Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Detailed Study of Cholinium Chloride and Levulinic Acid Deep Eutectic Solvent System for CO_2 Capture via Experimental and Molecular Simulation Approaches

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Electronic Supplementary Information

Table S1. Forcefield parameterization for compounds studied in this work.

The general form of the applied force field is:

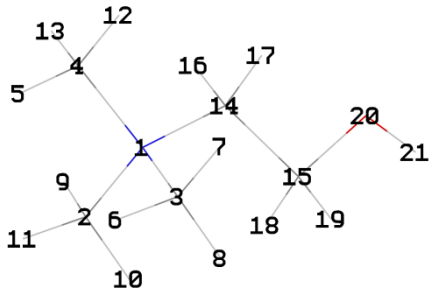
$$E = \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_\theta (\theta - \theta_{eq})^2 + E_{tor}$$
$$+ \sum_i \sum_j \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j e^2}{4\pi\varepsilon_0 r_{ij}} \right\}$$

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	0.362364	3.1000	0.8370
2	-0.218014	3.4500	0.3350
3	-0.295250	3.4500	0.3350
4	-0.404630	3.4500	0.3350
5	0.169077	2.2100	0.0920
6	0.151459	2.2100	0.0920
7	0.107947	2.2100	0.0920
8	0.177096	2.2100	0.0920
9	0.120926	2.2100	0.0920
10	0.161115	2.2100	0.0920
11	0.105308	2.2100	0.0920
12	0.145579	2.2100	0.0920
13	0.148409	2.2100	0.0920
14	-0.192072	3.6400	0.2300
15	0.546587	3.6400	0.2300
16	0.064004	2.2100	0.0920
17	0.107567	2.2100	0.0920
18	-0.073028	0.0000	0.0200
19	-0.029581	0.0000	0.0200
20	-0.733393	3.1538	0.6364
21	0.403941	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	

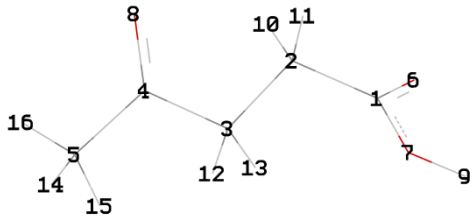
Dihedrals

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

Chlorine

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	-0.684915	3.5000	0.9276



LEV

LEV_1

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	0.842712	3.56359	0.460240
2	-0.174511	3.87541	0.230120
3	-0.011592	3.87541	0.230120
4	0.625023	3.56359	0.460240
5	-0.359483	3.87541	0.230120
6	-0.681608	3.02905	0.502080
7	-0.664781	3.15378	0.636386
8	-0.540244	3.02905	0.502080
9	0.459424	0.40001	0.192464
10	0.047030	2.35197	0.092048
11	0.065710	2.35197	0.092048
12	0.003217	2.35197	0.092048
13	0.038073	2.35197	0.092048
14	0.093589	2.35197	0.092048
15	0.083983	2.35197	0.092048
16	0.107231	2.35197	0.092048

LEV_2

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	0.813266	3.56359	0.460240
2	-0.172891	3.87541	0.230120
3	-0.019347	3.87541	0.230120
4	0.629431	3.56359	0.460240
5	-0.362507	3.87541	0.230120
6	-0.662318	3.02905	0.502080
7	-0.617997	3.15378	0.636386
8	-0.542801	3.02905	0.502080
9	0.412877	0.40001	0.192464
10	0.067413	2.35197	0.092048
11	0.047718	2.35197	0.092048
12	0.035982	2.35197	0.092048
13	0.009219	2.35197	0.092048
14	0.086208	2.35197	0.092048
15	0.093383	2.35197	0.092048
16	0.108096	2.35197	0.092048

LEV_1 and LEV_2

Bonds

Atom Numbers		r_{eq} /Å	k_r/ kJ mol^{-1} Å^{-2}
1	7	1.3550	1746.7
1	6	1.2220	3899.3
1	2	1.4920	1261.6
2	3	1.5080	1282.1
2	11	1.0930	1435.1
2	10	1.0930	1435.1
3	12	1.0930	1435.1
3	13	1.0930	1435.1
3	4	1.4920	1261.6
4	8	1.2220	3899.3
4	5	1.4920	1261.6
5	15	1.0930	1435.1
5	14	1.0930	1435.1
5	16	1.0930	1435.1
7	9	0.9810	2229.1

Angles

Atom Numbers			θ_{eq} / deg	k_θ / kJ mol^{-1} rad^{-2}
6	1	2	124.41	282.44
7	1	2	109.72	314.05
7	1	6	124.43	347.78
1	2	3	107.52	233.96
1	2	10	108.39	195.72
1	2	11	108.39	195.72
3	2	10	110.55	191.50
3	2	11	110.55	191.50
11	2	10	108.84	155.37
2	3	4	107.52	233.96
2	3	12	110.55	191.50
2	3	13	110.55	191.50
12	3	4	108.39	195.72
13	3	4	108.39	195.72
12	3	13	108.84	155.37
3	4	5	118.02	346.57
3	4	8	124.41	282.44
8	4	5	124.41	282.44
4	5	14	108.39	195.72
4	5	15	108.39	195.72
4	5	16	108.39	195.72
15	5	14	108.84	155.37
14	5	16	108.84	155.37
15	5	16	108.84	155.37
1	7	9	111.95	175.55

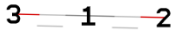
Dihedrals

Atom Numbers				δ / deg	k_φ / kJ mol^{-1}	m
1	2	3	4	0	0.9288	1
1	2	3	4	0	-2.3849	3
1	2	3	12	0	-0.5356	1
1	2	3	12	180	0.1213	2
1	2	3	13	0	-0.5356	1
1	2	3	13	180	0.1213	2
2	1	7	9	0	-2.4393	1
2	1	7	9	180	10.6232	2
2	1	7	9	0	-1.1422	3
2	3	4	5	0	0.2134	1
2	3	4	5	180	0.3682	2
2	3	4	5	0	1.1422	3
2	3	4	8	0	1.7238	1
2	3	4	8	180	0.2929	2
2	3	4	8	0	0.6820	3
3	2	1	6	0	1.7238	1
3	2	1	6	180	0.2929	2
3	2	1	6	0	0.6820	3
3	2	1	7	0	-0.2469	1
3	2	1	7	180	-0.6987	2
3	2	1	7	0	0.4226	3
3	4	5	14	0	-0.1506	1
3	4	5	14	180	0.1799	2
3	4	5	14	0	1.1129	3
3	4	5	15	0	-0.1506	1
3	4	5	15	180	0.1799	2
3	4	5	15	0	1.1129	3
3	4	5	16	0	-0.1506	1
3	4	5	16	180	0.1799	2
3	4	5	16	0	1.1129	3
4	3	2	10	0	-0.5356	1
4	3	2	10	180	0.1213	2
4	3	2	11	0	-0.5356	1
4	3	2	11	180	0.1213	2
5	4	3	12	0	-0.1506	1
5	4	3	12	180	0.1799	2
5	4	3	12	0	1.1129	3
5	4	3	13	0	-0.1506	1
5	4	3	13	180	0.1799	2
5	4	3	13	0	1.1129	3
6	1	2	10	0	1.3807	1
6	1	2	10	180	-2.9455	2
6	1	2	10	0	0.6443	3
6	1	2	11	0	1.3807	1
6	1	2	11	180	-2.9455	2
6	1	2	11	0	0.6443	3
6	1	7	9	0	3.4769	1
6	1	7	9	180	12.8700	2
6	1	7	9	0	-0.1213	3
7	1	2	10	180	-1.3054	2
7	1	2	10	0	0.6904	3
7	1	2	11	180	-1.3054	2
7	1	2	11	0	0.6904	3
8	4	3	12	0	1.3807	1
8	4	3	12	180	-2.9455	2
8	4	3	12	0	0.6443	3
8	4	3	13	0	1.3807	1
8	4	3	13	180	-2.9455	2
8	4	3	13	0	0.6443	3
8	4	5	14	0	1.3807	1
8	4	5	14	180	-2.9455	2
8	4	5	14	0	0.6443	3
8	4	5	15	0	1.3807	1
8	4	5	15	180	-2.9455	2
8	4	5	15	0	0.6443	3
8	4	5	16	0	1.3807	1

8	4	5	16	180	-2.9455	2
8	4	5	16	0	0.6443	3
10	2	3	12	0	0.5941	1
10	2	3	12	180	-2.8995	2
10	2	3	12	0	0.6569	3
10	2	3	13	0	0.5941	1
10	2	3	13	180	-2.8995	2
10	2	3	13	0	0.6569	3
11	2	3	12	0	0.5941	1
11	2	3	12	180	-2.8995	2
11	2	3	12	0	0.6569	3
11	2	3	13	0	0.5941	1
11	2	3	13	180	-2.8995	2
11	2	3	13	0	0.6569	3

improper

Atom Numbers				ϕ_0 / deg	k_φ / kJ mol^{-1} rad^{-2}
1	2	6	7	0.	42.455
4	3	5	8	0.	43.961



CO_2

#	q	σ_{ii} / Å	ε_{ii} / kJ mol^{-1}
1	0.7000	3.14290	0.221800
2	-0.3500	3.42350	0.656900
3	-0.3500	3.42350	0.656900

Bonds

Atom Numbers		r_{eq} /Å	k_r/ kJ mol^{-1} Å^{-2}
1	2	1.16000	4309.50
1	3	1.16000	4309.50

Angles

Atom Numbers			θ_{eq} / deg	k_θ / kJ mol^{-1} rad^{-2}
2	1	3	180.0000	234.30

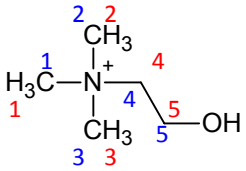
Table S2. Samples used for molecular dynamics simulations of CHCL_LEV_1_2 DES + CO_2 systems. All simulations were carried out at 298 K and for the pressures reported for each system.

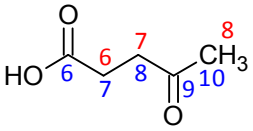
name	p / MPa	$N_{[CH][Cl]}$	N_{LEV}	N_{CO2}
CHCl_LEV_1_2_CO_2_I	0.1	250	500	9
CHCl_LEV_1_2_CO_2_I	0.4	250	500	37
CHCl_LEV_1_2_CO_2_I	0.7	250	500	69
CHCl_LEV_1_2_CO_2_I	1.0	250	500	105

Table S3. Density, ρ, refraction index (for sodium D-line), n_D, and viscosity, η, data for CHCL_LEV_1_2 DES synthesized in this work.

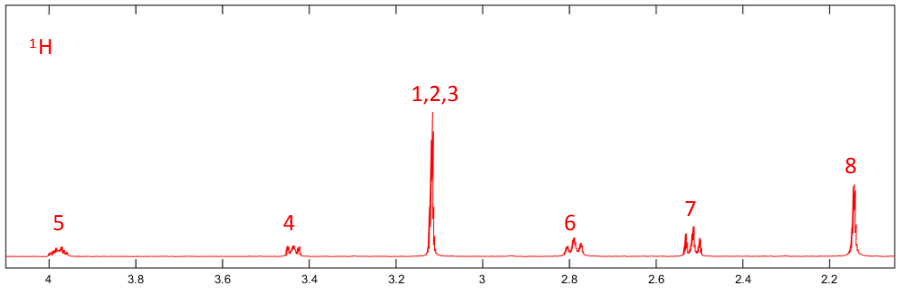
T / K	ρ / g×cm^{-3}	η / mPa×s	n_D
293.18	1.14044		
298.13	1.13709	171.3	1.46618
303.13	1.13370	118.7	1.46483
308.13	1.13031	87.1	1.46340
313.13	1.12694	64.6	1.46195
318.13	1.12359	50.6	1.46055
323.13	1.12025	40.7	1.45916
328.13	1.11693	33.0	1.45765
333.12	1.11362	26.3	1.45630
338.13	1.11032	22.1	1.45494
343.13	1.10705	18.9	
348.13	1.10378	16.1	
353.13	1.10053		
358.13	1.09729		
363.12	1.09406		

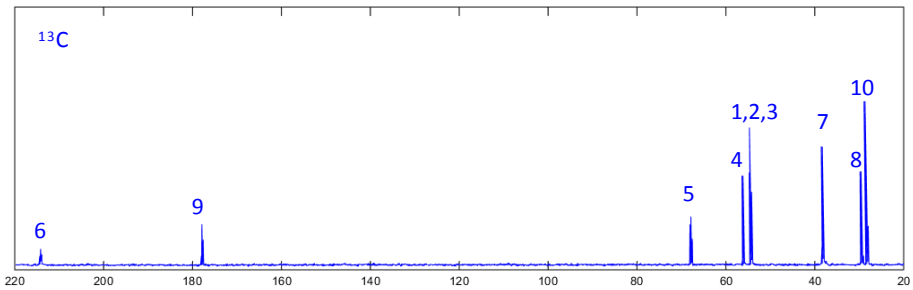
Table S4. ^{1}H and ^{13}C NMR chemical shifts, δ, for CHCL_LEV_1_2 synthesized in this work.





atoms	δ / ppm ^{1}H	atoms	δ / ppm ^{13}C
1,2,3	3.12	1,2,3	53.9
4	3.43	4	55.7
5	3.97	5	67.8
6	2.79	6	213.9
7	2.51	7	38.0
8	2.16	8	29.6
		9	177.5
		10	27.8





δ / ppm

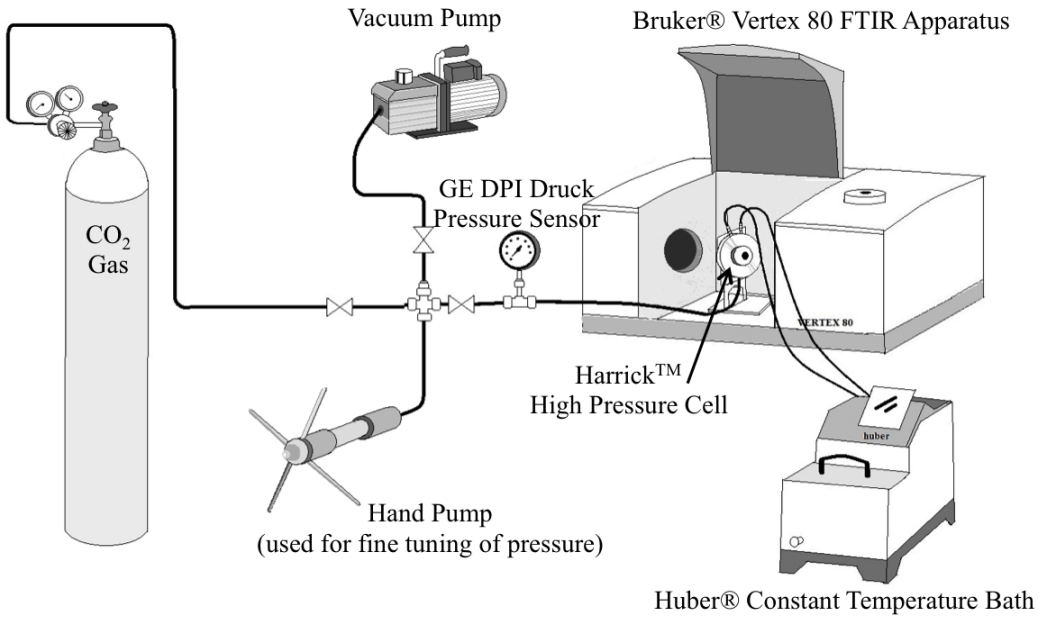


Figure S1. In-situ FTIR experimental setup schematics.

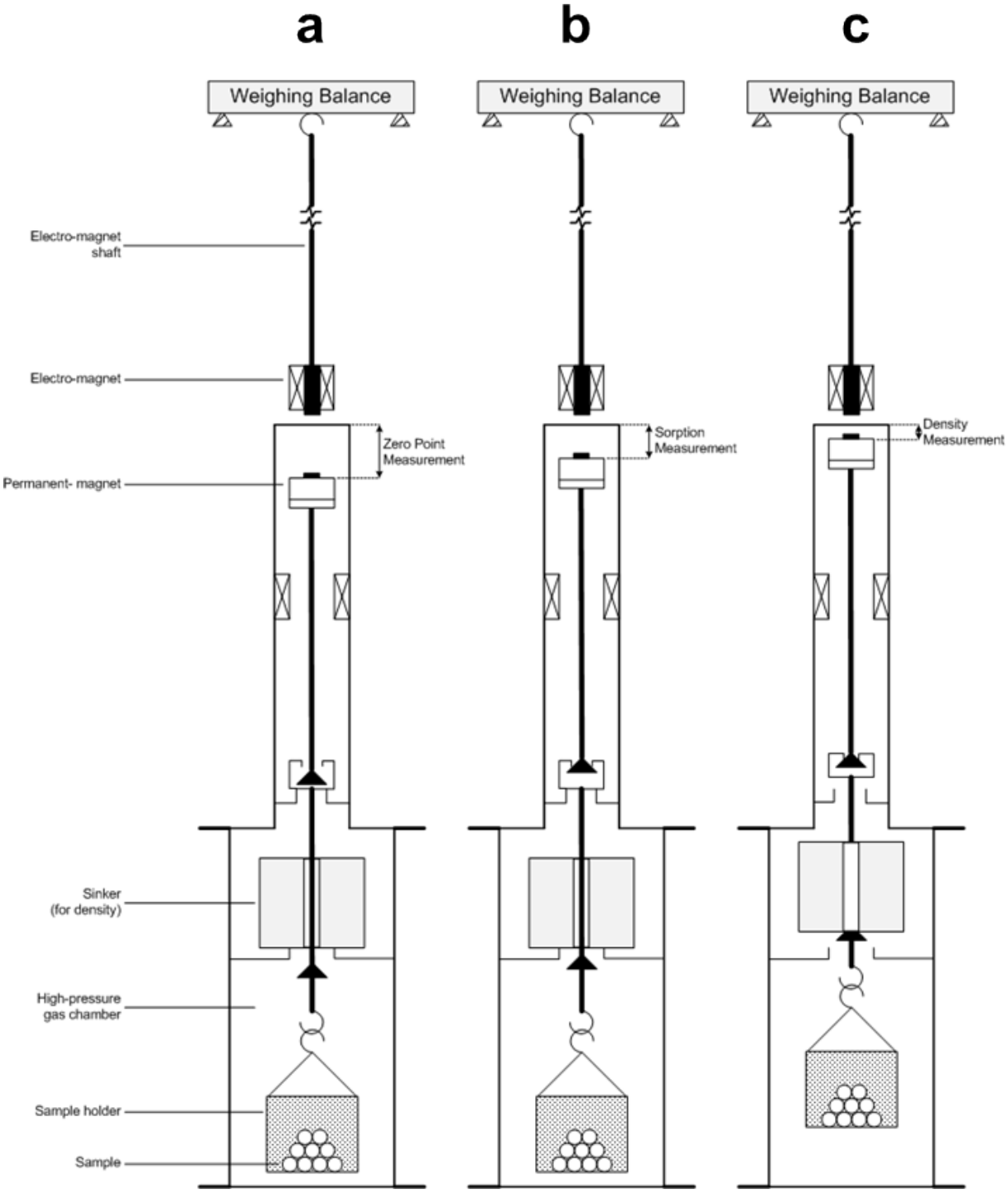


Figure S2. Gas absorption apparatus (MSA) schematics and its operating principle. (a) sample loaded to measuring basket in high pressure cell; (b) Measurement point 1 (MP1) - magnetic coupling is on and mass of the sample is measured; (c) Measurement point 2 (MP2) – in-situ density of the adsorbed gas is measured.

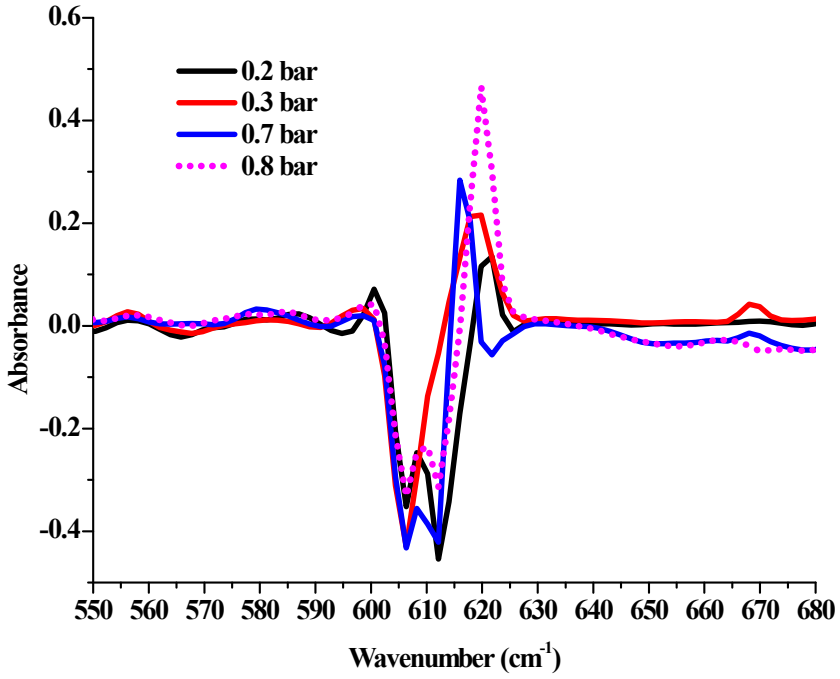


Figure S3.

Figure S3. In-situ FTIR experimental findings of CHCL_LEV_1_2 DES with the presence of pressurized CO_2 at different pressures.