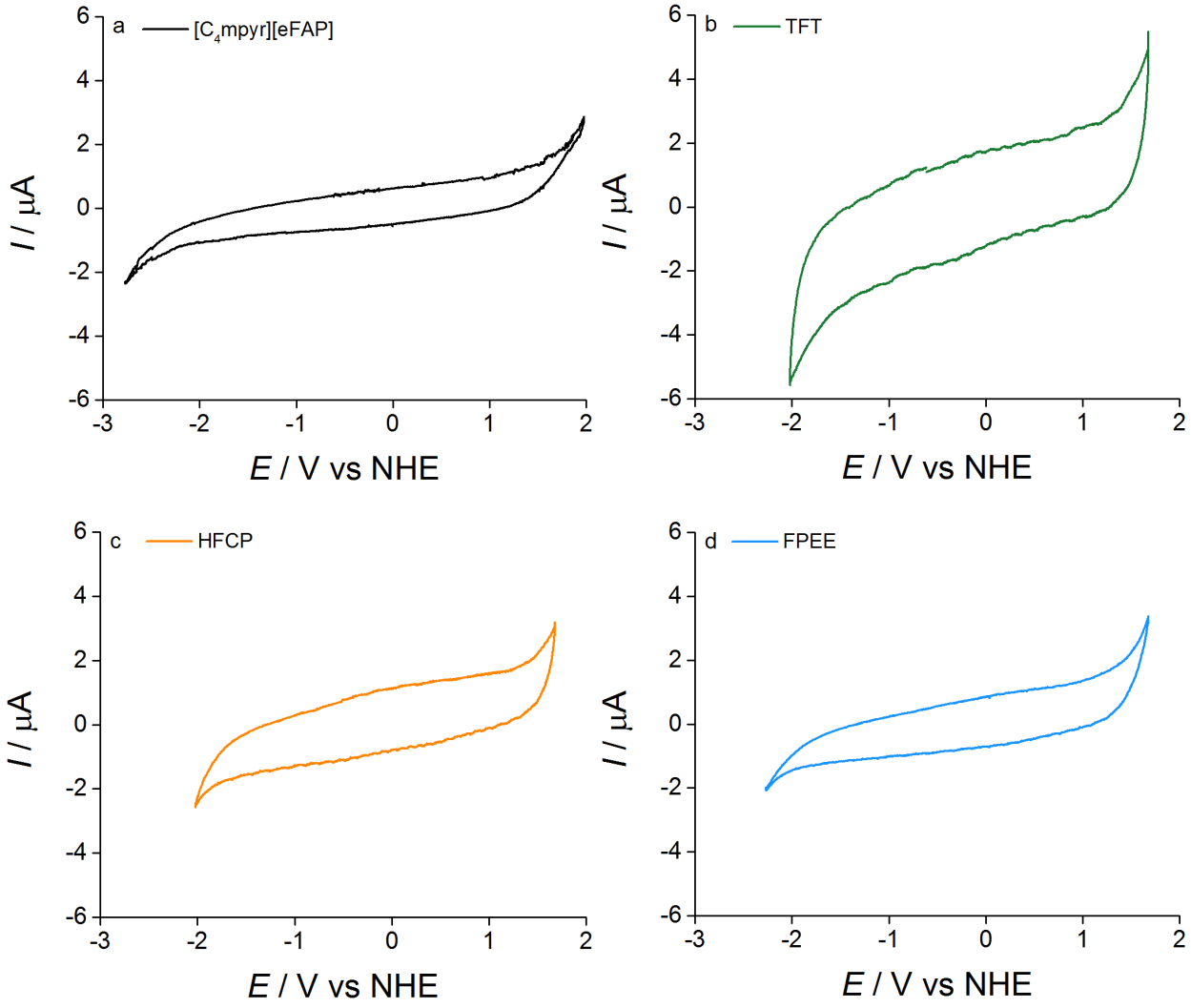
(c) Lastly, the moles of N_2 that is dissolved in the liquid sample is determined by the difference of N_2 admitted, and N_2 in the headspace:

$$n_{N_2}^{absorbed} = n_{N_2}^{admitted} - n_{N_2}^{headspace} \qquad (4)$$

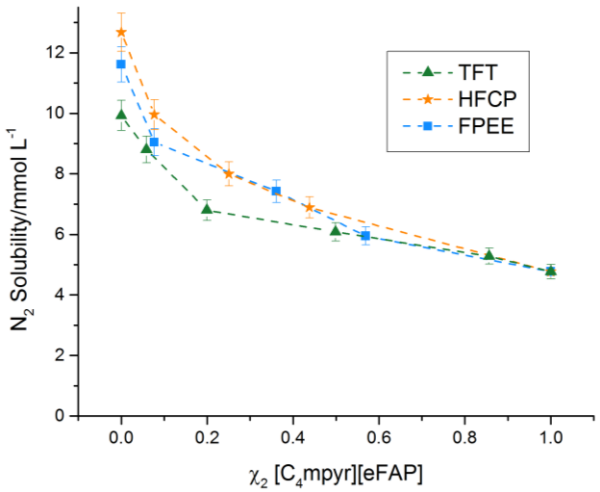
Supporting Table S1. Experimental values of N_2 solubility, corrected to a partial pressure of 101325 Pa where P_{eq} is the experimental equilibrium pressure, in [C_4mpyr][eFAP] binary mixtures at 30°C, as a function of [C_4mpyr][eFAP] mass fraction wt_2, volume fraction Φ, and mole fraction χ_2, expressed as molar concentration C_{N_2}, mole fraction $\chi_{2_{N_2}}$, and molal concentration b_{N_2}.

Sample Mixture	wt_2	Φ	χ_2	P_{eq} /10^4 Pa	P_{sample} /10^4 Pa	C_{N_2} /mmol L^{-1}	$\chi_{2_{N_2}}$ /10^{-3}	b_{N_2} /mmol kg^{-1}
[C_4mpyr][eFAP]	1.00	1.00	1.00	9.79	-	4.8	1.8	3.0
	1.00	1.00	1.00	9.67	-	4.7	1.7	3.0
[C_4mpyr][eFAP]/ TFT	0.96	0.95	0.86	10.04	0.32	5.5	1.8	3.5
	0.96	0.95	0.86	9.82	0.33	5.6	1.9	3.6
	0.80	0.75	0.50	9.60	0.51	5.7	1.4	3.8
	0.80	0.75	0.50	9.78	0.58	5.5	1.4	3.7
	0.80	0.75	0.50	9.57	0.63	5.5	1.4	3.7
	0.50	0.43	0.20	9.72	0.67	6.8	1.2	5.0
	0.50	0.43	0.20	9.43	0.78	6.7	1.1	4.9
	0.20	0.16	0.06	8.70	0.82	8.8	1.2	7.1
	0.20	0.16	0.06	8.95	0.80	8.8	1.2	7.1
	0.00	0.00	0.00	8.24	0.81	9.9	1.2	8.4
	0.00	0.00	0.00	8.99	0.82	9.9	1.2	8.5
	0.00	0.00	0.00	8.73	0.77	10.2	1.3	8.7
[C_4mpyr][eFAP]/ HFCP	0.70	0.70	0.44	9.49	0.76	6.9	1.6	4.4
	0.70	0.70	0.44	9.45	0.83	6.9	1.6	4.3
	0.50	0.50	0.25	9.10	1.10	8.1	1.5	5.0
	0.50	0.50	0.25	9.08	1.10	8.1	1.5	5.1
	0.20	0.20	0.08	8.55	1.30	10.0	1.4	6.2
	0.20	0.20	0.08	8.54	1.35	9.9	1.4	6.3
	0.00	0.00	0.00	7.75	1.41	12.2	1.6	7.8
	0.00	0.00	0.00	8.14	1.49	12.3	1.6	7.8
[C_4mpyr][eFAP]/ FPEE	0.70	0.71	0.57	9.81	0.27	6.5	1.9	4.1
	0.70	0.71	0.57	9.82	0.24	6.6	2.0	4.1
	0.50	0.51	0.36	9.39	0.23	7.4	1.9	4.6
	0.50	0.51	0.36	9.38	0.26	7.5	1.9	4.6
	0.20	0.21	0.08	9.18	0.26	9.0	2.0	5.5
	0.20	0.21	0.08	9.16	0.26	9.1	2.0	5.6

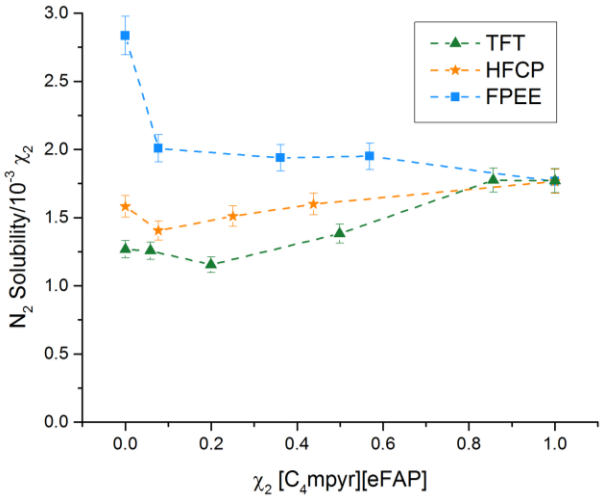
Sample Mixture	wt_2	Φ	χ_2	P_{eq} /10^4 Pa	P_{sample} /10^4 Pa	C_{N_2} /mmol L^{-1}	$\chi 2_{N_2}$ /10^{-3}	b_{N_2} /mmol kg^{-1}
	0.00	0.00	0.00	8.68	0.24	11.6	2.4	7.1
	0.00	0.00	0.00	8.71	0.25	11.6	2.4	7.1



Supporting Figure S1. Electrochemical potential ranges vs. NHE of a) [C_4mpyr][eFAP], and binary mixtures in a 1:1 volumetric ratio of b) [C_4mpyr][eFAP]–TFT, c) [C_4mpyr][eFAP]–HFCP, and d) [C_4mpyr][eFAP]–FPEE. Cyclic voltammetry was conducted on a 1 mm glassy carbon working electrode at a scan rate of 100 mV s^{-1} under N_2 atmosphere.



Supporting Figure S2. N_2 solubility (mmol L^{-1}) of [C_4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with TFT (▲), HFCP (★) and FPEE (■) at 30°C and P = 1 atm. Lines serve as a guide only.



Supporting Figure S3. N_2 solubility ($\chi_{2_{N_2}}$) of [C_4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with TFT (▲), HFCP (★) and FPEE (■) at 30°C and P = 1 atm. Lines serve as a guide only.

Supporting Table S2. Experimental values of density (ρ), excess molar volume (V^E), reduced excess molar volume ($V^E(\chi_1\chi_2)^{-1}$), partial molar volume of TFT ($\overline{V_1}$) and [C_4mpyr][eFAP] ($\overline{V_2}$) in [C_4mpyr][eFAP] binary mixtures with TFT as a function of mole fraction χ_2 and weight fraction wt_2 at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
			25 °C			
1.00	1.00	1.5877	-	-	-	-
0.86	0.96	1.5634	0.6	4.7	120.8	371.0
0.77	0.93	1.5504	0.0	-0.1	118.0	371.6
0.69	0.90	1.5389	-0.8	-3.7	117.9	371.6
0.50	0.80	1.4947	-1.5	-6.1	120.2	370.0
0.37	0.70	1.4529	-2.0	-8.7	121.4	368.4
0.27	0.60	1.4107	-2.0	-10.3	122.1	367.0
0.20	0.50	1.3694	-1.9	-11.7	122.5	365.4
0.14	0.40	1.3288	-1.5	-12.6	123.0	363.4
0.10	0.30	1.2893	-1.1	-13.0	123.3	361.0
0.06	0.20	1.2530	-0.9	-16.3	123.5	358.1
0.03	0.10	1.2166	-0.5	-18.1	123.7	355.0
0.01	0.05	1.1973	-0.1	-7.2	123.7	353.4
0.00	0.00	1.1811	-	-	-	-
			30 °C			
1.00	1.00	1.5824	-	-	-	-
0.86	0.96	1.5580	0.6	4.7	120.8	371.0
0.77	0.93	1.5450	0.0	-0.1	118.0	371.6
0.69	0.90	1.5334	-0.8	-3.7	117.9	371.6
0.50	0.80	1.4890	-1.6	-6.1	120.2	370.0
0.37	0.70	1.4470	-2.1	-8.7	121.4	368.4
0.27	0.60	1.4047	-2.1	-10.3	122.1	367.0
0.20	0.50	1.3632	-1.9	-11.7	122.5	365.4

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.14	0.40	1.3224	-1.6	-12.6	123.0	363.4
0.10	0.30	1.2827	-1.2	-13.0	123.3	361.0
0.06	0.20	1.2463	-0.9	-16.3	123.5	358.1
0.03	0.10	1.2097	-0.5	-18.1	123.7	355.0
0.01	0.05	1.1904	-0.1	-7.2	123.7	353.4
0.00	0.00	1.1741	-	-	-	-
			35 °C			
1.00	1.00	1.5771	-	-	-	-
0.86	0.96	1.5526	0.6	4.6	122.1	373.5
0.77	0.93	1.5395	-0.1	-0.3	119.3	374.1
0.69	0.90	1.5280	-0.9	-4.0	119.1	374.1
0.50	0.80	1.4834	-1.6	-6.6	121.5	372.4
0.37	0.70	1.4411	-2.2	-9.3	122.8	370.8
0.27	0.60	1.3987	-2.2	-11.1	123.4	369.3
0.20	0.50	1.3570	-2.0	-12.6	124.0	367.6
0.14	0.40	1.3160	-1.7	-13.5	124.4	365.4
0.10	0.30	1.2761	-1.2	-14.0	124.8	362.8
0.06	0.20	1.2396	-1.0	-17.6	125.0	359.7
0.03	0.10	1.2028	-0.5	-19.7	125.2	356.3
0.01	0.05	1.1834	-0.1	-9.0	125.2	354.6
0.00	0.00	1.1670	-	-	-	-
			40 °C			
1.00	1.00	1.5719	-	-	-	-
0.86	0.96	1.5473	0.6	4.6	122.7	374.7
0.77	0.93	1.5341	-0.1	-0.4	119.9	375.3
0.69	0.90	1.5225	-0.9	-4.1	119.8	375.4
0.50	0.80	1.4777	-1.7	-6.8	122.1	373.7
0.37	0.70	1.4353	-2.2	-9.6	123.4	372.0
0.27	0.60	1.3926	-2.3	-11.5	124.1	370.5
0.20	0.50	1.3507	-2.1	-13.0	124.7	368.7

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.14	0.40	1.3096	-1.7	-14.0	125.1	366.4
0.10	0.30	1.2695	-1.3	-14.6	125.5	363.7
0.06	0.20	1.2328	-1.0	-18.2	125.8	360.5
0.03	0.10	1.1959	-0.5	-20.5	125.9	357.0
0.01	0.05	1.1764	-0.1	-9.8	126.0	355.2
0.00	0.00	1.1598	-	-	-	-
			45 °C			
1.00	1.00	1.5666	-	-	-	-
0.86	0.96	1.5419	0.5	4.5	123.3	376.0
0.77	0.93	1.5287	-0.1	-0.6	120.5	376.6
0.69	0.90	1.5170	-0.9	-4.3	120.4	376.6
0.50	0.80	1.4720	-1.8	-7.1	122.8	374.9
0.37	0.70	1.4294	-2.3	-10.0	124.1	373.2
0.27	0.60	1.3866	-2.3	-11.8	124.8	371.7
0.20	0.50	1.3445	-2.2	-13.5	125.4	369.8
0.14	0.40	1.3032	-1.8	-14.6	125.9	367.4
0.10	0.30	1.2629	-1.3	-15.2	126.3	364.5
0.06	0.20	1.2260	-1.0	-19.0	126.6	361.2
0.03	0.10	1.1889	-0.6	-21.3	126.7	357.6
0.01	0.05	1.1693	-0.1	-10.8	126.8	355.7
0.00	0.00	1.1526	-	-	-	-
			50 °C			
1.00	1.00	1.5614	-	-	-	-
0.86	0.96	1.5366	0.5	4.3	124.0	377.3
0.77	0.93	1.5233	-0.1	-0.7	121.1	377.9
0.69	0.90	1.5115	-1.0	-4.6	121.0	377.9
0.50	0.80	1.4664	-1.8	-7.4	123.5	376.1
0.37	0.70	1.4236	-2.4	-10.4	124.8	374.4
0.27	0.60	1.3805	-2.4	-12.3	125.6	372.8
0.20	0.50	1.3383	-2.2	-14.0	126.1	370.9

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.14	0.40	1.2967	-1.9	-15.2	126.6	368.4
0.10	0.30	1.2563	-1.4	-15.8	127.1	365.4
0.06	0.20	1.2192	-1.1	-19.7	127.3	361.9
0.03	0.10	1.1819	-0.6	-22.3	127.5	358.1
0.01	0.05	1.1622	-0.2	-11.8	127.6	356.1
0.00	0.00	1.1454	-	-	-	-

Supporting Table S3. Experimental values of density (ρ), excess molar volume (V^E), reduced excess molar volume ($V^E(\chi_1\chi_2)^{-1}$), partial molar volume of HFCP ($\overline{V_1}$) and [C_4mpyr][eFAP] ($\overline{V_2}$) in [C_4mpyr][eFAP] binary mixtures with HFCP as a function of mole fraction χ_2 and weight fraction wt_2 at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
			25 °C			
1.00	1.00	1.5877	-	-	-	-
0.84	0.94	1.5837	0.7	4.9	123.5	370.9
0.65	0.85	1.5857	0.0	-0.1	122.0	371.2
0.44	0.70	1.5884	-0.7	-2.9	122.7	370.7
0.33	0.60	1.5901	-1.0	-4.7	122.7	370.7
0.25	0.50	1.5912	-1.2	-6.6	122.8	370.2
0.18	0.40	1.5914	-1.3	-8.7	123.2	368.7
0.13	0.30	1.5900	-1.2	-10.8	123.7	366.0
0.08	0.20	1.5875	-1.0	-14.0	124.2	361.9
0.04	0.10	1.5825	-0.6	-18.0	124.5	356.8
0.02	0.05	1.5796	-0.4	-24.8	124.6	353.8
0.00	0.00	1.5738	-	-	-	-
			30 °C			
1.00	1.00	1.5824	-	-	-	-

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.84	0.94	1.5782	0.6	4.7	124.1	372.1
0.65	0.85	1.5799	-0.1	-0.4	122.7	372.5
0.44	0.70	1.5821	-0.8	-3.3	123.4	371.9
0.33	0.60	1.5834	-1.2	-5.2	123.4	371.9
0.25	0.50	1.5840	-1.3	-7.2	123.6	371.4
0.18	0.40	1.5836	-1.4	-9.4	124.0	369.7
0.13	0.30	1.5816	-1.3	-11.6	124.6	366.8
0.08	0.20	1.5784	-1.1	-15.0	125.0	362.5
0.04	0.10	1.5726	-0.7	-19.2	125.3	357.1
0.02	0.05	1.5693	-0.4	-26.5	125.4	354.0
0.00	0.00	1.5629	-	-	-	-
			35 °C			
1.00	1.00	1.5771	-	-	-	-
0.84	0.94	1.5727	0.6	4.5	124.8	373.4
0.65	0.85	1.5741	-0.1	-0.7	123.3	373.7
0.44	0.70	1.5757	-0.9	-3.8	124.1	373.1
0.33	0.60	1.5766	-1.3	-5.7	124.1	373.1
0.25	0.50	1.5769	-1.5	-7.9	124.4	372.5
0.18	0.40	1.5758	-1.5	-10.1	124.8	370.7
0.13	0.30	1.5732	-1.4	-12.5	125.4	367.6
0.08	0.20	1.5693	-1.1	-16.0	125.9	363.1
0.04	0.10	1.5627	-0.7	-20.5	126.2	357.4
0.02	0.05	1.5590	-0.5	-28.2	126.3	354.1
0.00	0.00	1.5520	-	-	-	-
			40 °C			
1.00	1.00	1.5719	-	-	-	-
0.84	0.94	1.5673	0.6	4.2	125.5	374.6
0.65	0.85	1.5684	-0.2	-1.0	124.1	374.9
0.44	0.70	1.5694	-1.0	-4.2	124.8	374.4
0.33	0.60	1.5698	-1.4	-6.3	124.8	374.3

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.25	0.50	1.5699	-1.6	-8.7	125.1	373.6
0.18	0.40	1.5680	-1.6	-10.9	125.6	371.6
0.13	0.30	1.5647	-1.5	-13.4	126.2	368.3
0.08	0.20	1.5601	-1.2	-17.2	126.8	363.5
0.04	0.10	1.5527	-0.8	-21.9	127.1	357.5
0.02	0.05	1.5485	-0.5	-30.0	127.2	354.1
0.00	0.00	1.5410	-	-	-	-
			45 °C			
1.00	1.00	1.5666	-	-	-	-
0.84	0.94	1.5619	0.5	4.0	126.1	375.9
0.65	0.85	1.5626	-0.3	-1.3	124.8	376.2
0.44	0.70	1.5631	-1.2	-4.7	125.5	375.6
0.33	0.60	1.5631	-1.5	-6.9	125.6	375.5
0.25	0.50	1.5625	-1.8	-9.4	125.9	374.7
0.18	0.40	1.5601	-1.7	-11.7	126.5	372.6
0.13	0.30	1.5562	-1.6	-14.5	127.1	369.1
0.08	0.20	1.5509	-1.3	-18.4	127.7	364.0
0.04	0.10	1.5426	-0.8	-23.3	128.0	357.7
0.02	0.05	1.5380	-0.5	-32.0	128.1	354.1
0.00	0.00	1.5299	-	-	-	-
			50 °C			
1.00	1.00	1.5614	-	-	-	-
0.84	0.94	1.5564	0.5	3.7	126.8	377.2
0.65	0.85	1.5568	-0.4	-1.7	125.5	377.4
0.44	0.70	1.5567	-1.3	-5.2	126.3	376.8
0.33	0.60	1.5563	-1.7	-7.5	126.4	376.7
0.25	0.50	1.5553	-1.9	-10.2	126.7	375.8
0.18	0.40	1.5522	-1.9	-12.6	127.3	373.6
0.13	0.30	1.5477	-1.7	-15.6	128.0	369.8
0.08	0.20	1.5417	-1.4	-19.8	128.6	364.4

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.04	0.10	1.5324	-0.9	-24.9	129.0	357.7
0.02	0.05	1.5274	-0.6	-34.1	129.1	353.9
0.00	0.00	1.5187	-	-	-	-

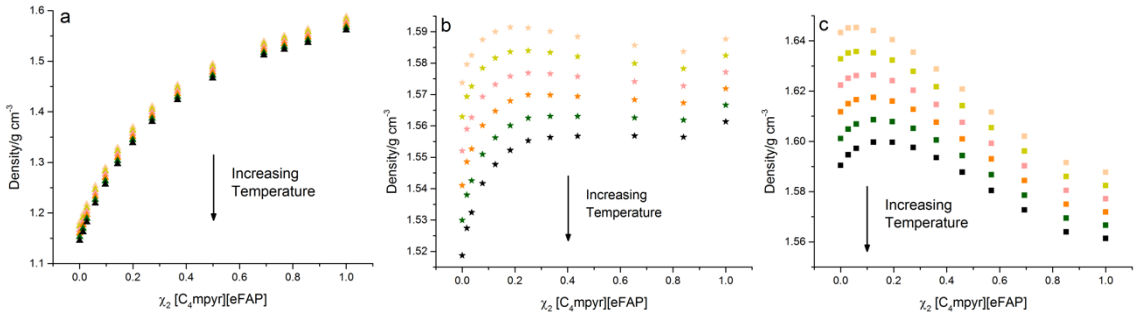
Supporting Table S4. Experimental values of density (ρ), excess molar volume (V^E), reduced excess molar volume ($V^E(\chi_1\chi_2)^{-1}$), partial molar volume of FPEE ($\overline{V_1}$) and [C_4mpyr][eFAP] ($\overline{V_2}$) in [C_4mpyr][eFAP] binary mixtures with FPEE as a function of mole fraction χ_2 and weight fraction wt_2 at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
			25 °C			
1.00	1.00	1.5877	-	-	-	-
0.85	0.91	1.5915	0.2	1.7	199.1	370.7
0.69	0.80	1.6020	-0.7	-3.3	196.9	371.2
0.57	0.70	1.6116	-1.4	-5.8	197.6	370.8
0.46	0.60	1.6208	-2.0	-7.9	198.5	369.9
0.36	0.50	1.6288	-2.2	-9.6	199.3	368.7
0.27	0.40	1.6354	-2.3	-11.3	200.0	367.1
0.20	0.30	1.6404	-2.0	-13.0	200.8	364.8
0.12	0.20	1.6441	-1.7	-15.3	201.4	361.3
0.06	0.10	1.6452	-1.0	-17.9	201.9	356.3
0.03	0.05	1.6451	-0.6	-20.9	202.0	353.2
0.00	0.00	1.6433	-	-	-	-
			30 °C			
1.00	1.00	1.5824	-	-	-	-
0.85	0.91	1.5860	0.2	1.4	200.1	371.9
0.69	0.80	1.5961	-0.8	-3.7	197.9	372.4

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.57	0.70	1.6054	-1.5	-6.2	198.6	372.0
0.46	0.60	1.6142	-2.1	-8.4	199.6	371.1
0.36	0.50	1.6217	-2.4	-10.2	200.5	369.8
0.27	0.40	1.6279	-2.4	-12.0	201.2	368.1
0.20	0.30	1.6323	-2.2	-13.7	202.0	365.7
0.12	0.20	1.6352	-1.7	-16.1	202.7	362.0
0.06	0.10	1.6357	-1.1	-18.9	203.2	356.8
0.03	0.05	1.6351	-0.6	-22.1	203.3	353.5
0.00	0.00	1.6328	-	-	-	-
			35 °C			
1.00	1.00	1.5771	-	-	-	-
0.85	0.91	1.5805	0.1	1.0	201.1	373.1
0.69	0.80	1.5903	-0.9	-4.1	199.0	373.7
0.57	0.70	1.5992	-1.6	-6.7	199.7	373.2
0.46	0.60	1.6076	-2.2	-8.9	200.7	372.2
0.36	0.50	1.6146	-2.5	-10.9	201.6	371.0
0.27	0.40	1.6203	-2.5	-12.7	202.4	369.2
0.20	0.30	1.6241	-2.3	-14.6	203.2	366.6
0.12	0.20	1.6264	-1.8	-17.0	203.9	362.7
0.06	0.10	1.6261	-1.1	-20.1	204.5	357.2
0.03	0.05	1.6251	-0.7	-23.3	204.6	353.7
0.00	0.00	1.6223	-	-	-	-
			40 °C			
1.00	1.00	1.5719	-	-	-	-
0.85	0.91	1.5750	0.1	0.8	202.2	374.4
0.69	0.80	1.5844	-1.0	-4.5	200.0	374.9
0.57	0.70	1.5930	-1.8	-7.2	200.8	374.4
0.46	0.60	1.6009	-2.4	-9.5	201.9	373.4
0.36	0.50	1.6076	-2.7	-11.5	202.8	372.1
0.27	0.40	1.6127	-2.7	-13.5	203.6	370.2

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.20	0.30	1.6160	-2.4	-15.4	204.5	367.4
0.12	0.20	1.6175	-1.9	-17.9	205.2	363.3
0.06	0.10	1.6165	-1.2	-21.3	205.8	357.5
0.03	0.05	1.6150	-0.7	-24.5	206.0	353.9
0.00	0.00	1.6117	-	-	-	-
			45 °C			
1.00	1.00	1.5666	-	-	-	-
0.85	0.91	1.5694	0.0	0.4	203.2	375.7
0.69	0.80	1.5785	-1.1	-5.0	201.1	376.2
0.57	0.70	1.5867	-1.9	-7.7	201.9	375.6
0.46	0.60	1.5943	-2.5	-10.1	203.0	374.6
0.36	0.50	1.6005	-2.8	-12.2	204.0	373.2
0.27	0.40	1.6051	-2.8	-14.3	204.9	371.2
0.20	0.30	1.6078	-2.6	-16.4	205.8	368.3
0.12	0.20	1.6086	-2.1	-18.9	206.6	364.0
0.06	0.10	1.6069	-1.3	-22.6	207.2	357.9
0.03	0.05	1.6048	-0.7	-25.8	207.3	354.0
0.00	0.00	1.6011	-	-	-	-
			50 °C			
1.00	1.00	1.5614	-	-	-	-
0.85	0.91	1.5639	0.0	0.0	204.3	376.9
0.69	0.80	1.5727	-1.2	-5.5	202.2	377.4
0.57	0.70	1.5804	-2.0	-8.2	203.1	376.9
0.46	0.60	1.5877	-2.7	-10.8	204.2	375.8
0.36	0.50	1.5935	-3.0	-13.0	205.2	374.4
0.27	0.40	1.5975	-3.0	-15.1	206.1	372.3
0.20	0.30	1.5996	-2.7	-17.3	207.1	369.2
0.12	0.20	1.5997	-2.2	-20.0	207.9	364.6
0.06	0.10	1.5972	-1.3	-24.0	208.6	358.1
0.03	0.05	1.5946	-0.8	-27.3	208.7	354.1

χ_2	wt_2	ρ /g cm^{-3}	V^E /cm^3 mol^{-1}	$V^E(\chi_1\chi_2)^{-1}$ /cm^3 mol^{-1}	$\overline{V_1}$ /cm^3 mol^{-1}	$\overline{V_2}$ /cm^3 mol^{-1}
0.00	0.00	1.5904	-	-	-	-



Supporting Figure S4. Density of [C$_4$mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, in a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

Supporting Table S5. Redlich–Kister fitting coefficients A_n of the excess molar volumes of [C$_4$mpyr][eFAP] binary mixtures in TFT, HFCP, FPEE at 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, and 50 °C, and the associated fitting deviation calculated by **equation 5**.

T/°C	A0	A1	A2	A3	σ
TFT					
25	-6.861	-7.192	4.987	-9.091	0.101
30	-7.071	-7.437	4.903	-9.228	0.102
35	-7.312	-7.621	4.791	-9.425	0.103
40	-7.545	-7.841	4.714	-9.631	0.103
45	-7.817	-8.008	4.613	-9.923	0.103
50	-8.106	-8.235	4.474	-10.125	0.104
HFCP					
25	-2.224	-5.733	-0.354	-10.895	0.048

T/°C	A0	A1	A2	A3	σ
30	-2.557	-6.021	-0.658	-11.194	0.052
35	-2.940	-6.346	-0.927	-11.533	0.055
40	-3.327	-6.792	-1.360	-11.608	0.061
45	-3.764	-7.042	-1.670	-12.154	0.064
50	-4.236	-7.410	-2.064	-12.546	0.069
FPEE					
25	-7.138	-8.598	1.453	-6.021	0.025
30	-7.612	-8.925	1.284	-6.129	0.027
35	-8.138	-9.237	1.071	-6.298	0.028
40	-8.676	-9.588	0.912	-6.537	0.029
45	-9.252	-9.962	0.662	-6.664	0.032
50	-9.843	-10.413	0.351	-6.694	0.037

The standard deviation of the polynomial fit is calculated by the following expression:

$$\sigma V^E = \left[\frac{\Sigma(V^E_{exp} - V^E_{calc})^2}{N-n}\right]^{1/2} \quad (5)$$

Where N is the number of data points, n is the order of fitting Redlich–Kister polynomial equation.

10. Reduced Excess Molar Volume

The reduced V^E, calculated from $V^E/\chi_1\chi_2$, aids in describing non–ideal interactions between the IL and solvent, particularly as it is more sensitive at lower concentrations.[4] Papović and co–workers[5] studied the reduced V^E of IL mixtures containing imidazolium cations of varying alkyl chain length and γ–butyrolactone. For the cations of alkyl chain length > 4, the reduced V^E changes upon addition of IL which was attributed due to imperfect packing and free volume. On the other hand, for ILs with cation alkyl chain length < 4, the reduced V^E was constant across the studied composition range between χ_2 = 0.1—0.9; this suggested that a smaller extent of free volume is

present when the IL exhibits a higher degree of order. In our [C4mpyr][eFAP]–fluorinated solvent systems shown in **Figure S5**, the reduced V^E values are changing across all compositions, suggesting the presence of such free volume within the IL and solvent.

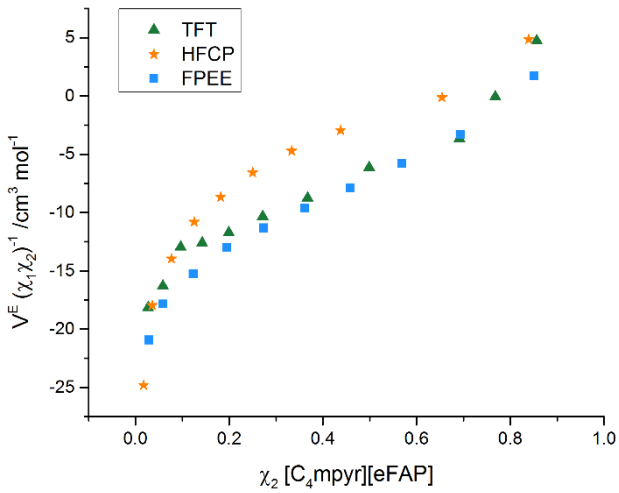
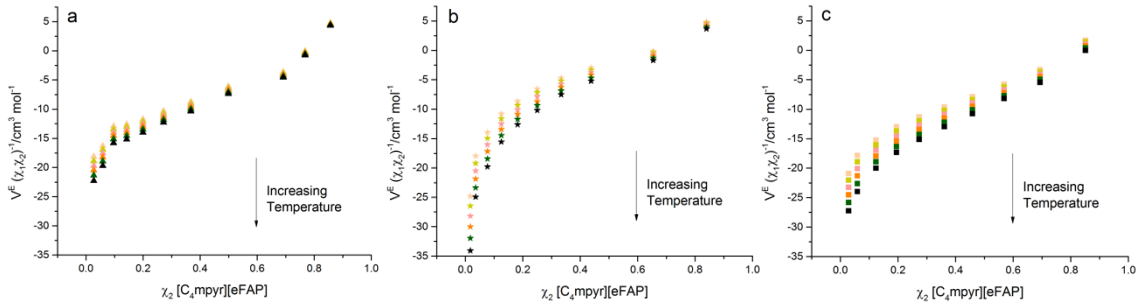


Figure S5. Reduced excess molar volumes ($V^E(\chi_1\chi_2)^{-1}$) of [C4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with TFT (▲), HFCP (★) and FPEE (■) at 25°C.

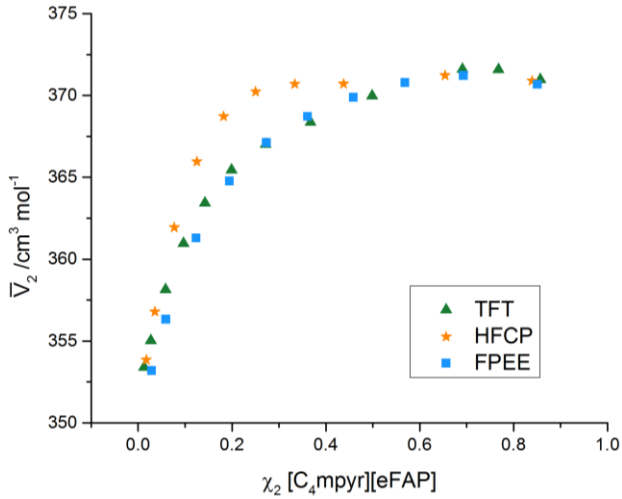
However, at very low concentrations of either IL or fluorinated solvent, a steep change in the magnitude of $V^E/\chi_1\chi_2$ values below $\chi_2 < 0.1$ (and $\chi > 0.8$) is observed for all three [C4mpyr][eFAP]–solvent mixtures. This may reflect the different nature of [C4mpyr][eFAP] compared to the fluorinated solvent (in terms of their interactions), and at either extreme, the complete solvation of each component is likely to be unfavorable. In contrast to this behavior, the reduced V^E of water and dioxane,[6] where the two liquids share similar interactions, display a minimum of -5 cm^3 mol^{-1}. Our fluorinated ionic liquid electrolyte system, of dissimilar interactions, display minima values of <-17 cm^3 mol^{-1} at $\chi_2 < 0.05$. Lastly, temperature does not appear to affect such trends other than the increase in magnitude of the reduced V^E (see **Figure S6**).



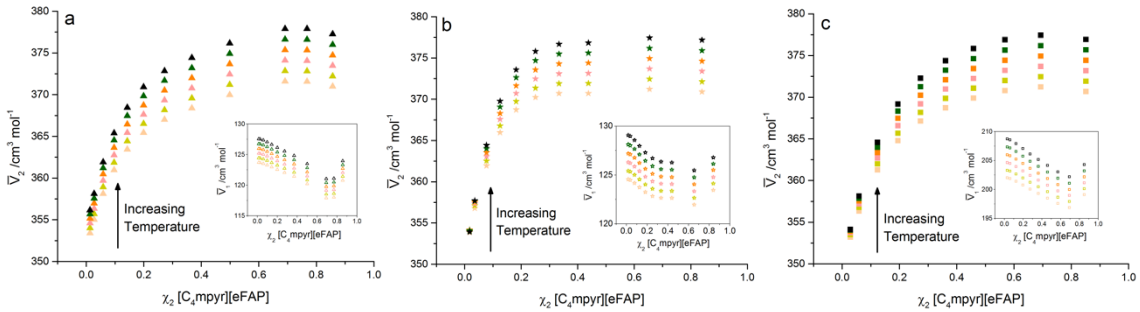
Supporting Figure S6. Reduced excess molar volume ($V^E (\chi_1\chi_2)^{-1}$) of [C4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

11. Partial Molar Volume

Comparison of the partial molar volume of [C4mpyr][eFAP] in TFT, HFCP, and FPEE mixtures across a range of compositions at 25°C are shown in **Supporting Figure S7**. With subsequent addition of [C4mpyr][eFAP], the partial molar volume initially rises sharply and then slowly increases toward the pure IL molar volume. The sharp differences in partial molar volume can reflect a change in the intermolecular interactions between the IL and fluorinated solvent due to the variation in environment as described before. The insets in **Supporting Figure S8** show the partial molar volume of the fluorinated solvents TFT, HFCP and FPEE decreases upon initial addition of [C4mpyr][eFAP] and similarly follows the inverse trend of the IL partial molar volume corresponding to each solvent. Again, an increase in temperature does not appear to greatly affect such trends with regard to the partial molar volumes of either component as shown in **Supporting Figure S8.**



Supporting Figure S7. Comparison of partial molar volume of [C4mpyr][eFAP] in a binary mixture, as a function of mole fraction χ_2, with TFT (▲), HFCP (★) and FPEE (■) at 25°C.



Supporting Figure S8. Partial molar volume of [C4mpyr][eFAP] in a binary mixture, as a function of mole fraction χ_2, with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C. Insets show the partial molar volume of the respective fluorinated solvent in the binary mixture.

12. Free Volume Calculations of TFT and Toluene

To investigate the difference in attributed N_2 solubility, the free volume of TFT and toluene is estimated by the difference in molar volume, from the crystal structure to liquid. The molar

volumes are calculated from the density at its crystal structure state, and the liquid density measured at 30 °C. We assume the crystal structure will exhibit a free volume close to zero, compared to the liquid form at which the crystalline packing structure is broken and free volume exists between such molecules. **Supporting Table S6** shows the estimated free volume, from the density and molar volume, of TFT, toluene and [C_2mim][BF_4] at the crystalline and liquid state.

Supporting Table S6: The estimated free volume (FV) and % change of TFT, toluene, and [C_2mim][BF_4] calculated from the molecular weight (MW), density (ρ) and molar volume (V_m) of the crystal structure and liquid at 30 °C.

Sample	MW /g mol^{-1}	ρ (crystal) /g cm^{-3}	V_m (crystal) /cm^3 mol^{-1}	ρ (30 °C) /g cm^{-3}	V_m (liquid) /cm^3 mol^{-1}	FV /cm^3 mol^{-1}	FV%
TFT	146.1	1.473 (at -60 °C)[7]	**99.2**	1.176	**124.2**	25.0	20.2
Toluene	92.1	1.070 (at -123 °C)[7]	**86.1**	0.858	**107.4**	21.3	19.8
[C_2mim][BF_4]	198.0	1.450 (at -173 °C)[8]	**136.5**	1.280[9]	**154.7**	18.2	11.8

* FV ≅ V_m (liquid) – V_m (crystal)

Calculations for the free volume required to dissolve N_2

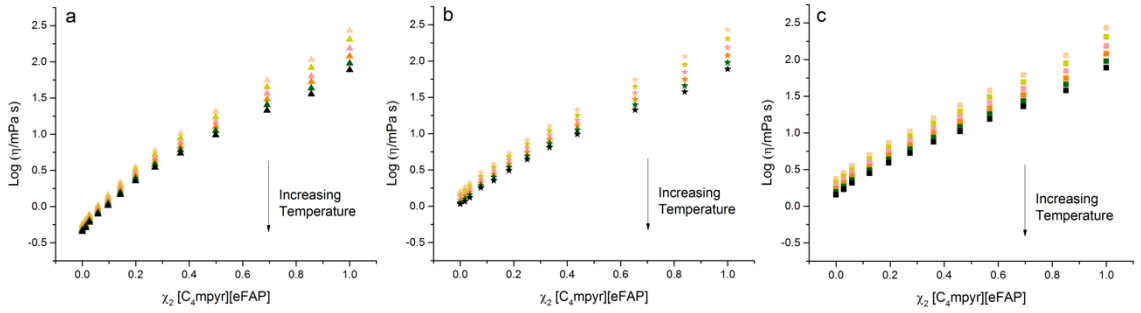
The amount of free volume present in one mole of TFT is 25 cm^3 mol^{-1} compared to a total molar volume of 124.2 cm^3 mol^{-1} (see Table S6 above). Therefore, in one liter of TFT, the amount of free volume present is:

FV = 25 cm^3 (FV) mol^{-1} x 1000 cm^3/124.2 cm^3 (TFT) mol^{-1} = 201.3 cm^3

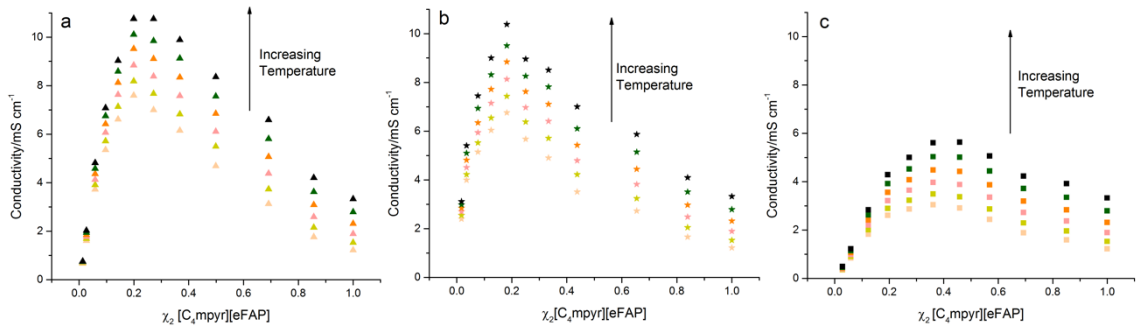
If we consider the molar volume of N_2 as a liquid:

28 g mol^{-1}/0.808 g cm^{-3} = 34.7 cm^3 mol^{-1}

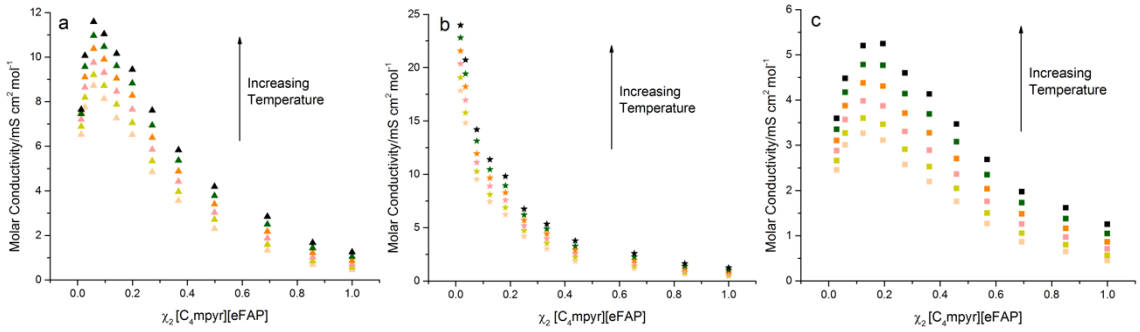
And given the N_2 solubility in TFT is measured to be 10 mmol L^{-1}, the molar volume that is required to dissolve this amount of N_2 is ~0.35 cm^3.



Supporting Figure S9. Log viscosity of [C_4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.



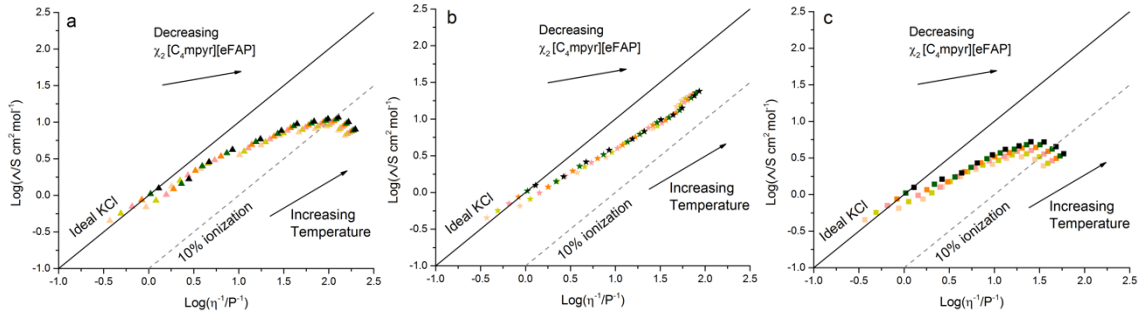
Supporting Figure S10. Ionic conductivity of [C_4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.



Supporting Figure S11. Molar conductivity of [C4mpyr][eFAP] binary mixtures, as a function of mole fraction χ_2, with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

Supporting Table S7. Self–diffusion coefficients (m^2s^{-1}) of each component in [C4mpyr][eFAP] mixtures in TFT and HFCP, as a function of mole fraction χ_2 and mass fraction wt_2, and the degree of ionicity at 25°C

Binary Mixture	χ_2	wt_2	D_{cation} /10^{-10} m^2s^{-1} ± 5%	D_{anion} /10^{-10} m^2s^{-1} ± 5%	$D_{solvent}$ /10^{-10} m^2s^{-1} ± 5%	$\Lambda_{imp}/\Lambda_{NMR}$ ± 10%
[C4mpyr][eFAP]	1.00	1.00	0.074	0.049	-	0.97
[C4mpyr][eFAP]/ TFT	0.27	0.60	1.6	1.1	5.2	0.48
	0.20	0.50	2.5	1.5	7.5	0.42
	0.14	0.40	3.2	2.2	9.9	0.36
	0.10	0.30	4.9	3.1	14	0.27
	0.06	0.20	6.3	4.3	16	0.22
	0.03	0.10	8.5	5.2	20	0.15
	0.00	0.00	-	-	24	-
[C4mpyr][eFAP]/ HFCP	0.33	0.60	0.99	0.67	2.0	0.48
	0.25	0.50	1.3	0.95	2.5	0.50
	0.18	0.40	1.6	1.3	3.1	0.57
	0.13	0.30	2.7	1.7	4.3	0.45
	0.08	0.20	3.9	2.3	5.4	0.42
	0.04	0.10	5.6	3.0	6.7	0.46
	0.00	0.00	-	-	8.6	-



Supporting Figure S12. Walden plot of [C_4mpyr][eFAP] binary mixtures, in various compositions* with a) TFT (▲), b) HFCP (★) and c) FPEE (■) at 25°C, 30°C, 35°C, 40°C, 45°C and 50°C.

*The range of χ_2 compositions of [C_4mpyr][eFAP] mixtures shown above:

[C_4mpyr][eFAP]–TFT, χ_2 = 1.00, 0.86, 0.77, 0.69, 0.50, 0.37, 0.27, 0.20, 0.14, 0.10, 0.06, 0.03, 0.01

[C_4mpyr][eFAP]–HFCP, χ_2 = 1.00, 0.84, 0.65, 0.44, 0.33, 0.25, 0.18, 0.13, 0.08, 0.04, 0.02

[C_4mpyr][eFAP]–FPEE, χ_2 = 1.00, 0.85, 0.69, 0.57, 0.46, 0.36, 0.27, 0.20, 0.12, 0.06, 0.03

19. References

1. Kang, C. S. M.; Zhang, X.; MacFarlane, D. R., Synthesis and Physicochemical Properties of Fluorinated Ionic Liquids with High Nitrogen Gas Solubility. *J. Phys. Chem. C* **2018**, *122*, 24550–24558.
2. Poling, B. E.; Prausnitz, J. M.; O'connell, J. P., *The Properties of Gases and Liquids*; McGraw-Hill: New York, 2001; Vol. 5.
3. Dymond, J. H., *The Virial Coefficients of Gases: A Critical Compilation*; Clarendon Press: Oxford, 1969; Vol. 2.
4. Desnoyers, J. E.; Perron, G., Treatment of Excess Thermodynamic Quantities for Liquid Mixtures. *J. Solution Chem.* **1997**, *26*, 749–755.
5. Papović, S.; Gadžurić, S.; Bešter-Rogač, M.; Jović, B.; Vraneš, M., A Systematic Study on Physicochemical and Transport Properties of Imidazolium-Based Ionic Liquids with Γ-Butyrolactone. *J. Chem. Thermodyn.* **2018**, *116*, 330–340.
6. Ouerfelli, N.; Barhoumi, Z.; Besbes, R.; Amdouni, N., The Reduced Redlich–Kister Excess Molar Gibbs Energy of Activation of Viscous Flow and Derived Properties in 1,4-Dioxane + Water Binary Mixtures from 293.15 to 309.15 K. *Phys. Chem. Liq.* **2011**, *49*, 777–800.
7. Merz, K.; Evers, M. V.; Uhl, F.; Zubatyuk, R. I.; Shishkin, O. V., Role of Chf2- and Cf3-Substituents on Molecular Arrangement in the Solid State: Experimental and Theoretical Crystal

Structure Analysis of Ch3/Chf2/Cf3-Substituted Benzene. *Cryst. Growth Des.* **2014**, *14*, 3124–3130.
8. Matsumoto, K.; Hagiwara, R.; Mazej, Z.; Benkič, P.; Žemva, B., Crystal Structures of Frozen Room Temperature Ionic Liquids, 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (Emimbf4), Hexafluoroniobate (Emimnbf6) and Hexafluorotantalate (Emimtaf6), Determined by Low-Temperature X-Ray Diffraction. *Solid State Sci.* **2006**, *8*, 1250–1257.
9. Neves, C. M. S. S.; Kurnia, K. A.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Freire, M. G.; Rebelo, L. P. N., Systematic Study of the Thermophysical Properties of Imidazolium-Based Ionic Liquids with Cyano-Functionalized Anions. *J. Phys. Chem. B* **2013**, *117*, 10271–10283.