Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Insights into choline chloride – phenylacetic acid deep eutectic solvent for CO_2 absorption

Tausif Altamash,[a] Mert Atilhan,[a*] Amal Aliyan,[a] Ruh Ullah,[a] Gregorio García[b] and Santiago Aparicio[b*]

[a] Department of Chemical Engineering, Qatar University, Doha, Qatar

[b] Department of Chemistry, University of Burgos, Burgos, Spain

[*]Corresponding authors: mert.atilhan@qu.edu.qa (M. A.) and sapar@ubu.es (S. A.).

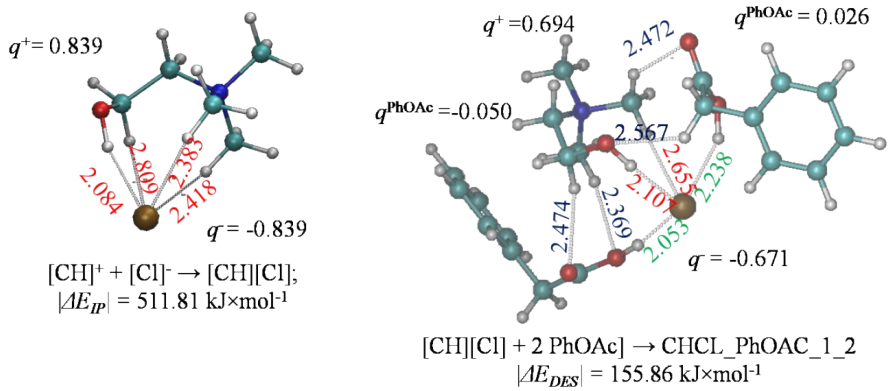


Fig. S1 Optimized structures for [CH][Cl] (left) and CHCl_PhOAc_1_2 (right) at B3LYP-D2/6-31+G** level, along the main structural parameters related with intermolecular interactions. Computed charges over choline (q^+), chloride (q^-) and phenyl acetic (q^{PhOAc}) motifs, as well as the binding energy for ionic pair interaction (ΔE_{IP}) DES formation (ΔE_{DES}) are also shown**.** Intermolecular bond lengths are in Å.

Table S1 Systems used for MD simulations of CHCl_PhOAc_1_2 + CO_2 mixtures. x_{CO2} stands for CO_2 mole fraction, and *N* for the number of molecules used in each system. All simulation were carried out at 298 K

p / bar	x_{CO2}	N_{CO2}	$N_{[CH][Cl]}$	N_{PhOAc}
0.93	0.027	7	250	500
4.93	0.113	32	250	500
9.92	0.209	66	250	500
14.92	0.290	102	250	500
19.91	0.361	141	250	500
24.91	0.424	184	250	500
29.91	0.478	229	250	500

Mixture compositions for obtaining CO_2 mole fractions used in building simulation boxes were obtained from unpublished experimental results obtained using a magnetic sorption apparatus (MSA) of Rubotherm präzisionsmesstechnik GmbH.

Table S2 Forcefield parameterization for compounds studied in this work

The general form of the applied force field is:

$$E = \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_\theta (\theta - \theta_{eq})^2 + E_{tor}$$

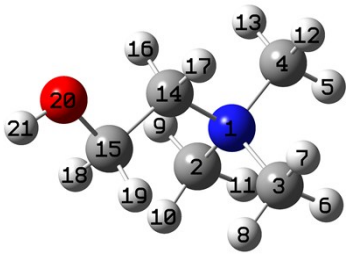
$$+ \sum_i \sum_j \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} \right\}$$

Dihedrals (E_{tor}) were described according to:

$$E_{tor} = \sum_{torsions} k_\phi (1 + \cos(m\phi - \delta))$$

Improper dihedrals were described according to:

$$E_{improper} = k_\phi (\phi - \phi_0)^2$$



[CH]$^+$

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	0.319516	3.1000	0.8370
2	-0.270228	3.4500	0.3350
3	-0.245586	3.4500	0.3350
4	-0.190790	3.4500	0.3350
5	0.105401	2.2100	0.0920
6	0.111574	2.2100	0.0920
7	0.154988	2.2100	0.0920
8	0.140103	2.2100	0.0920
9	0.088173	2.2100	0.0920
10	0.142721	2.2100	0.0920
11	0.108039	2.2100	0.0920
12	0.107796	2.2100	0.0920
13	0.090485	2.2100	0.0920
14	-0.299507	3.6400	0.2300

15	0.688986	3.6400	0.2300
16	0.067734	2.2100	0.0920
17	0.137039	2.2100	0.0920
18	-0.035466	0.0000	0.0200
19	-0.127488	0.0000	0.0200
20	-0.778949	3.9500	0.6370
21	0.379517	0.4000	0.1925

Bonds

Atom Numbers		r_{eq} /Å	k_r/ kJ mol^{-1} Å^{-2}
1	2	1.5100	1092.80
1	3	1.5100	1092.80
1	14	1.5320	1092.80
1	4	1.5100	1092.80
2	9	1.0890	1422.56
2	10	1.0890	1422.56
2	11	1.0890	1422.56
3	6	1.0890	1422.56
3	7	1.0890	1422.56
3	8	1.0890	1422.56
4	5	1.0890	1422.56
4	12	1.0890	1422.56
4	13	1.0890	1422.56
14	15	1.5200	931.60
14	16	1.0910	1422.56
14	17	1.0910	1422.56
15	18	1.0960	1422.56
15	19	1.0960	1422.56
15	20	1.4180	1792.00
20	21	0.9650	2313.80

Angles

Atom Numbers			θ_{eq} / deg	k_θ / kJ mol^{-1} rad^{-2}
2	1	3	108.9000	209.30
2	1	14	110.7000	209.30
2	1	4	108.9000	209.30
3	1	14	110.7000	209.30
3	1	4	108.9000	209.30
14	1	4	110.7000	209.30
1	2	10	109.0000	201.00
1	2	11	109.0000	201.00
1	2	9	109.0000	201.00
10	2	11	109.3000	148.60
10	2	9	109.3000	148.60
11	2	9	109.3000	148.60
1	3	8	109.0000	201.00
1	3	7	109.0000	201.00
1	3	6	109.0000	201.00
8	3	7	109.3000	148.60
8	3	6	109.3000	148.60

7	3	6	109.3000	148.60
1	4	13	109.0000	201.00
1	4	12	109.0000	201.00
1	4	5	109.0000	201.00
13	4	12	109.3000	148.60
13	4	5	109.3000	148.60
12	4	5	109.3000	148.60
1	14	15	110.6000	334.90
1	14	16	106.2000	215.60
1	14	17	106.2000	215.60
15	14	16	110.6000	110.90
15	14	17	110.6000	110.90
16	14	17	108.4000	148.60
14	15	18	105.8000	148.60
14	15	19	105.8000	148.60
14	15	20	109.4000	316.90
18	15	19	107.2000	148.60
18	15	20	111.8000	192.20
19	15	20	111.8000	192.20
15	20	21	111.9000	240.70

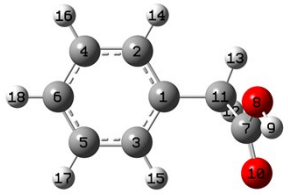
Dihedrals

Atom Numbers				δ / deg	k_φ / kJ mol^{-1}	m
3	1	2	10	0.00	0.335	3
3	1	2	11	0.00	0.335	3
3	1	2	9	0.00	0.335	3
14	1	2	10	0.00	0.335	3
14	1	2	11	0.00	0.335	3
14	1	2	9	0.00	0.335	3
4	1	2	10	0.00	0.335	3
4	1	2	11	0.00	0.335	3
4	1	2	9	0.00	0.335	3
2	1	3	8	0.00	0.335	3
2	1	3	7	0.00	0.335	3
2	1	3	6	0.00	0.335	3
14	1	3	8	0.00	0.335	3
14	1	3	7	0.00	0.335	3
14	1	3	6	0.00	0.335	3
4	1	3	8	0.00	0.335	3
4	1	3	7	0.00	0.335	3
4	1	3	6	0.00	0.335	3
2	1	14	15	180.00	10.500	3
2	1	14	16	0.00	0.335	3
2	1	14	17	0.00	0.335	3
3	1	14	15	180.00	10.500	3
3	1	14	16	0.00	0.335	3
3	1	14	17	0.00	0.335	3
4	1	14	15	180.00	10.500	3
4	1	14	16	0.00	0.335	3
4	1	14	17	0.00	0.335	3
2	1	4	13	0.00	0.335	3
2	1	4	12	0.00	0.335	3

2	1	4	5	0.00	0.335	3
3	1	4	13	0.00	0.335	3
3	1	4	12	0.00	0.335	3
3	1	4	5	0.00	0.335	3
14	1	4	13	0.00	0.335	3
14	1	4	12	0.00	0.335	3
14	1	4	5	0.00	0.335	3
1	14	15	18	0.00	2.510	2
1	14	15	19	0.00	2.510	2
1	14	15	20	0.00	0.000	1
16	14	15	18	180.00	10.500	2
16	14	15	19	180.00	10.500	2
16	14	15	20	180.00	0.000	2
17	14	15	18	180.00	10.500	2
17	14	15	19	180.00	10.500	2
17	14	15	20	180.00	0.000	2
14	15	20	21	0.00	5.440	1
18	15	20	21	0.00	1.260	2
19	15	20	21	0.00	1.260	2

Cl^-

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	-0.670677	2.47000	0.418400



PhOAc

#	q^{A*}	q^{B*}	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	-0.264165	0.183385	3.55005	0.292880
2	-0.178686	-0.188848	3.55005	0.292880
3	-0.216083	-0.180233	3.55005	0.292880
4	-0.066347	-0.056783	3.55005	0.292880
5	-0.019907	-0.066088	3.55005	0.292880
6	-0.125358	-0.112415	3.55005	0.292880
7	0.902700	0.904824	3.56359	0.460240
8	-0.695191	-0.664886	3.15378	0.636386
9	0.448147	0.397551	0.40001	0.192464
10	-0.619056	-0.629716	3.02905	0.502080
11	-0.325380	-0.306781	3.87541	0.230120
12	0.071478	0.076447	2.35197	0.092048

13	0.107196	0.113611	2.35197	0.092048
14	0.105377	0.128552	2.35197	0.092048
15	0.118409	0.104622	2.35197	0.092048
16	0.088348	0.083506	2.35197	0.092048
17	0.073632	0.081079	2.35197	0.092048
18	0.092823	0.082629	2.35197	0.092048

* Two different parameters sets for charges (q^A and q^B) because of the two different PhOAc molecules interacting with the salt.

Bonds

Atom Numbers		r_{eq} /Å	k_r/ kJ mol^{-1} Å^{-2}
7	10	1.2220	3899.3
7	8	1.3550	1746.7
7	11	1.4920	1261.6
8	9	0.9810	2229.1
11	1	1.4860	1492.6
11	12	1.0930	1435.1
11	13	1.0930	1435.1
1	3	1.3740	1678.1
1	2	1.3740	1678.1
2	4	1.3740	1678.1
2	14	1.0840	1597.7
3	5	1.3740	1678.1
3	15	1.0840	1597.7
4	6	1.3740	1678.1
4	16	1.0840	1597.7
5	17	1.0840	1597.7
5	6	1.3740	1678.1
6	18	1.0840	1597.7

Angles

Atom Numbers			θ_{eq} / deg	k_θ / kJ mol^{-1} rad^{-2}
2	1	3	119.98	402.88
2	1	11	120.42	483.57
3	1	11	120.42	483.57
1	2	4	119.98	402.88
1	2	14	120.57	339.05
4	2	14	120.57	339.05
1	3	5	119.98	402.88
1	3	15	120.57	339.05
5	3	15	120.57	339.05
2	4	6	119.98	402.88
2	4	16	120.57	339.05
6	4	16	120.57	339.05
3	5	6	119.98	402.88
3	5	17	120.57	339.05
6	5	17	120.57	339.05
4	6	5	119.98	402.88
4	6	18	120.57	339.05
5	6	18	120.57	339.05
8	7	10	124.43	695.55

8	7	11	109.72	628.10
10	7	11	124.41	564.87
7	8	9	111.95	351.09
1	11	7	109.83	608.83
1	11	12	109.49	377.58
1	11	13	109.49	377.58
7	11	12	108.39	391.44
7	11	13	108.39	391.44
12	11	13	108.84	310.74

Dihedrals

Atom Numbers				δ / deg	k_φ / kJ mol^{-1}	m
1	2	4	6	180.00	14.6440	2
1	2	4	16	180.00	14.6440	2
1	3	5	6	180.00	14.6440	2
1	3	5	17	180.00	14.6440	2
1	11	7	8	180.00	0.8368	2
1	11	7	8	0.00	0.6276	3
1	11	7	10	180.00	0.8368	2
1	11	7	10	0.00	0.8368	3
2	1	3	5	180.00	14.6440	2
2	1	3	15	180.00	14.6440	2
2	1	11	7	0.00	0.4184	3
2	1	11	12	180.00	-0.8786	2
2	1	11	12	0.00	0.8201	3
2	1	11	13	180.00	-0.8786	2
2	1	11	13	0.00	0.8201	3
2	4	6	5	180.00	14.6440	2
2	4	6	18	180.00	14.6440	2
3	1	2	4	180.00	14.6440	2
3	1	2	14	180.00	14.6440	2
3	1	11	7	0.00	0.4184	3
3	1	11	12	180.00	-0.8786	2
3	1	11	12	0.00	0.8201	3
3	1	11	13	180.00	-0.8786	2
3	1	11	13	0.00	0.8201	3
3	5	6	4	180.00	14.6440	2
3	5	6	18	180.00	14.6440	2
4	2	1	11	180.00	14.6440	2
4	6	5	17	180.00	14.6440	2
5	3	1	11	180.00	14.6440	2
5	6	4	16	180.00	14.6440	2
6	4	2	14	180.00	14.6440	2
6	5	3	15	180.00	14.6440	2
8	7	11	12	180.00	-1.3054	2
8	7	11	12	0.00	0.6904	3
8	7	11	13	180.00	-1.3054	2
8	7	11	13	0.00	0.6904	3
9	8	7	10	0.00	3.4769	1
9	8	7	10	180.00	12.8700	2
9	8	7	10	0.00	-0.1213	3
9	8	7	11	0.00	-2.4393	1

9	8	7	11	180.00	10.6232	2
9	8	7	11	0.00	-1.1422	3
10	7	11	12	0.00	1.3807	1
10	7	11	12	180.00	-2.9455	2
10	7	11	12	0.00	0.6443	3
10	7	11	13	0.00	1.3807	1
10	7	11	13	180.00	-2.9455	2
10	7	11	13	0.00	0.6443	3
11	1	2	14	180.00	14.6440	2
11	1	3	15	180.00	14.6440	2
14	2	4	16	180.00	14.6440	2
15	3	5	17	180.00	14.6440	2
16	4	6	18	180.00	14.6440	2
17	5	6	18	180.00	14.6440	2

improper

Atom Numbers				ϕ_0 / deg	k_φ / kJ mol^{-1} rad^{-2}
1	3	11	2	0.00	24.0915
2	4	1	14	0.00	9.0291
3	5	1	15	0.00	9.0291
4	6	2	16	0.00	9.0291
11	7	1	12	0.00	0.0000
11	7	1	13	0.00	0.0000
7	8	11	10	0.00	84.9101
5	6	3	17	0.00	9.0291
6	5	4	18	0.00	9.0291

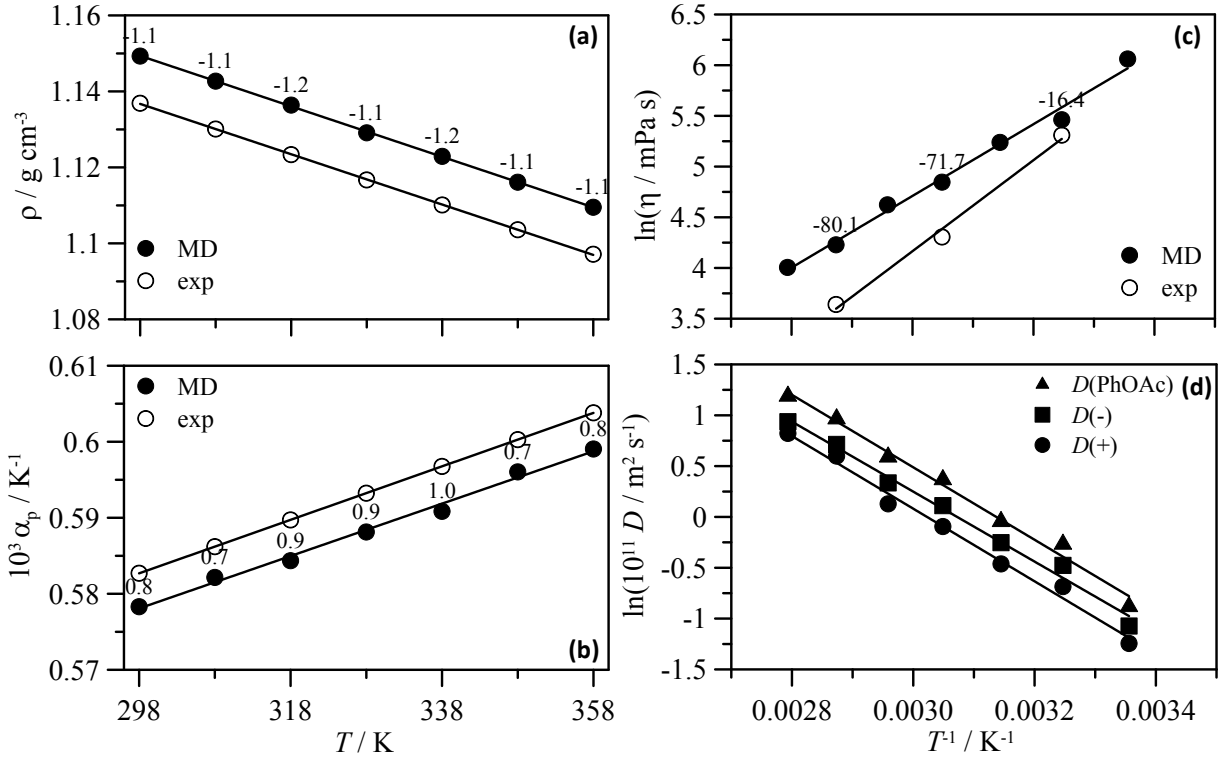


Fig. S2 Thermophysical properties of CHCl_PhOAc_1_2 at 1 bar as a function of temperature. MD and exp stand from values obtained from molecular dynamics simulations and measured in this work, respectively. Value sin panel d are only for MD because experimental data are not available. Numbers inside each panel show percentage deviations between MD and exp data. Lines are linear fits for guiding purposes. In panel d, + stands for $[CH]^+$ and – for Cl^-. P stands for density, α_p for thermal expansion coefficient, η for dynamic viscosity, and *D* for center-of-mass self-diffusion coefficient.

Experimental data come from unpublished results obtained in our laboratories using an Anton Paar DMA 4500M densimeter (±0.00005 g cm^{-3}) and an Anton Paar Rheometer Model MCR 302 (± 5%).

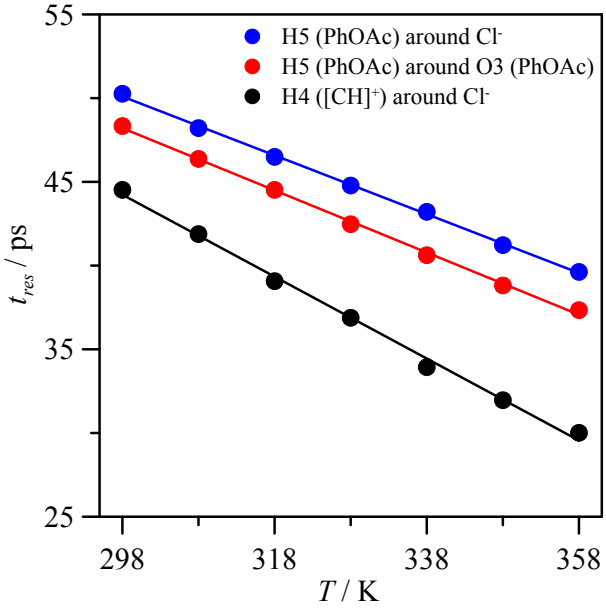


Fig. S3 Residence time, t_{res}, of selected atoms around other atoms obtained from molecular dynamics simulations for CHCl_PhOAc_1_2 at 298 K and 1 bar. t_{res} was calculated from the exponential decay of conditional probability P with R = 6.0 Å.

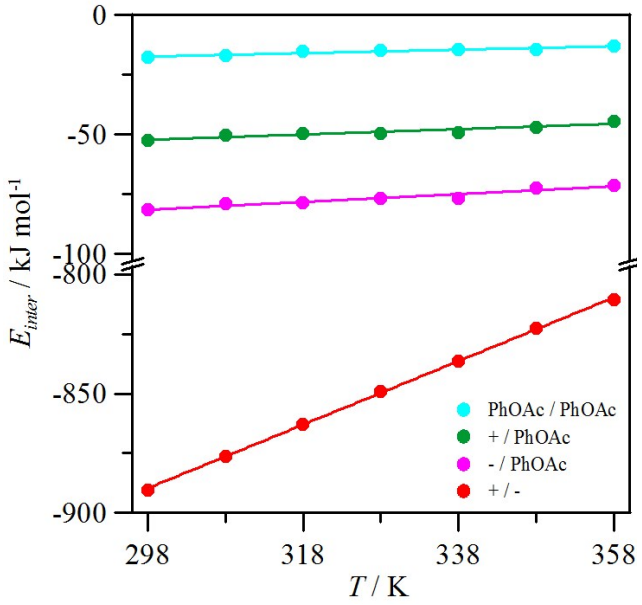


Fig. S4 Intermolecular interaction energy, E_{inter}, sum of Lennard-Jones and coulombic terms, for CHCl_PhOAc_1_2 at 298 K and 1 bar.

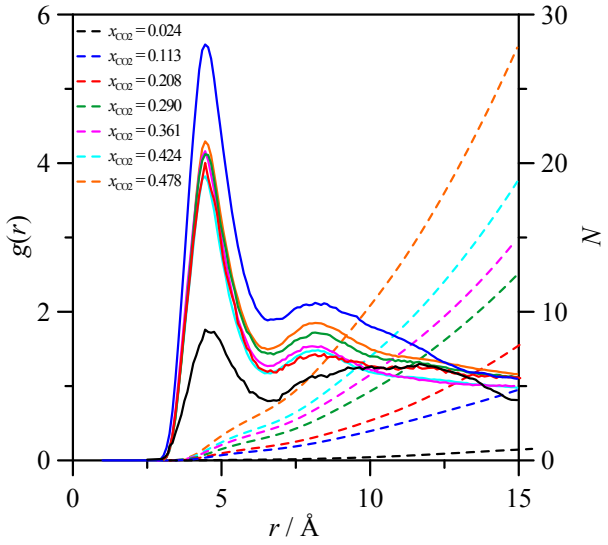


Fig. S5 CD–CD site–site radial distribution functions, $g(r)$ (continuous lines, left axis), and the corresponding running integrals, N (dashed lines, right axis), for CHCl_PhOAc_1_2 + CO_2 systems at 298 K as a function of CO_2 mole fraction.

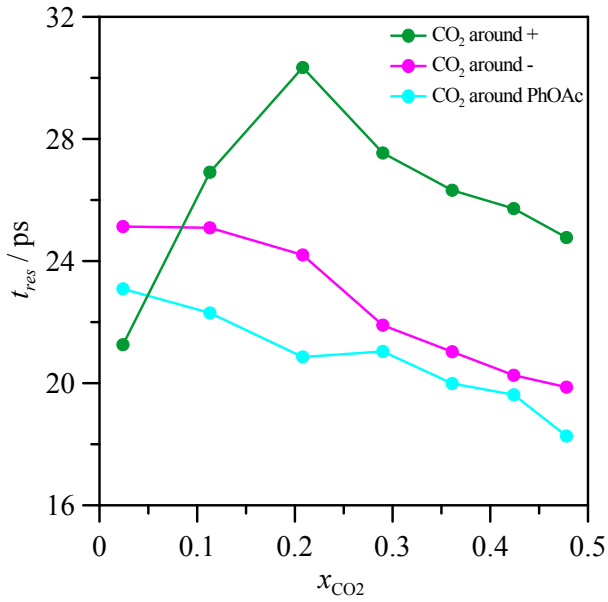


Fig. S6 Residence time, t_{res}, of CO_2 carbon atoms around the center of mass of $[CH]^+$, Cl^-, and PhOAc molecules for CHCl_PhOAc_1_2 + CO_2 systems at 298 K as a function of CO_2 mole fraction. t_{res} was calculated from the exponential decay of conditional probability P with R = 6.0 Å.

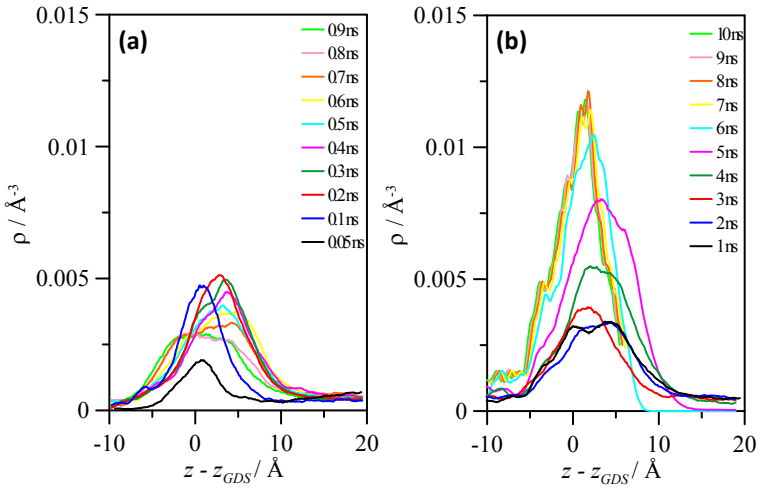


Fig. S7 Density profiles for CO_2 molecules in CHCl_PhOAc_1_2 + CO_2 interface system calculated from molecular dynamics simulations at 298 K. *z* stands for the coordinate perpendicular to the corresponding interfaces, and z_{GDS} for the coordinate of the Gibbs dividing surface. Profiles obtained for the reported simulation times.

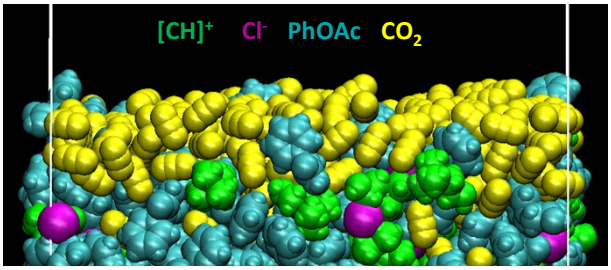


Fig. S8 Snapshot of the CHCl_PhOAc _1_2 + CO_2 interfaces calculated from molecular dynamics simulations at 298 K.

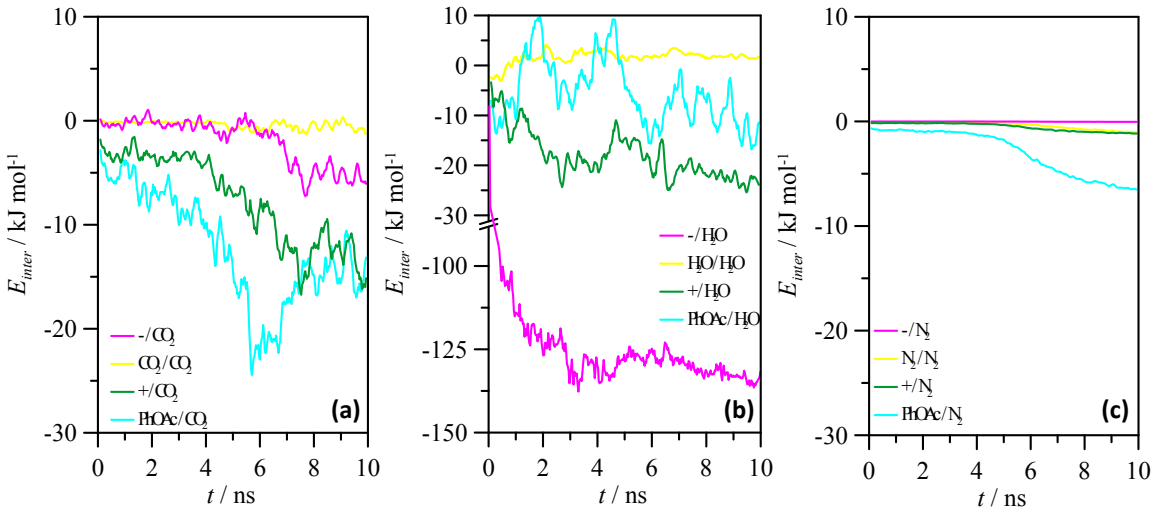


Fig. S9 Intermolecular interaction energy, E_{int}, between CO_2, H_2O and N_2 and molecules in CHCl_PhOAc_1_2 + flue gas interface system as a function of simulation time, calculated from molecular dynamics simulations at 298 K.