Supporting Information:

Monte Carlo Simulations of Pure and Mixed Gas Solubilities of CO_2 and CH_4 in NonIdeal Ionic Liquid-Ionic Liquid Mixtures

Utkarsh Kapoor and Jindal K. Shah*

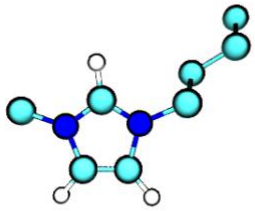
School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078 USA

* *corresponding author*: *jindal.shah@okstate.edu*

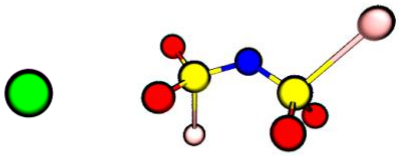
Simulation protocol adopted to compute Henry's constants using BAR approach

Henry's constants for CH_4 in binary ionic liquid mixture system of $[C_4mim]\ Cl_x\ [NTf_2]_{1-x}$ were assessed by computing the excess chemical potential using BAR approach. In this method, a series of simulations were conducted by varying the interaction strength, from non-interacting to fully interacting, between the solute CH_4 and the ionic liquid solvent through a coupling parameter λ. A complete molecular dynamics (MD) simulation is carried out at each λ. Then, the free energy change between the successive λ values is evaluated by BAR method, and the total free energy change is obtained by taking the sum over all the λ values. As the CH_4 force field is comprised only of the van der Waal terms, only these interactions were scaled from the ideal gas state (λ=0) to a fully coupled state (λ=1). This was done using an equidistant spacing of λ=0.05, thereby giving 21 λ points.

All the MD simulations were done at a temperature and pressure of 353 K and 1 bar using GROMACS 5.0.4. The initial configurations were generated using PACKMOL by inserting 1 molecule of CH_4 with 256 (or 250 for 10:90 and 90:10 compositions) ion pairs for an ionic liquid in a cubic box with periodic boundary conditions. As the first estimate, the ionic liquid box sizes were obtained from our previous study. The initial configurations were subjected to the steepest descent minimization followed by a 2 ns annealing scheme where the temperature of the whole system was iteratively changed from 353 K to 553 K at the rate of 1 K/ps. Following, each system was then equilibrated in canonical (*NVT*) and isothermal-isobaric (*NPT*) ensembles for 10 ns each, followed by a subsequent production run of 20 ns in the *NPT* ensemble, using a Langevin dynamics integrator. A 0.002 ps time step was used for integrating the equations of motion, as the fast-vibrational modes comprising the hydrogen atoms were constrained. The temperature and pressure were controlled using Nose-Hoover thermostat and Parrinello-Rahman barostat respectively, with coupling time constants of τ_T = 0.4 ps and τ_P = 2.0 ps. With a potential cutoff of 12 Å, appropriate tail corrections were applied for non-bonded LJ interactions while electrostatic interactions were handled using the Particle Mesh Ewald (PME) method. The free energy difference or μ^{ex} was evaluated using gmx bar utility of GROMACS. Three independent simulation trials were conducted to determine the standard deviations at each value of λ.



(a) Cation :: 1-butyl-3-methylimidazolium $[C_4mim]^+$



(b) Anions :: Chloride, Cl^- and bis(trifluoromethanesulfonyl)imide$[NTf_2]^-$

(c) Gas Molecules :: carbon dioxide (CO_2) and methane (CH_4)

Figure S1: Chemical structure schematic used in this work (a) 1-butyl-3-methylimidazolium $[C_4mim]^+$, (b) chloride Cl^-, and $[NTf_2]^-$, respectively and (c) carbon dioxide (CO_2) and methane (CH_4). Please note that these atomic representations are chosen to enforce the employed force field models.

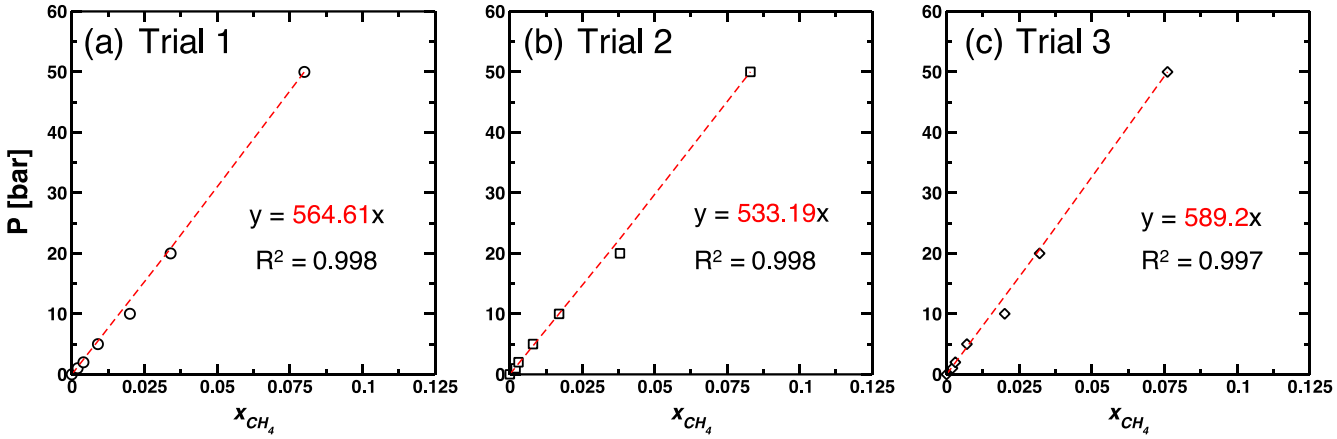


Figure S2: An example showing linear fit procedure for the calculation of Henry's constants of CH_4 in $[C_4mim][NTf_2]$ ionic liquid. (a), (b) and (c) represents data obtained from three different simulation trials. R^2 is the correlation coefficient and y = mx is the linear fit between pressure and mole fraction of CH_4, thus, slope (m) gives the Henry's constant value. The obtained Henry's constant values are shown in red color. The average and standard deviation value of 562.33 ± 28.07 is computed using these values, as reported in this work.

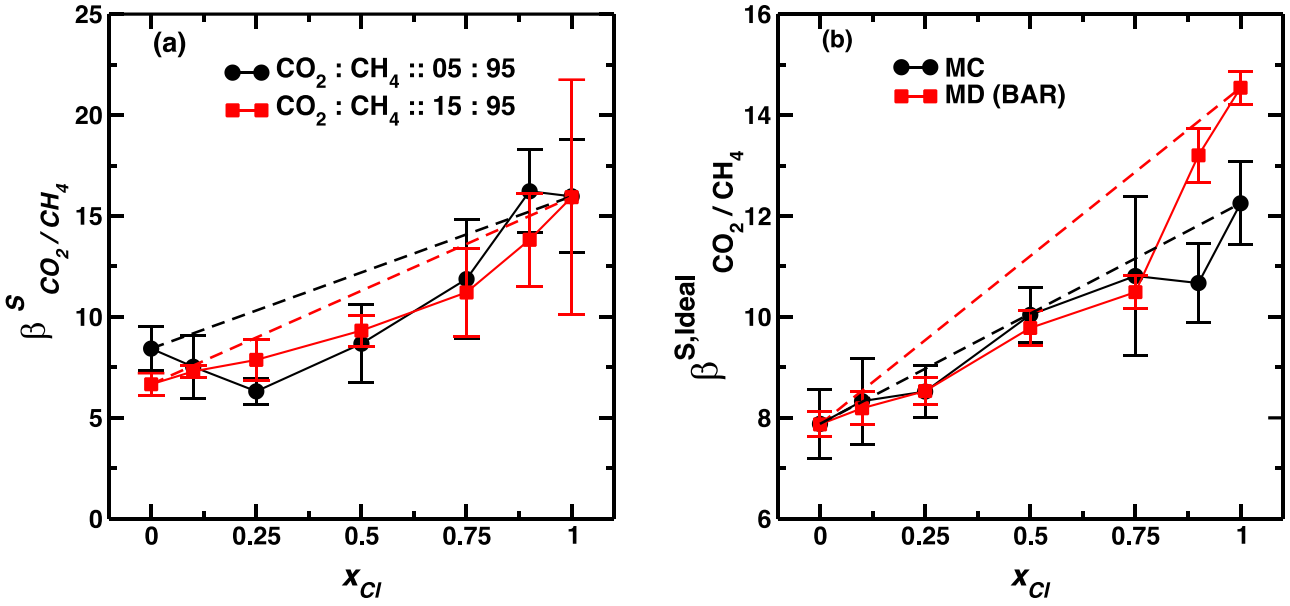


Figure S3: (a) CO_2/CH_4 gas mixture solubility selectivities ($\beta^{S}_{CO2/CH4}$) in binary ionic liquid mixture of $[C_4mim]Cl_x[NTf_2]_{1-x}$ as a function of molar composition computed at 353 K and a total pressure of 100 bar. (b) Comparison of CO_2/CH_4 gas mixture ideal solubility selectivities ($\beta^{S,Ideal}_{CO2/CH4}$) computed using the ratio of Henry's law constants using both Monte Carlo and Molecular Dynamics (BAR) techniques. Standard deviations were calculated from three independent trials for all the mixture compositions. Note that the continuous lines joining data points are only guide to the eye while dotted lines represent the linear mixing rule.

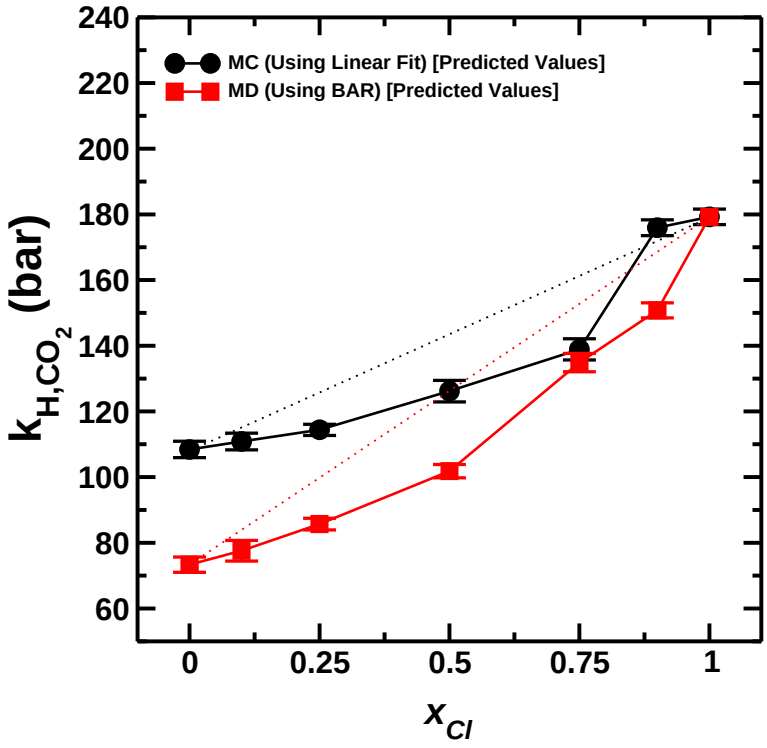


Figure S4: Comparison of Henry's constants of CO_2 calculated using MC simulations, by taking linear fits from P = 0 to P = 50 bar and those computed using the BAR technique employed in MD simulations for the mixture system of $[C_4mim]\ Cl_x\ [NTf_2]_{1-x}$. Standard deviations were calculated from three independent trials for all mixture compositions. Note that the continuous lines joining data points are only guide to the eye while dotted lines represent linear mixing rule. The values for CO_2-MD(BAR) are taken from our previous work. [1]

Table S1: Solubility data of CO_2 in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and P = 1, 2, 5, 10, 20, 50, 80, 100 bar. The statistical uncertainties are obtained using three independent trail runs.

Pressure	Binary Ionic Liquid Mixture	x	Mole Fraction of CO_2	
			AV	STDEV
1 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.017	0.003
		0.10	0.015	0.002
		0.25	0.020	0.002
		0.50	0.016	0.004
		0.75	0.016	0.002
		0.90	0.013	0.003
		1.00	0.015	0.002
2 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.033	0.003
		0.10	0.031	0.002
		0.25	0.030	0.005
		0.50	0.026	0.002
		0.75	0.024	0.004
		0.90	0.020	0.003
		1.00	0.021	0.004
5 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.067	0.007
		0.10	0.069	0.006
		0.25	0.059	0.006
		0.50	0.059	0.006
		0.75	0.055	0.006
		0.90	0.053	0.005
		1.00	0.047	0.010
10 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.123	0.009
		0.10	0.125	0.006
		0.25	0.118	0.004
		0.50	0.104	0.009
		0.75	0.106	0.011
		0.90	0.097	0.008
		1.00	0.086	0.004

20 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.227	0.009
		0.10	0.225	0.006
		0.25	0.220	0.009
		0.50	0.197	0.004
		0.75	0.180	0.008
		0.90	0.186	0.009
		1.00	0.155	0.021
50 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.425	0.006
		0.10	0.411	0.013
		0.25	0.398	0.007
		0.50	0.363	0.016
		0.75	0.324	0.001
		0.90	0.304	0.006
		1.00	0.305	0.012
80 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.536	0.009
		0.10	0.522	0.007
		0.25	0.500	0.007
		0.50	0.485	0.033
		0.75	0.445	0.018
		0.90	0.390	0.001
		1.00	0.398	0.014
100 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.589	0.005
		0.10	0.567	0.012
		0.25	0.547	0.023
		0.50	0.514	0.011
		0.75	0.485	0.004
		0.90	0.445	0.034
		1.00	0.427	0.012

Table S2: Solubility data of CH_4 in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and P = 1, 2, 5, 10, 20, 50, 80, 100 bar. The statistical uncertainties are obtained using three independent trail runs.

Pressure	Binary Ionic Liquid Mixture	x	Mole Fraction of CH_4	
			AV	STDEV
1 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.002	0.000
		0.10	0.002	0.000
		0.25	0.001	0.000
		0.50	0.001	0.000
		0.75	0.001	0.000
		0.90	0.001	0.000
		1.00	0.001	0.000
2 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.003	0.001
		0.10	0.003	0.001
		0.25	0.003	0.000
		0.50	0.002	0.000
		0.75	0.002	0.000
		0.90	0.001	0.000
		1.00	0.001	0.000
5 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.008	0.001
		0.10	0.009	0.001
		0.25	0.007	0.001
		0.50	0.006	0.001
		0.75	0.004	0.001
		0.90	0.003	0.000
		1.00	0.003	0.001
10 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.019	0.002
		0.10	0.018	0.001
		0.25	0.015	0.000
		0.50	0.011	0.002
		0.75	0.009	0.002
		0.90	0.008	0.000
		1.00	0.005	0.001

20 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.035	0.003
		0.10	0.032	0.003
		0.25	0.028	0.002
		0.50	0.019	0.001
		0.75	0.017	0.004
		0.90	0.012	0.002
		1.00	0.011	0.002
50 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.035	0.003
		0.10	0.032	0.003
		0.25	0.028	0.002
		0.50	0.019	0.001
		0.75	0.017	0.004
		0.90	0.012	0.002
		1.00	0.011	0.002
80 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.112	0.001
		0.10	0.111	0.011
		0.25	0.097	0.005
		0.50	0.079	0.009
		0.75	0.059	0.009
		0.90	0.044	0.002
		1.00	0.042	0.007
100 bar	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.149	0.012
		0.10	0.126	0.016
		0.25	0.115	0.005
		0.50	0.094	0.016
		0.75	0.063	0.001
		0.90	0.072	0.005
		1.00	0.040	0.001

Table S3: Data for Henry's law constants, k_H, of CO_2 in binary ionic liquid mixture of $[C_4mim]Cl_x[NTf_2]_{1-x}$ computed using (1) Monte Carlo (MC) Simulations and the pressure range used for linear fit and (2) Molecular Dynamics (MD) using BAR technique.

Binary Ionic Liquid Mixture	x	Chosen Pressure Range for linear fit	$K_{H, CO2}$ (MC)		$K_{H, CO2}$ (MD-BAR)	
			AV	STDEV	AV	STDEV
$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0-10	71.37	5.06	73.35	2.34
	0.10	0-10	77.34	3.22	77.58	3.15
	0.25	0-10	82.87	0.48	85.71	1.78
	0.50	0-10	98.47	0.94	101.82	2.04
	0.75	0-10	105.46	7.14	134.87	2.79
	0.90	0-20	144.33	3.46	150.77	2.30
	1.00	0-20	153.10	8.79	179.23	0.00

Please note that the above $K_{H, CO2}$ data is taken directly from our previous study.[1]

1. Kapoor, U. & Shah, J. K. Molecular Origins of the Apparent Ideal CO2 Solubilities J. Phys. Chem. B 122 (42) (2018) 9763–9774

Table S4: Data for Henry's law constants, k_H, of CH_4 in binary ionic liquid mixture of $[C_4mim]Cl_x[NTf_2]_{1-x}$ computed using (1) Monte Carlo (MC) Simulations and the pressure range used for linear fit (2) Molecular Dynamics (MD) using BAR technique.

Binary Ionic Liquid Mixture	x	Chosen Pressure range for linear fit	$K_{H, CH4}$ (MC)		$K_{H, CH4}$ (MD-BAR)	
			AV	STDEV	AV	STDEV
$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0-50	562.33	28.07	577.19	0.00
	0.10	0-50	644.00	60.20	635.33	0.00
	0.25	0-50	706.03	42.54	730.97	16.77
	0.50	0-50	988.53	52.08	995.58	29.86
	0.75	0-50	1140.22	146.25	1414.21	32.87
	0.90	0-50	1539.80	106.32	1990.60	76.10
	1.00	0-50	1876.07	65.70	2605.80	59.77

Table S5: CO_2/CH_4 gas mixture solubility data of CO_2 in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and Total pressure of 100 bar. The standard deviations were calculated from three independent trials for all mixture compositions except x_{Cl} = 0.75, 0.90 and 1.00 where two additional independent runs were considered.

	Binary Ionic Liquid Mixture	x	X_CO_2		Y_CO_2	
			AV	STDEV	AV	STDEV
P = 100 bar; $CO_2 : CH_4$ :: 05 : 95	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.049	0.006	0.044	0.001
		0.10	0.051	0.007	0.043	0.001
		0.25	0.038	0.003	0.045	0.000
		0.50	0.042	0.009	0.045	0.001
		0.75	0.041	0.009	0.045	0.001
		0.90	0.051	0.005	0.044	0.001
		1.00	0.037	0.006	0.045	0.001
P = 100 bar; $CO_2 : CH_4$ :: 15 : 85	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.118	0.007	0.120	0.003
		0.10	0.115	0.002	0.122	0.001
		0.25	0.112	0.013	0.122	0.004
		0.50	0.113	0.002	0.122	0.001
		0.75	0.099	0.006	0.126	0.002
		0.90	0.106	0.002	0.124	0.001
		1.00	0.088	0.019	0.129	0.006

Table S6: CO_2/CH_4 gas mixture solubility data of CH_4 in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and Total pressure of 100 bar. The standard deviations were calculated from three independent trials for all mixture compositions except x_{Cl} = 0.75, 0.90 and 1.00 where two additional independent runs were considered.

	Binary Ionic Liquid Mixture	x	X_CH_4		Y_CH_4	
			AV	STDEV	AV	STDEV
P = 100 bar; CO_2 : CH_4 :: 05 : 95	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.128	0.004	0.956	0.001
		0.10	0.148	0.023	0.957	0.001
		0.25	0.128	0.008	0.955	0.000
		0.50	0.105	0.003	0.955	0.001
		0.75	0.073	0.006	0.955	0.001
		0.90	0.069	0.006	0.956	0.001
		1.00	0.049	0.002	0.955	0.001
P = 100 bar; CO_2 : CH_4 :: 15 : 85	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	0.130	0.006	0.880	0.003
		0.10	0.114	0.004	0.878	0.001
		0.25	0.103	0.004	0.878	0.004
		0.50	0.088	0.007	0.878	0.001
		0.75	0.061	0.011	0.874	0.002
		0.90	0.054	0.009	0.876	0.001
		1.00	0.037	0.011	0.871	0.006

Table S7: CO_2/CH_4 solubility selectivity (β^S) in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and Total pressure of 100 bar. The standard deviations were calculated from three independent trials for all mixture compositions except x_{Cl} = 0.75, 0.90 and 1.00 where two additional independent runs were considered.

	Binary Ionic Liquid Mixture	x	β^S	
			AV	STDEV
P = 100 bar; $CO_2 : CH_4$ :: 05 : 95	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	8.43	1.11
		0.10	7.53	1.57
		0.25	6.31	0.63
		0.50	8.67	1.93
		0.75	11.87	2.96
		0.90	16.22	2.05
		1.00	15.97	2.80
P = 100 bar; $CO_2 : CH_4$ :: 15 : 85	$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	6.66	0.55
		0.10	7.30	0.31
		0.25	7.87	1.00
		0.50	9.32	0.77
		0.75	11.21	2.16
		0.90	13.82	2.30
		1.00	15.93	5.82

Table S8: CO_2/CH_4 ideal solubility selectivity (calculated using Henry's law constants - ($\beta^{S,Ideal}$)) in binary ionic liquid mixture of and $[C_4mim]Cl_x[NTf_2]_{1-x}$ at 353 K and Total pressure of 100 bar. The statistical uncertainties are obtained using three independent trail runs.

Binary Ionic Liquid Mixture	x	$\beta^{S,Ideal}$ (MC)		$\beta^{S,Ideal}$ (MD-BAR)	
		AV	STDEV	AV	STDEV
$[C_4mim]Cl_x[NTf_2]_{1-x}$	0.00	7.88	0.68	7.87	0.25
	0.10	8.33	0.85	8.19	0.33
	0.25	8.52	0.52	8.53	0.26
	0.50	10.04	0.54	9.78	0.35
	0.75	10.81	1.57	10.49	0.33
	0.90	10.67	0.78	13.20	0.54
	1.00	12.25	0.82	14.54	0.33