

Reaction Kinetics of CO₂ Absorption of Phosphonium Based Anion-Functionalized Ionic Liquids

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Supplementary Information

I. Confirmation of tetraglyme being inert during CO₂ absorption reaction of ILs

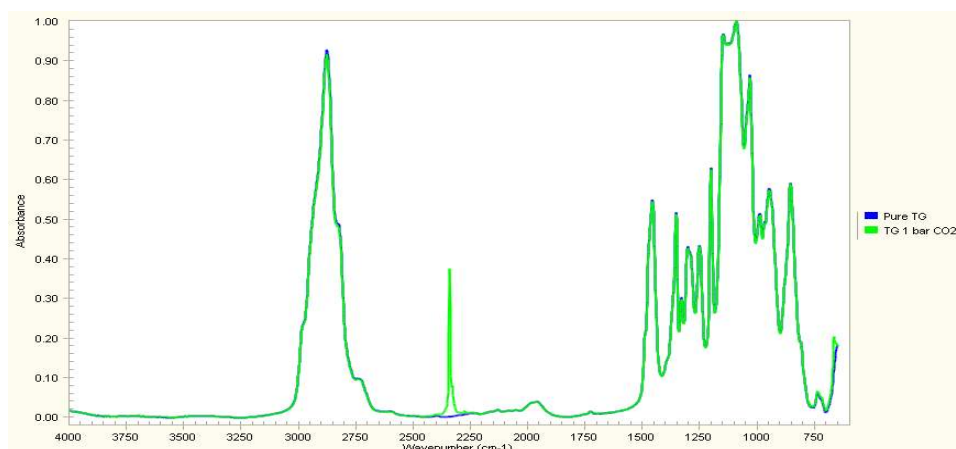


Fig S. 1 IR spectra of neat tetraglyme with (green) and without (blue) CO₂

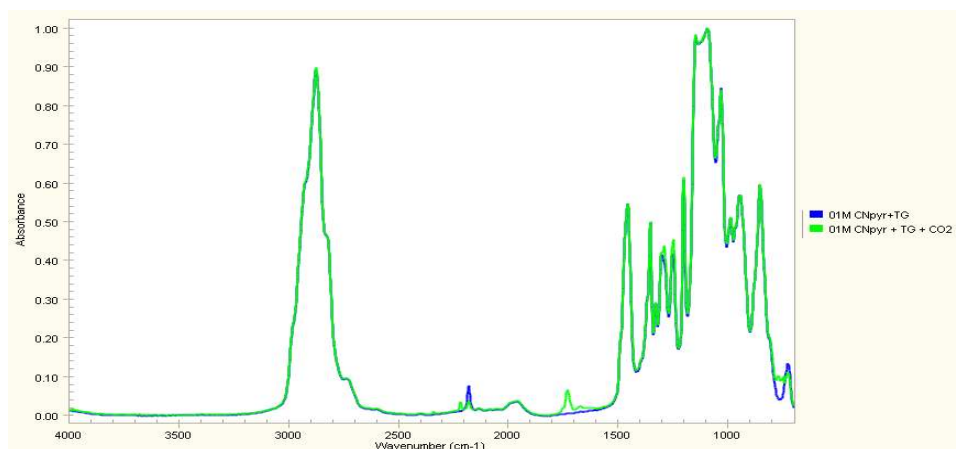


Fig S. 2 IR spectra of neat 0.1 M [P₆₆₆₁₄][2-CNpyr] in tetraglyme with (green) and without (blue) CO₂

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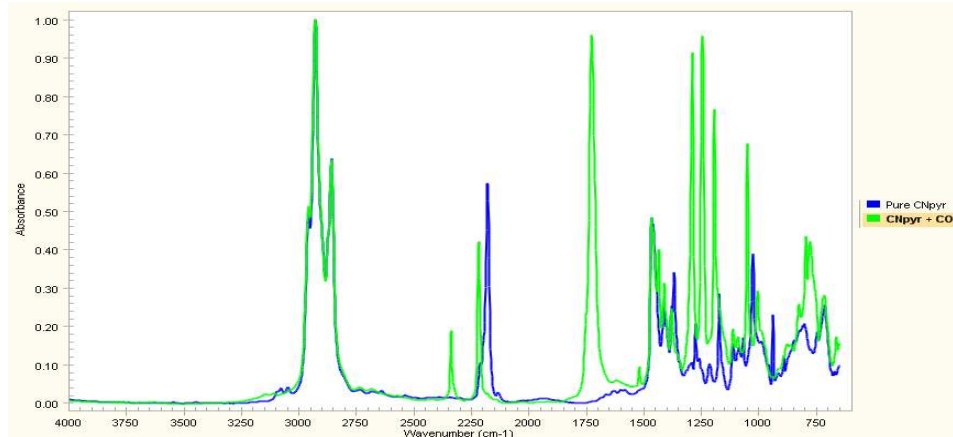


Fig S. 3 IR spectra of neat [P₆₆₆₁₄][2-CNpyr] with (green) and without (blue) CO₂

The IR spectrum between 700 and 4000 cm⁻¹ shown in Fig S.1 is observed for tetraglyme before and after it is exposed to CO₂. The only additional peak observed upon CO₂ addition is the physically dissolved CO₂ that appears between 2300 and 2400 cm⁻¹. In the presence of ionic liquid, (e.g. 0.1 M [P₆₆₆₁₄][2-CNpyr]), two additional peaks appear around 1700 cm⁻¹ (C=O stretch of reaction product between CO₂ and IL) and the peak around 2200 cm⁻¹ (CN of the cyanopyrrolide) shifts to higher wavenumbers, as seen in Fig S.2. The physically dissolved CO₂ peak in this case is not observable since these IL/TG+CO₂ reaction measurements were done at very low CO₂ pressures. These changes observed in Fig S.2 are identical to those obtained for the pure IL reacting with CO₂, as shown in Fig. S.3. Because the solution is very dilute in IL, the characteristic peaks for the IL and CO₂ reaction in Fig. S.2 are observed to be weak in intensity. The additional peaks between 1100 and 1300 cm⁻¹ from the IL + CO₂ reaction are not observed in Fig S.1 since the neat tetraglyme has very strong peaks that overlap and dominate in this region.

II. Reactor design and the details of the experimental methods:

The schematics shown in Fig S.4 detail the design of the reactor used for both kinetic and gas solubility measurements. The typical CO₂ pressure drop observed in the supply vessel during a kinetic run to maintain a constant pressure in the reactor is shown in Fig S.5.

Physico-chemical properties are either measured or estimated using appropriate approximations. The validation of the method employed in this study for the measurement of gas solubilities is shown in Table S.1. The CO₂ solubility in [hmim][Tf₂N] is measured and compared with the literature. The raw data measured at 10 and 25 °C are given in Table S.2. For the diffusivity of CO₂, the correlation (eqn. 16) adapted from the literature is used. The review of literature and the applicability of the correlation are provided in Table S.3 and Fig S.6, respectively.

Materials illustrating the discussions of the in-situ IR observations during the kinetic runs, fit of the activation energies and the details of the calculation of the desorption rates are provided at the end of this section.

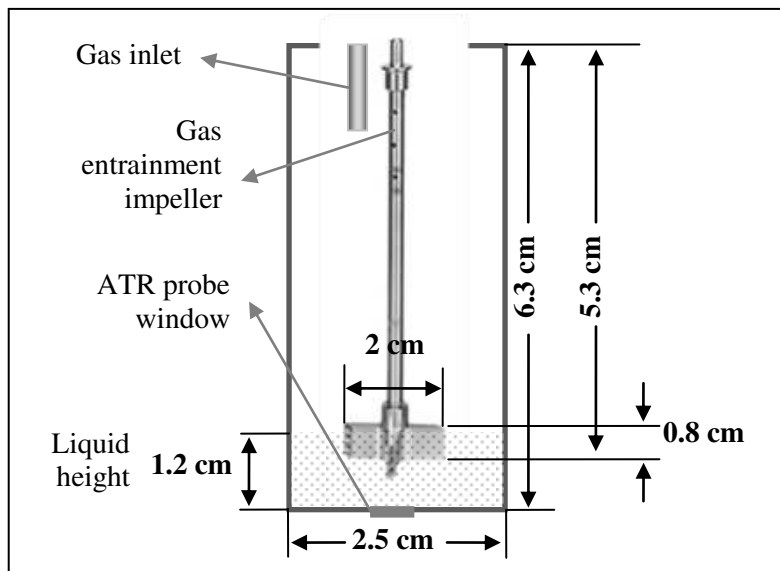


Fig S. 4 Schematics of IR-reactor showing the stirrer location in the liquid

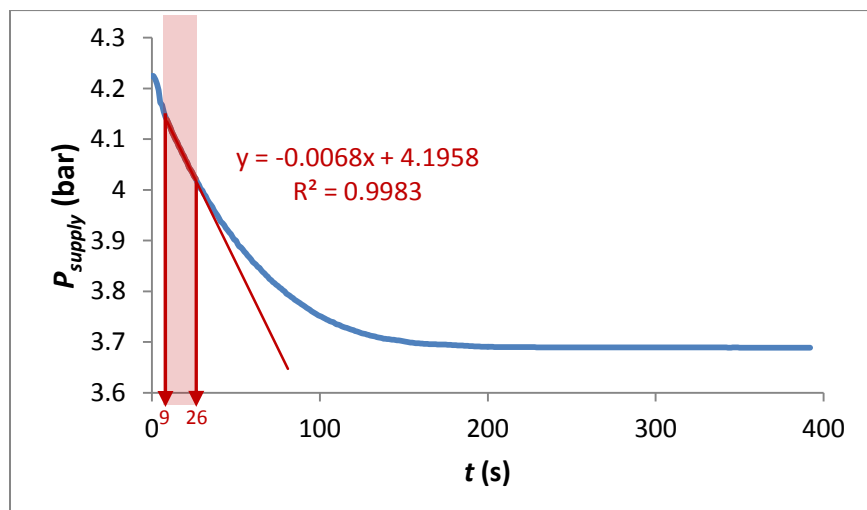


Fig S. 5 Observed pressure drop in the supply vessel during a typical rate experiment. The average flux is calculated from the slope of the linear line fitted to the selected highlighted interval. Data collected for the 0.1M [P₆₆₆₁₄][Pro] / TG system at 22 °C is shown.

Table S. 1 Comparison of measured and literature Henry's Law constants, H , for CO₂ in [hmim][Tf₂N] at 10 and 25 °C

	10 °C	25 °C
H (bar) this study	25	33
H (bar) literature ¹	24.2	31.6
% difference	3.3	4.4

Table S. 2 CO₂ solubility of [hmim][Tf₂N] at 10 and 25 °C measured in this study

P (bar)	T (°C)	x_{CO_2}	P (bar)	T (°C)	x_{CO_2}
0.850	25.2	0.0261	0.471	10	0.020
1.560	25.3	0.0482	0.527	10	0.022
2.510	25.1	0.0767	0.801	10	0.033
0.186	25.3	0.0054	0.935	10	0.038
0.519	25.1	0.0156	1.100	10	0.045
1.147	25.3	0.0346	1.220	10.1	0.050
1.567	25.2	0.0472	1.459	10	0.060
1.986	25.1	0.0591	1.650	10.1	0.067
--	--	--	1.734	10.1	0.071
--	--	--	1.998	10.1	0.081

Table S. 3 Comparison of experimental and predicted (using eqn. 15) CO₂ diffusivities for some organics and ILs. The highlighted compounds are the ones that fall beyond the applicable range of the correlation provided in eqn. 15 and the ones that display special interactions such as water and ethylene glycol.

	T (°C)	molar volume (L/mol)	viscosity (cP)	diffusion coefficient $\times 10^6$ (cm ² /s)	D_{CO_2} predicted	% error
<i>water</i> ²	25	0.018	0.8903	19.25	38.28	99
<i>water</i> ³	20	0.018	1.002	15.0	36.21	141
<i>ethylene glycol</i> ⁴	25	0.056	16	2.79	9.85	253
ethanol ⁵	25	0.063	1.2	34.20	33.27	-3
isobutyl alcohol ⁵	25	0.073	3.36	22.00	20.50	-7
toluene ^{6,7}	25	0.118	0.552	40.25	47.92	19
heptane ⁵	25	0.146	0.411	60.30	55.04	-9
hexadecane ⁶	50	0.301	2.04	22.10	25.92	17
[emim][TfO] ⁸	30	0.192	45	5.20	6.06	16
[bmim][BF ₄] ⁹	30	0.189 ¹⁰	75	4.10	4.76	16
[bmim][BF₄] ¹¹	30	0.189¹⁰	75	1.14	4.76	318

Table S.3 Continued

	T (° C)	molar volume (L/mol)	viscosity (cP)	diffusion coefficient $\times 10^6$ (cm ² /s)	D_{CO_2} predicted	% error
[bmim][PF ₆] ⁸	30	0.211	176	2.70	3.19	18
[bmim][PF₆]¹¹	30	0.211	176	0.8	3.19	297
<i>[desmim][TfO]⁸</i>	30	0.210	554	1.10	1.86	69
[emim][Tf ₂ N] ⁸	30	0.258	26	6.60	7.84	19
[pmmim][Tf ₂ N] ⁹	30	0.288 ¹²	66.6	5.60	5.04	-10
[N ₁₁₁₄][Tf ₂ N] ¹³	30	0.290	71	4.87	4.89	0
[bmim][Tf ₂ N] ⁹	30	0.292 ¹²	37.4	8.50	6.61	-22
[bmim][BETI] ⁸	30	0.294	77	4.50	4.71	5
[bmpy][Tf ₂ N] ⁹	30	0.306	51	6.00	5.71	-5
[N ₁₁₃₄][Tf ₂ N] ¹³	30	0.315	85	4.83	4.49	-7
[P ₂₄₄₄][DEP] ¹⁴	30	0.323	207	3.50	2.96	-16
[N ₁₁₁₆][Tf ₂ N] ¹³	30	0.325	100	4.38	4.16	-5
[N ₁₁₃₆][Tf ₂ N] ¹³	30	0.353	126	3.72	3.73	0
[N ₂₂₂₆][Tf ₂ N] ¹³	30	0.366	167	4.68	3.27	-30
<i>[N₄₄₄₁][Tf₂N]¹³</i>	30	0.384	386	3.41	2.21	-35
[N ₁₁₁₁₀][Tf ₂ N] ¹³	30	0.393	173	4.60	3.22	-30
[N ₁₁₃₁₀][Tf ₂ N] ¹³	30	0.425	183	3.78	3.13	-17
[P ₆₆₆₁₄][DCA] ¹⁴	30	0.578	213	3.00	2.92	-3
<i>[thtdp][Cl]⁸</i>	30	0.590	919	2.20	1.47	-33
<i>[P₆₆₆₁₄][Cl]¹⁴</i>	30	0.590	1316	3.00	1.24	-59
<i>[N₁₈₈₈][Tf₂N]¹³</i>	30	0.601	532	3.43	1.90	-45
<i>[emim][EtSO₄]¹⁵</i>	30	0.641	76	2.19	4.73	116
<i>[P₆₆₆₁₄][DBS]¹⁴</i>	30	0.731	3011	1.70	0.84	-51
<i>[P₆₆₆₁₄][Tf₂N]¹⁴</i>	30	0.804	243	6.20	2.74	-56

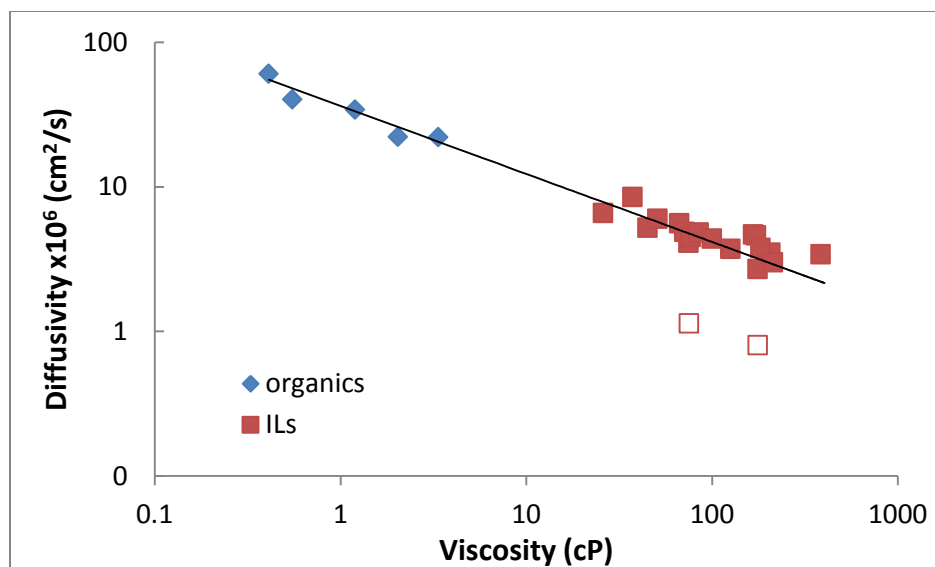


Fig S. 6 Correlation between diffusivity of CO₂ and the viscosity of organics. The correlation is extrapolated to higher viscosities and the experimental CO₂ diffusivities measured for ILs fall on this line with a maximum of 35 % error, including [N₄₄₄₁][Tf₂N]. The diffusivities obtained by Shiflett and Yokozeki ¹¹ are represented with open symbols. ILs with molar volumes above 0.59 L/mol and viscosities above 386 cP are excluded.

Table S. 4 First order reaction rate constants measured for [P₆₆₆₁₄][Pro] / TG solutions

<i>C</i> _{IL} (mol / L)	run #	<i>P</i> _{CO₂} (mbar)	<i>T</i> (°C)	<i>k</i> (1/s)	<i>k</i> _{average} (1/s)
0.05	1	10.6	21.2	1100	1000
	2	14.2	21.4	990	
	3	14.1	21.8	980	
0.1	1	15.1	22.6	1800	1900
	2	14.8	21.7	2200	
	3	15.6	22.2	1800	
0.15	1	14.9	22.2	4000	4200
	2	15.0	22.1	4300	
	3	14.7	22.2	4500	
0.1	1	16.4	29.9	4300	4400
	2	16.4	30.0	4300	
	3	16.2	29.8	4500	
0.1	1	16.9	39.8	5900	6200
	2	16.2	39.5	6200	
	3	16.1	39.6	6500	
0.1	1	17.1	49.8	8000	8600
	2	17.0	49.4	8600	
	3	16.7	49.6	9100	
0.1	1	15.9	60.0	11100	11000
	2	18.2	60.0	9600	
	3	17.3	60.8	12100	

Table S. 5 First order reaction rate constants measured for [P₆₆₆₁₄][2-CNpyr] / TG solutions

<i>C_{IL}</i> (mol / L)	run #	<i>P_{CO2}</i> (mbar)	<i>T</i> (°C)	<i>k</i> (1/s)	<i>k_{average}</i> (1/s)
0.05	1	15.4	21.8	390	370
	2	15.1	21.9	370	
	3	15.0	23.0	340	
0.1	1	16.2	22.5	790	850
	2	14.9	21.1	880	
	3	14.8	22.1	870	
0.15	1	15.2	21.6	1600	1500
	2	15.2	21.9	1500	
	3	14.6	21.1	1300	
0.1	1	16.0	30.0	910	910
	2	16.0	29.9	940	
	3	16.5	29.9	890	
0.1	1	11.6	39.8	1000	1100
	2	15.4	39.8	1100	
	3	16.6	39.8	1100	
0.1	1	14.7	49.5	1200	1200
	2	15.6	49.1	1300	
	3	16.1	49.7	1200	
0.1	1	14.2	59.5	1300	1600
	2	16.9	59.7	1700	
	3	16.1	59.5	1400	

Table S. 6 First order reaction rate constants measured for [P₆₆₆₁₄][3-CF₃pyra] / TG solutions

<i>C_{IL}</i> (mol / L)	run #	<i>P_{CO2}</i> (mbar)	<i>T</i> (°C)	<i>k</i> (1/s)	<i>k_{average}</i> (1/s)
0.05	1	15.4	22.6	160	150
	2	15.4	22.0	140	
	3	15.4	23.2	140	
0.1	1	15.5	22.0	320	320
	2	15.7	22.6	300	
	3	15.1	22.7	330	
0.15	1	15.0	22.3	530	500
	2	15.2	21.3	490	
	3	15.4	23.2	490	
0.1	1	16.4	29.9	320	340
	2	16.7	29.9	340	
	3	15.3	29.9	350	
0.1	1	14.3	39.7	510	490
	2	16.9	39.9	490	
	3	17.1	39.9	470	
0.1	1	17.5	49.3	560	530
	2	16.9	50.0	500	
	3	16.3	49.0	520	
	4	16.4	48.4	550	
0.1	1	15.1	58.8	740	740

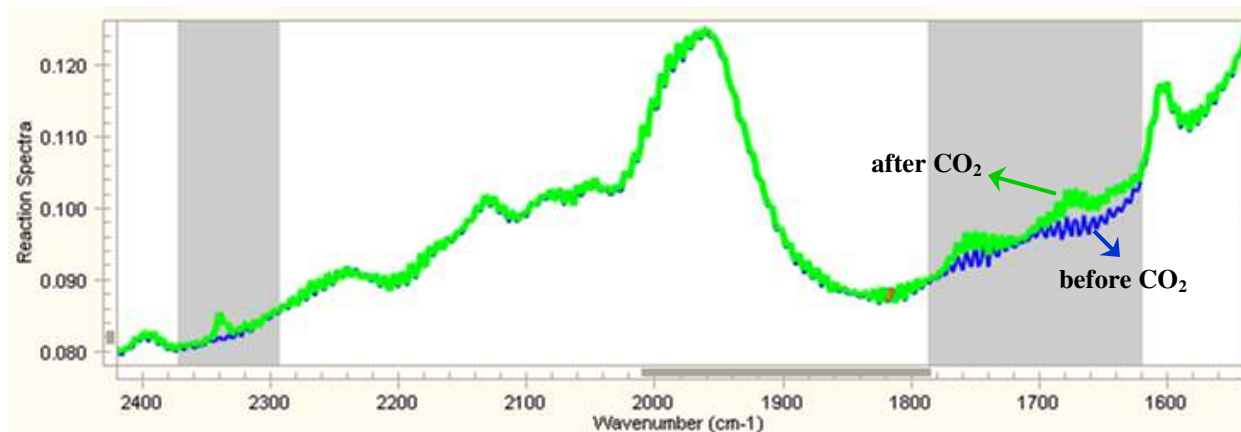


Fig S. 7 IR spectra of 0.1M [P₆₆₆₁₄][3-CF₃pyra] / TG at 60 °C before and after reaction with CO₂. Highlighted regions (2370 – 2310) cm⁻¹ and (1780 – 1620) cm⁻¹ correspond to the dissolved CO₂ and the newly formed -COO⁻ peaks, respectively.

The in-situ IR observations during kinetic measurements helped determine the conditions where the pseudo first order approximation was valid and select the time interval for kinetic analysis. Fig S.7 illustrates the observed absorbance between 2400 and 1500 cm⁻¹ for 0.1 M [P₆₆₆₁₄][3-CF₃pyra] at 60 °C. Due to the low CO₂ capacity of this IL, the changes in the IR spectrum are small. In other words, this is a ‘worst-case scenario’. In order to clearly see the changes, the selected interval is expanded in Fig S.7, which causes the spectra to appear noisy. The CO₂ and newly formed -COO⁻ peaks are highlighted in the figure.

Table S. 7 Arrhenius parameters fitted to the kinetic data shown in Figure 5. R² indicates the goodness of the fit

$k = A \cdot \exp\left(\frac{-E_a}{RT}\right)$	E_a (kJ/mol)	A	R^2
[P ₆₆₆₁₄][Pro]	43 ± 7	8.02 x 10 ⁸	0.9475
[P ₆₆₆₁₄][2-CNpyr]	11 ± 6	0.73 x 10 ³	0.8876
[P ₆₆₆₁₄][3-CF ₃ pyra]	18 ± 4	4.65 x 10 ³	0.9523

On the desorption rates:

CO₂ absorption r_{abs} and desorption r_{des} rate expressions can be written as

$$r_{abs} = k_2 C_{IL} C_{CO_2} \quad (S.1)$$

$$r_{des} = k_{-1} C_{IL-CO_2} \quad (S.2)$$

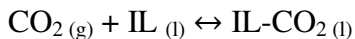
and

$$\frac{r_{des}}{r_{abs}} = \frac{k_{-1} C_{IL-CO_2}}{k_2 C_{IL} C_{CO_2}} = \frac{k_{-1} n_{IL-CO_2}}{k_2 n_{IL} n_{CO_2}} V_{sample} \quad (S.3)$$

where the moles of species i can be written in terms of their mole fraction: $n_i = x_i n_{total}$. Furthermore, the amount of CO₂ that is available to react with the IL can be written in terms of the Henry's Law constant ($P_{CO_2} = H x_{CO_2}$).

$$\frac{r_{des}}{r_{abs}} = \frac{k_{-1} x_{IL-CO_2} V_{sample}}{k_2 x_{IL} P_{CO_2} n_{total}} H \quad (S.4)$$

When we write the overall reaction between CO₂ and IL to form IL-CO₂



with forward and reverse rate constants as k_2 and k_{-1} , respectively, we can write the equilibrium constant for this reaction as

$$K = \left(\frac{f_{CO_2}}{f_{CO_2}^0} \right)^{-1} \left(\frac{f_{IL}}{f_{IL}^0} \right)^{-1} \left(\frac{f_{IL-CO_2}}{f_{IL-CO_2}^0} \right)^1 \quad (S.5)$$

Assuming the standard state as 1 bar ($f_{CO_2}^0 = 1$) and the fugacity of the pure liquid at the same temperature as the system (f_{IL}^0 and $f_{IL-CO_2}^0$) to be the vapor pressures of those pure components, eqn. (S.5) can be simplified as

$$K = \frac{(x_{IL-CO_2} \gamma_{IL-CO_2})}{(y_{CO_2} P_{CO_2})(x_{IL} \gamma_{IL})} \quad (S.6)$$

where γ_i is the activity coefficient and x_i is the mole fraction. Because the IL or the IL/tetraglyme mixture is essentially nonvolatile, the only specie present in the gas phase is CO₂. Therefore, the mole fraction of CO₂ in the gas phase is 1 ($y_{CO_2}=1$). When we further assume that the activity coefficients of the IL and that of the product are similar, eqn. (S.6) can be simplified to:

$$K = \frac{(x_{IL-CO_2})}{(P_{CO_2})(x_{IL})} \quad (S.7)$$

Returning to eqn. (S.4), the left hand side includes the familiar expression of the equilibrium constant derived in eqn. (S.7). At chemical equilibrium absorption and desorption rates are equal. Therefore,

$$1 = \frac{k_{-1}}{k_2} K \frac{V_{sample}}{n_{total}} H \quad (S.8)$$

Rearranging eqn. (S.8) in terms of the desorption rate constant (s^{-1}) yields:

$$k_{-1} = \frac{k_2}{K} \frac{1}{H} \frac{n_{total}}{V_{sample}} \quad (S.9)$$

The temperature dependence of the equilibrium constant is shown in Fig S.8 (data for [P₆₆₆₁₄][2-CNpyr] and [P₆₆₆₁₄][3-CF₃pyra] are given in Table 4 and those for [P₆₆₆₁₄][Pro] can be found in Goodrich, 2011¹⁶). The slope of $\ln K$ vs $1/T$ yields the reaction enthalpy in the form of $(-\Delta H/R)$ where R is the gas constant. The intercept corresponds to the change of entropy in the form of $(\Delta S/R)$. Accordingly, the reaction enthalpies of CO₂ absorption by [P₆₆₆₁₄][Pro] and [P₆₆₆₁₄][2-CNpyr] are -44 and -43 kJ / mol, respectively. Comparing the CO₂ isotherms for [P₆₆₆₁₄][Pro] in¹⁷ with that of [P₆₆₆₁₄][2-CNpyr] in¹⁸, it is clear that the reaction enthalpies for both ILs should be quite different. [P₆₆₆₁₄][Pro] has a higher affinity towards CO₂. Therefore, one would expect the reaction enthalpy for this IL to be more exothermic. The only explanation for this unexpected

enthalpy is that the assumed Langmuir-type model is not suitable to describe the CO₂ reaction with [P₆₆₆₁₄][Pro].

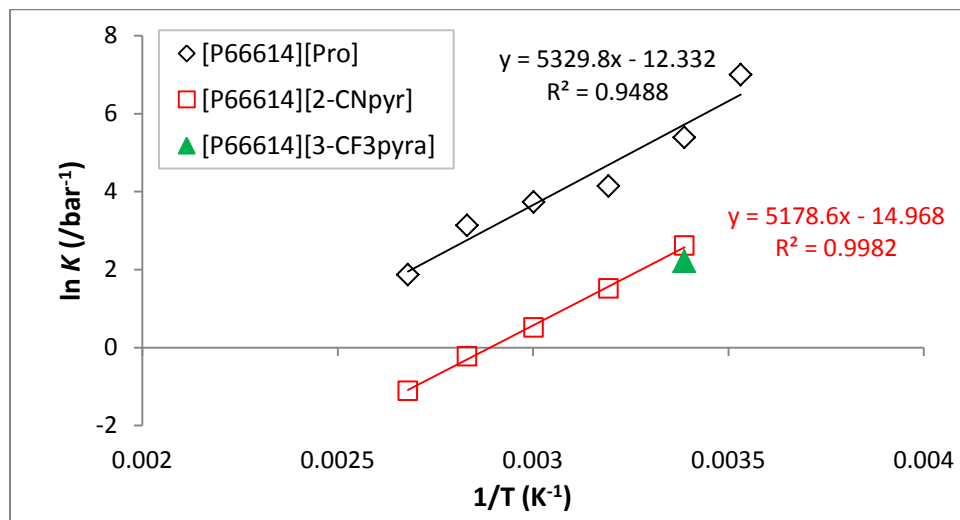


Fig S. 8 Dependence of the equilibrium constants for reaction of CO₂ with [P₆₆₆₁₄][Pro] and [P₆₆₆₁₄][2-CNpyr] on temperature.

To calculate the equilibrium constants at 80 and 100 °C, where data is not available, the relations obtained in Fig S.8 were used. It was assumed that temperature dependence of ΔH is negligible. For [P₆₆₆₁₄][3-CF₃pyra], the same change of entropy for [P₆₆₆₁₄][2-CNpyr] ($\Delta S = -130$ kJ / mol) was adapted to calculate the reaction enthalpy.

III. Other raw data for the measured properties:

Table S. 5 Experimental densities for the neat tetraglyme (TG) and IL/TG solutions. Kodama et al. ¹⁹. reported an uncertainty of $\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$ for their density measurement of TG; however, they did not report the water content of their sample. The discrepancy between our measurements and those reported by Kodama et al. can be explained by the difference in water content.

C_{IL} (mol/L)	water content (ppm)	density ($\text{g}\cdot\text{cm}^{-3}$)							
		22°C	25°C	30°C	35°C	40°C	45°C	50°C	60°C
[P₆₆₆₁₄][Pro]									
0.05	400	1.00568	1.00295	0.99841	0.99387	0.98936	0.9848	0.98029	0.97123
0.10	473	1.00289	1.00021	0.99571	0.99125	0.98675	0.98227	0.97782	0.96882
0.15	550	0.99989	0.99724	0.99281	0.98838	0.98398	0.97956	0.97514	0.9663
[P₆₆₆₁₄][2-CNpyr]									
0.05	470	1.00575	1.00304	0.9985	0.99398	0.98944	0.98488	0.98037	0.97132
0.10	477	1.00213	0.99945	0.99497	0.99049	0.98602	0.98162	0.9771	0.9682
0.15	490	0.99858	0.99596	0.99153	0.98712	0.98273	0.97831	0.97393	0.96514
[P₆₆₆₁₄][3-CF₃pyra]									
0.05	358	1.0071	1.00438	0.99984	0.99529	0.99073	0.98616	0.98163	0.97254
0.10	378	1.00501	1.00231	0.9978	0.9933	0.98882	0.98433	0.97983	0.9708
0.15	400	1.00298	1.00033	0.99587	0.99144	0.98698	0.98255	0.9781	0.96922
tetraglyme									
this work	224	1.00890	1.00618	1.00160	0.99700	0.99245	0.98786	0.98327	0.97409
¹⁹ Kodama et al., 2011			1.00743	1.00281		0.99356		0.98432	0.97507

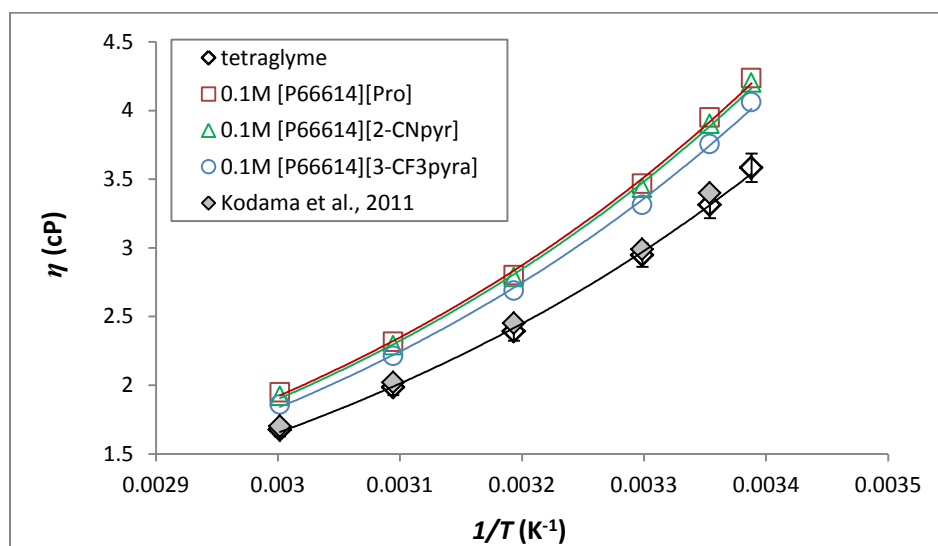


Fig S. 9 Arrhenius behavior of viscosities of tetraglyme and 0.1M IL / TG solutions. The lines represent fitted exponential trends.

Table S. 4 Data measured for the CO₂ solubility in tetraglyme.

P (bar)	T (°C)	x _{CO2}	P (bar)	T (°C)	x _{CO2}
0.381	22.1	0.0132	<i>0.149</i>	<i>23.5</i>	<i>0.005</i>
0.649	22.3	0.0225	0.272	24	0.0091
0.877	22.1	0.0308	0.385	24.2	0.0129
1.1	22.1	0.0388	0.69	24.4	0.0246
1.379	22.2	0.0483	0.976	24.2	0.0331
1.671	22.2	0.0581	1.76	24.2	0.0588
2.007	22.2	0.071	2.2	24.3	0.0725
2.277	22.2	0.08	2.941	24.6	0.0942
2.579	22.3	0.0905	3.906	24.8	0.1223
2.905	22.3	0.101	4.784	25.3	0.1521
0.382	21.9	0.0132	0.465	25	0.0153
0.838	22.1	0.0288	0.747	25.1	0.0249
1.167	22.2	0.0399	1.036	25	0.0349
1.493	22.3	0.0509	1.587	24.9	0.0538
1.854	22.2	0.0632	--	--	--
2.157	22.3	0.0733	--	--	--
2.926	22.3	0.0973	--	--	--
0.395	30.3	0.011	<i>0.162</i>	<i>38.9</i>	<i>0.0039</i>
0.602	30.3	0.0166	0.285	39.1	0.007
0.801	30.3	0.0221	0.397	39.1	0.0099
1.014	30.4	0.0279	0.51	39	0.0127
1.195	30.5	0.0328	0.938	39	0.0234
1.361	30.7	0.0373	1.857	39	0.0451
1.558	30.4	0.043	2.87	38.9	0.0719
1.776	30.4	0.0489	4.64	38.8	0.1137
2.072	30.4	0.0567	0.463	39.2	0.01
2.811	30.4	0.0756	0.488	39.4	0.0102
--	--	--	1.021	39.4	0.0224
--	--	--	1.401	39.6	0.0314
--	--	--	2.063	39.5	0.0466
--	--	--	3.173	39.5	0.0717
0.349	49.8	0.0064	0.255	59.5	0.0043
0.596	49.6	0.0114	0.392	59.6	0.0067
0.822	49.5	0.0157	0.504	59.6	0.0089
1.033	49.5	0.0201	0.617	59.3	0.0108
1.248	49.5	0.0251	0.727	59.3	0.0127
1.55	49.6	0.0316	0.836	59.2	0.0145
1.875	49.7	0.0382	1.031	59.1	0.0178
2.196	49.6	0.045	1.244	59	0.0214
2.617	49.7	0.0533	1.543	59.1	0.027
0.349	50.6	0.0063	2.108	59.1	0.0369
0.59	50.3	0.0109	3.161	59	0.0552
0.814	49.8	0.0154	0.604	59.1	0.0099
1.031	49.9	0.0201	0.962	58.9	0.0163
1.24	50	0.0253	1.158	58.9	0.0199
1.79	50	0.0372	1.726	59.1	0.0296
2.249	50	0.0474	2.325	59	0.0398
2.678	49.9	0.0582	3.09	59.1	0.0529

Table S. 5 N₂O solubility in tetraglyme measured in this study.

P (bar)	T (°C)	x _{N₂O}	P (bar)	T (°C)	x _{N₂O}
0.507	22.4	0.0112	0.432	39.5	0.0079
0.859	22.5	0.0204	0.606	39.4	0.0113
1.108	22.3	0.0273	0.812	39.4	0.0156
1.335	22.2	0.0335	1.027	39.4	0.02
1.556	22.3	0.0394	1.249	39.5	0.0252
1.814	22.2	0.0464	1.539	39.4	0.0318
2.064	22.2	0.054	1.862	39.4	0.0387
2.303	22.2	0.0608	3.384	39.3	0.0683
2.537	22.2	0.0669	0.436	39.8	0.0086
3.143	22.2	0.0826	0.871	39.7	0.0174
3.709	22.2	0.098	1.174	39.7	0.0242
4.04	22.3	0.1073	1.58	39.7	0.0336
0.48	22.1	0.0128	1.964	39.7	0.0429
0.854	22.2	0.0227	2.211	39.7	0.0505
1.23	22.4	0.0329	2.783	39.7	0.0648
1.607	22.2	0.0433	0.625	59	0.009
2.109	22.3	0.0565	1.004	58.9	0.0146
2.479	22.4	0.0666	1.243	59.1	0.019
3.248	22.4	0.087	1.649	59.1	0.0256
0.203	24.8	0.0052	2.054	59.1	0.0338
0.828	24.9	0.021	2.329	59	0.0388
1.148	25.1	0.0295	3.013	59	0.0493
1.599	25	0.0409	0.462	59.4	0.0066
2.066	25.15	0.0525	0.532	59.5	0.0075
2.841	25.23	0.0712	0.811	59.4	0.0117
--	--	--	1.04	58.9	0.0151
--	--	--	1.17	59.3	0.0173
--	--	--	1.372	59.3	0.0206
--	--	--	1.588	59.3	0.0239
--	--	--	1.71	58.9	0.0298
--	--	--	2.092	59	0.035
--	--	--	2.434	58.9	0.0399
--	--	--	3.12	58.8	0.0495

Table S. 6 Data measured for N₂O solubility in [hmim][Tf₂N] and [hmpy][Tf₂N]

[hmim][Tf ₂ N]			[hmpy][Tf ₂ N]		
P (bar)	T (°C)	x _{N2O}	P (bar)	T (°C)	x _{N2O}
0.187	24.8	0.006	0.154	24.9	0.005
0.429	24.8	0.014	0.34	25	0.012
0.803	24.9	0.031	0.591	24.9	0.02
1.035	24.9	0.038	0.838	25	0.029
1.277	25	0.046	1.045	25	0.037
1.367	25	0.049	1.437	24.9	0.052
0.146	25	0.004	1.792	24.9	0.064
0.272	25	0.008	0.113	49.7	0.002
0.5	25	0.016	0.272	49.7	0.006
0.831	25.1	0.027	0.4	50.1	0.008
1.244	25	0.041	0.523	50.1	0.011
1.854	25	0.061	0.876	50	0.019
1.289	25.1	0.044	1.243	50	0.028
0.105	50	0.002	1.612	50	0.036
0.332	50.1	0.006	1.866	50.1	0.043
0.642	50.1	0.013			
1	50.1	0.021			
1.201	50.1	0.026			
1.421	50.2	0.031			
1.93	50.2	0.043			

Table S. 7 Data measured for N₂O solubility in [P₆₆₆₁₄][Pro]

P (bar)	T (°C)	x _{N2O}	P (bar)	T (°C)	x _{N2O}
0.097	24.7	0.004	0.145	25.2	0.006
0.287	24.8	0.013	0.338	25.1	0.015
0.499	24.8	0.023	0.588	25.1	0.026
0.61	24.8	0.032	0.869	25	0.040
0.804	24.8	0.040	1.086	25	0.047
0.935	24.9	0.046	--	--	--
1.106	24.9	0.055	--	--	--
1.236	24.9	0.061	--	--	--

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